

## STRUCTURAL HIERARCHY IN SEMICRYSTALLINE POLYMERS

### atomic scale - crystal unit cell

- several Angstroms (<1 nm to a few nm)
- detailed crystal structure, conformation of individual bonds
- wide-angle XRD

### scale of crystal thickness

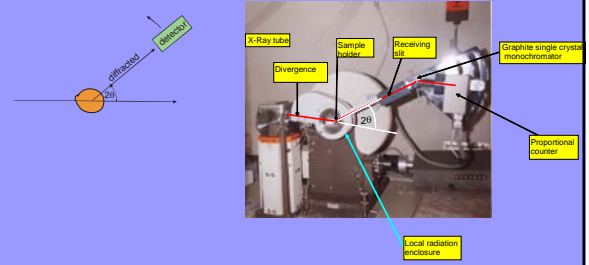
- 100-500 Å (10 - 50 nm)
- electron microscopy, small-angle XRD

### scale of crystal aggregates (spherulites etc.)

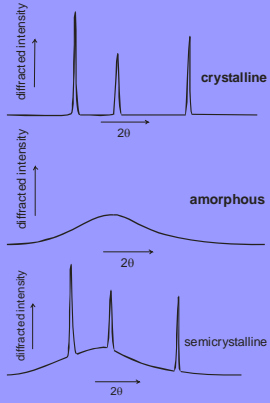
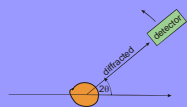
- μm scale
- optical microscopy

## Semicrystalline Polymers

### PHILIPS X-RAY DIFFRACTOMETER



## Semicrystalline Polymers



## Degree of crystallinity

$$\text{crystallinity: } X = \frac{v_c}{v_c + v_a} = \frac{I_c}{I_c + I_a}$$

$$\text{density: } \rho = \frac{\rho_c v_c + \rho_a v_a}{v_c + v_a}$$

$$= \rho_c X + \rho_a (1 - X) = \rho_a + (\rho_c - \rho_a) X$$

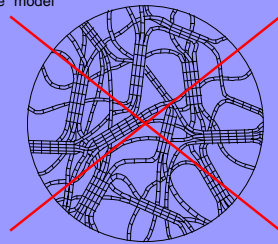
polyethylene:  $\rho_c = 1.00 \text{ gcm}^{-3}$ ,  $\rho_a = 0.85 \text{ gcm}^{-3}$

**Problem:** Crystallinities of HDPE and LDPE are typically 0.5 and 0.8. Calculate their densities.

Determination of X. Primary method: XRD  
Secondary: DSC, density, (NMR, IR)

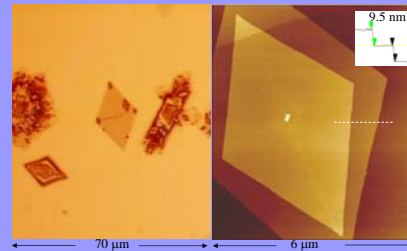
## How are the two phases arranged?

"Fringed micelle" model

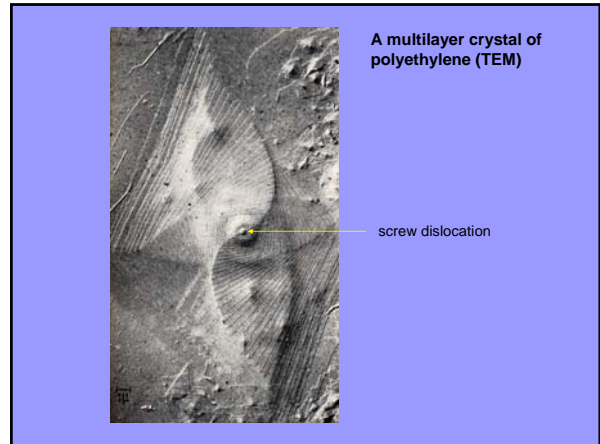
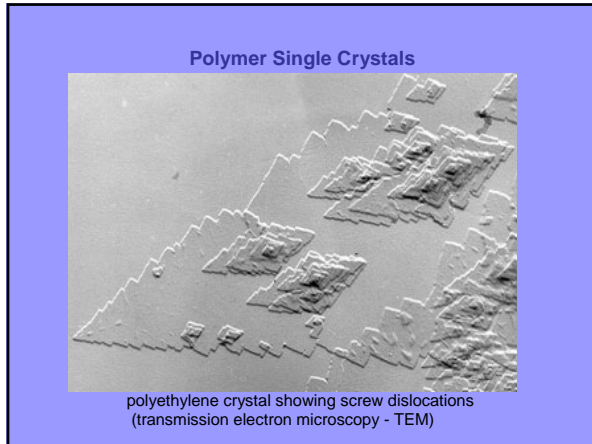


Today abandoned.

