Chapter 8

Crystallization

Xtallization rate

- Xtallization by
  - nucleation (at T < Tm) and
  - growth (diffusion of chain at T > Tg)

- nucleation
  - free energy change for nucleation
    - free E for Xtalliz’n nucleation (< 0) + surface energy (> 0)

$$\Delta G = \Delta g V_{\text{crystal}} + \sum_i A_i \sigma_i = \frac{4\pi r^3}{3} \cdot \Delta g + 4\pi r^2 \sigma$$

~ for spherical nucleus

$$\frac{\partial \Delta G}{\partial r} = 4\pi r^{*2} \Delta g + 8\pi r^* \sigma = 0$$

r* ~ critical radius for nucleation

$$\begin{tikzcd} r^* = -\frac{2\sigma}{\Delta g} \arrow[rr] & {} & r^* = -\frac{2\sigma T_m^0}{\Delta h^0 \Delta T} \\ & \Delta g = \frac{\Delta h^0 \Delta T}{T_m^0} \arrow[u] & \end{tikzcd}$$

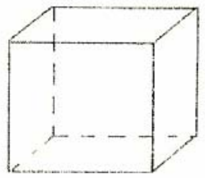
$\Delta T = T_m^0 - T_c$ ~ supercooling

- As ΔT increases,
  - r* decreases
  - G* decreases
  - easier nucleation

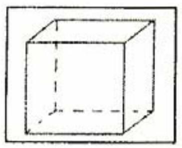
$$r^* = -\frac{2\sigma T_m^0}{\Delta h^0 \Delta T}$$

$$\Delta G^* = \frac{4\pi\sigma^3 (T_m^0)^2}{(\Delta h^0)^2 \Delta T^2}\left[-\frac{8}{3}+4\right] = \frac{16\pi\sigma^3 (T_m^0)^2}{3(\Delta h^0)^2 \Delta T^2}$$

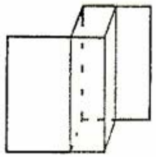
- homogeneous vs heterogeneous nucleation
  - ΔT for homogeneous primary nucleation ~ 50 – 100 K
    - occurs seldom
  - in practice, heterogeneous nucleation
    - followed by secondary and tertiary nucleation



Primary nucleation
(n=6)



Secondary nucleation
(n=4)



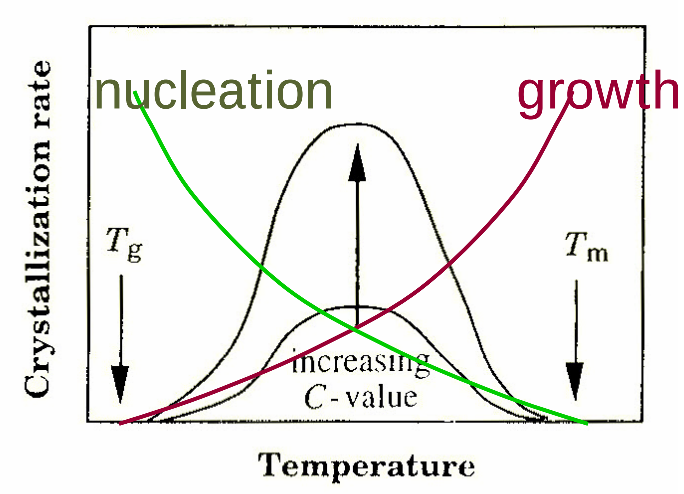
Tertiary nucleation
(n=2)

Crystal growth (view along the chains)

- overall crystallization rate

$$\dot{w}_c = \underbrace{C}\,\underbrace{\exp\left(-\frac{U^*}{R(T_c - T_\infty)}\right)}\,\underbrace{\exp\left(-\frac{K_g}{T_c(T_m^0 - T_c)}\right)}$$

  - C ~ structural factor
    - regularity and flexibility
    - C = 0 for atactic (amorphous)
    - small C for inflexible polymers
  - diffusion
    - segmental mobility, motion
    - WLF or reptation
    - zero at T_g
  - nucleation
    - zero at T_m



- measurement of Xtallization rate
  - dilatometry
  - microscopy

Equilibrium melting temperature

- T_m^0 is T_m of
  - infinitely thick crystal for high MW
  - extended-chain crystal for low MW

- determination
  - from Thompson-Gibbs eqn

$$T_m = T_m^0\left(1 - \frac{2\sigma}{L_c \rho_c \Delta h^0}\right) \qquad (7.21)$$

    - L_c measured and extrapolated to $1/L_c = 0$

    - crystal thickening
      - prevented by light Xlinking
    - superheating ~ Thick crystal melts slowly.
      - prevented by slow heating

determination (cont'd)

- from Δh_f and Δs_f

$$T_m^0 = \lim_{x\to\infty} \frac{\Delta h(x)}{\Delta s(x)} \qquad (8.11)$$

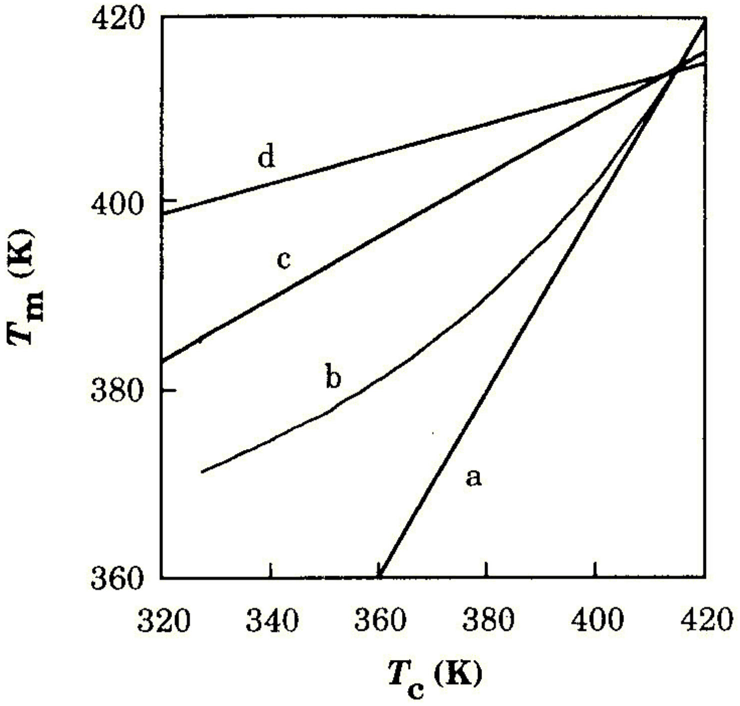
  - extrapolated to infinite MW
  - for PE

$$T_m = 414.3\left[\frac{x - 1.5}{x + 5.0}\right]$$

- Hoffman-Weeks plot
  - plot T_m vs T_c, and extrapolate to $T_m = T_c$