## Polymer Single Crystals

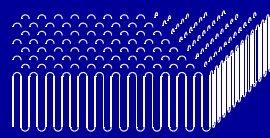


polyethylene from 0.1% xylene solution (AFM - atomic force microscopy)

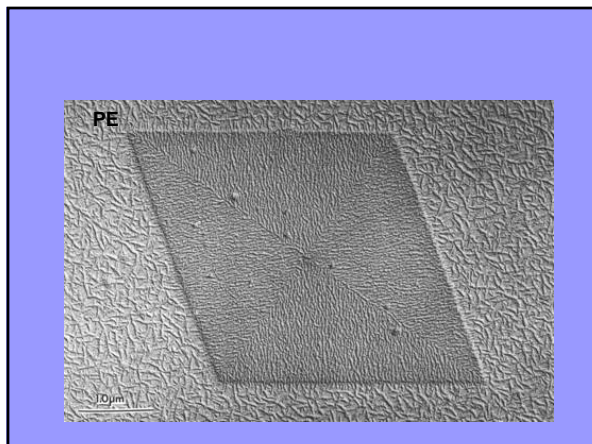
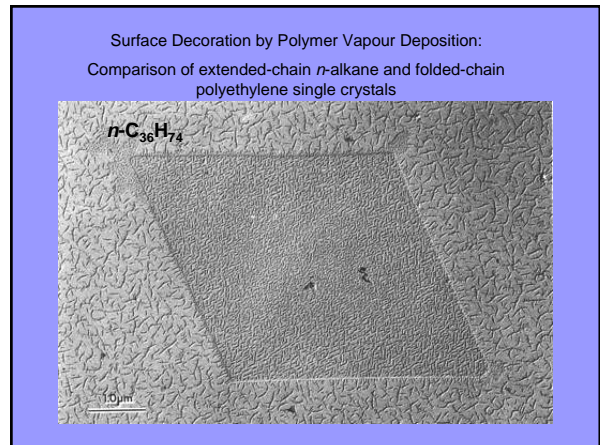


**Structure of lamellar polymer crystals**

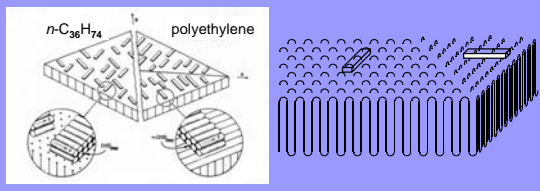
- lamellar crystals thickness 10 nm (typically from solution)
- polymer chains normal to lamellar surface
- typical length of extended polymer chain:  
 $1\mu\text{m} = 1000\text{ nm}$
- What is the structure?

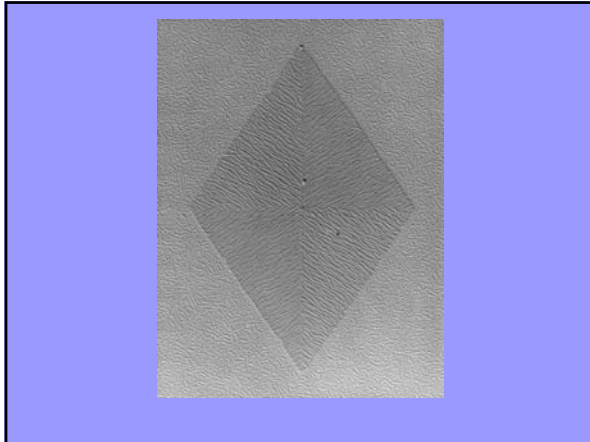


chain-folded lamellar crystal



Decorating PE lamellae crystallize epitaxially on top of chain folds





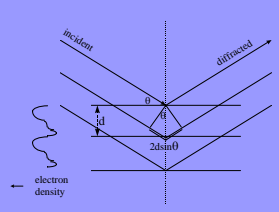
### What about **melt-crystallized** polymers?

- Also lamellar crystals?
- Small-angle X-ray scattering (SAXS) suggests so.
- Diffraction peak at small  $2\theta$  corresponds to d-spacing  $20 - 50$  nm.  
= "long period"  $l$

→ stacking of lamellar crystals

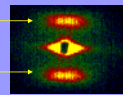
### Bragg equation relating diffraction angle $\theta$ to interplanar spacing $d$

$n\lambda = 2d \sin\theta$



**Small  $d$  - large  $\theta$**   
(wide angle XRD when layers are layers of atoms)

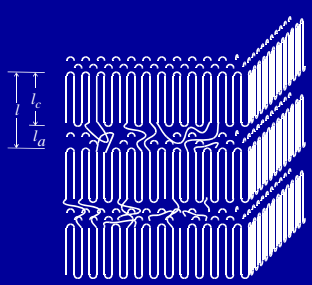
**Large  $d$  - small  $\theta$**   
(small-angle XRD when layers are thin crystals)



SAXS of oriented *i*PP

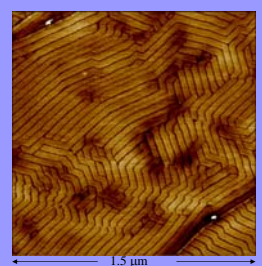
### Stacked melt-crystallized lamellae

$X = l_c/l$



- folds less regular
- amorphous phase more liquid-like
- tie-molecules – give mechanical integrity

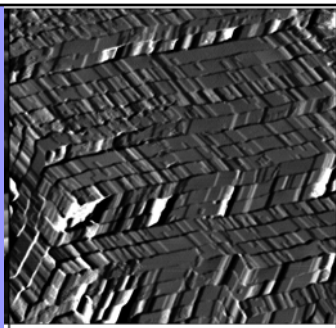
### Atomic Force Micrograph (AFM) of melt-crystallized PE



1.5  $\mu$ m

- thin layer on graphite
- lamellae edge-on
- chains tilted

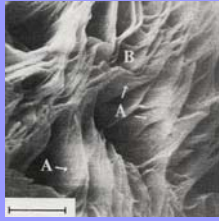
C390



1.00  $\mu$ m

AFM micrograph of fracture surface  
Note chain tilt.

## Lamellar structure in melt-crystallized PE

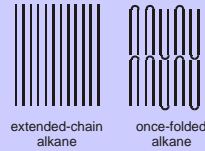


SEM of surface of PE from which low MW fraction was extracted

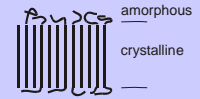
Part of MAT215 and MAT6102 modules  
Prof. G. Ungar, © University of Sheffield

## Why are polymers semicrystalline?

Monodisperse polymer  
(pure long chain alkane)

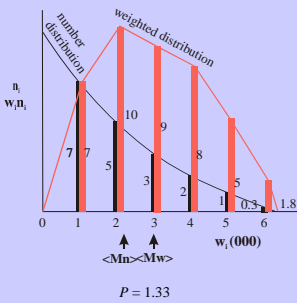


Binary alkane mixture



chain length up to 390 C-atoms  
(M.W. = 5462)

## Polydisperse polymers – molecular weight distribution



averages:

$$\langle M_n \rangle = \frac{\sum w_i n_i}{\sum n_i}$$

$$\langle M_w \rangle = \frac{\sum w_i^2 n_i}{\sum w_i n_i}$$

polydispersity:

$$P = \frac{\langle M_w \rangle}{\langle M_n \rangle}$$

## Polymer Crystallization

Why thin chain-folded crystals?  
Why not the more stable extended-chain crystals?

Most stable shapes of crystals are such that the total surfaces energy is minimised.

$$\sum A_i \sigma_i = \text{minimum}$$

In polymers:

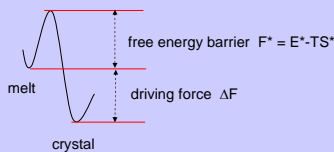
$$\sigma_c \cong 10\sigma$$



Minimum energy crystal

However, instead of being the smallest, the high energy surface (fold surface) is the **largest** in lamellar polymer crystals.

- thick crystal – more stable (lower free energy)
    - less surface = less surface energy
    - high thermodynamic **driving force** for crystallization
- $DF = F_{\text{crystal}} - F_{\text{melt}}$  is highly negative



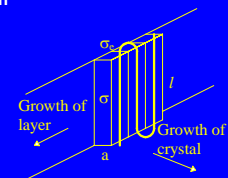
Lamellar crystals are favoured by **growth and nucleation**.

**Thinnest crystals grow fastest.**

Crystals grow **as thin as possible**.

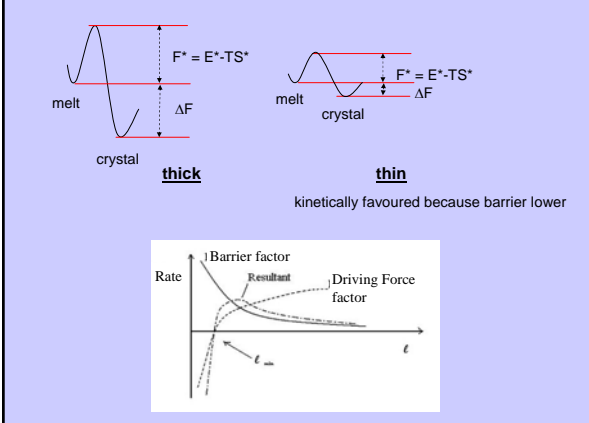
2 reasons for this:

- if  $l$  large - long chain segment must become straight
  - all bonds must be in correct conformation (e.g. *trans*)
  - probability low – chain extension is a **rare event**
- there is **no longitudinal growth**
  - chains deposit side-by-side
  - growth is 2-dimensional



Free energy **barrier** for chain attachment is mainly entropic

- Probability of 1 C-C bond being *trans* = 1/3
- Probability of 2 C-C bonds being *trans* = 1/3 × 1/3 = 1/3<sup>2</sup> = 1/9
- Probability of 100 C-C bonds being *trans* = 1/3<sup>100</sup>
- $S^* = k \ln(1/3^{100}) = -100 \ln 3 k$
- free energy barrier  $F^* = (E) - TS^* = kT \times (100 \ln 3)$   
 $F^* = kT \times L$  (L = crystal thickness)
- frequency of chain attachments  
 $\exp(-F^*/kT) = \exp(-L)$



**thick** **thin**  
kinetically favoured because barrier lower

### How does lamellar thickness depend on $T_c$ ?

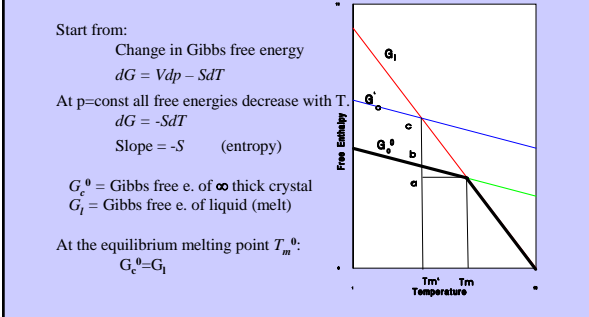
- For a given  $T_c$  the minimum allowed  $l$  is  $l_{min}$ .
- $l_{min}$  = thickness of crystals whose  $T_m = T_c$ .
- Growth rate of crystals with  $l = l_{min}$  is zero. (Driving force  $G_c - G_l = 0$ .)
- Hence:  
 $l > l_{min}$
- To find  $l(T_c)$  need find  $l_{min}(T_c)$ .
- Find inverse:  $T_m(l)$

### MELTING TEMPERATURE OF LAMELLAR POLYMER CRYSTALS

Start from:  
 Change in Gibbs free energy  
 $dG = Vdp - SdT$   
 At  $p = \text{const}$  all free energies decrease with T.  
 $dG = -SdT$   
 Slope =  $-S$  (entropy)

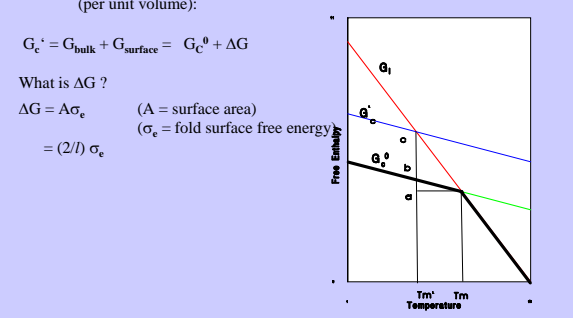
$G_c^0$  = Gibbs free e. of  $\infty$  thick crystal  
 $G_l$  = Gibbs free e. of liquid (melt)

At the equilibrium melting point  $T_m^0$ :  
 $G_c^0 = G_l$



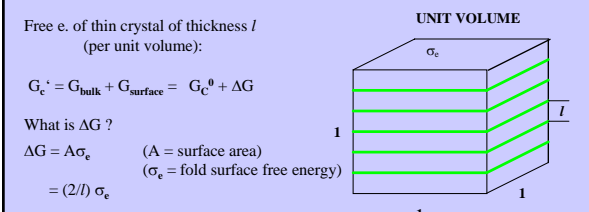
Free e. of thin crystal of thickness  $l$  (per unit volume):  
 $G_c^* = G_{\text{bulk}} + G_{\text{surface}} = G_c^0 + \Delta G$

What is  $\Delta G$ ?  
 $\Delta G = A\sigma_e$  (A = surface area)  
 $= (2/l)\sigma_e$  ( $\sigma_e$  = fold surface free energy)



Free e. of thin crystal of thickness  $l$  (per unit volume):  
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**UNIT VOLUME**

No. of layers =  $1/l$   
 Total area of layers (both surfaces)  
 $A = 2/l$   
 Total surface free energy per unit volume of polymer  
 $= A\sigma_e = 2\sigma_e/l$

Free e. of thin crystal of thickness  $l$  (per unit volume):

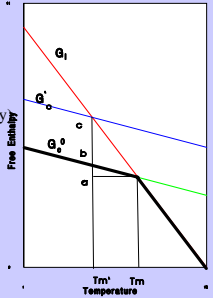
$$G_c^* = G_{\text{bulk}} + G_{\text{surface}} = G_c^0 + \Delta G$$

What is  $\Delta G$  ?

$$\Delta G = A\sigma_e \quad (A = \text{surface area})$$

$$= (2l)\sigma_e \quad (\sigma_e = \text{fold surface free energy})$$

Now determine melting point depression

$$\Delta T = T_m^0 - T_m$$


Geometry:

$$bc = \Delta G$$

$$ac = \Delta T S_l$$

$$ab = \Delta T S_c$$

$$bc = ac - ab$$

$$\Delta G = \Delta T S_l - \Delta T S_c = \Delta T (S_l - S_c)$$

$$\Delta G = \Delta T \Delta S_f \quad (\Delta S_f = \text{entropy of fusion})$$

Substitute  $\Delta G$ :

$$(2l)\sigma_e = \Delta T \Delta S_f$$

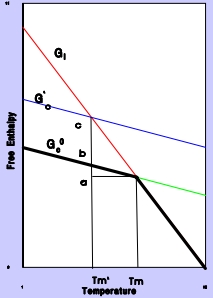
Thus melting point depression  $\Delta T$  is:

$$\Delta T = \frac{2\sigma_e}{l\Delta S_f} = \frac{2\sigma_e T_m}{l\Delta H_f}$$

since

$$\Delta S_f = \frac{\Delta H_f}{T_m}$$

where  $\Delta H_f$  = heat of fusion



$$T_m^0 - T_m = \frac{2\sigma_e T_m}{l\Delta H_f}$$

- Melting point depression is **inversely proportional to crystal thickness**.
- Thin crystals: high free energy = low stability = low  $T_m$

### How does $l$ depend on $T_c$ ?

- For a given supercooling  $\Delta T$  the minimum allowed  $l$  is  $l_{\text{min}}$ .
- Hence:

$$l \geq l_{\text{min}}$$

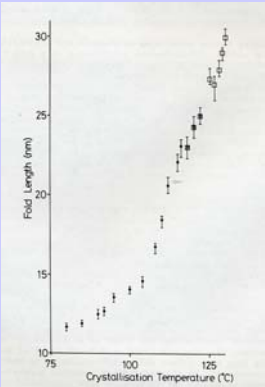
since:

$$\Delta T = \frac{2\sigma_e T_m}{l\Delta H_f}$$

$$\rightarrow l_{\text{min}} = \frac{2\sigma_e T_m}{\Delta H_f \Delta T}$$

$\rightarrow l \propto 1/\Delta T$

### Lamellar thickness $l$ vs. crystallization temperature for polyethylene



### Crystallization rate vs. temperature

Close to  $T_m^0$ :  
Only thick crystals can grow. Growth is slow.

With increasing  $\Delta T$  - growth accelerates exponentially.  
2 reasons:

- Driving force  $|G_c - G_l|$  increases.
- Entropic barrier decreases since thinner crystals can grow.

At still lower temperatures, close to  $T_g$ , melt viscosity increases  
 $\rightarrow$  crystallisation rate  $\rightarrow 0$ .

Typical crystallization rate vs.  $T_c$  for polymers:

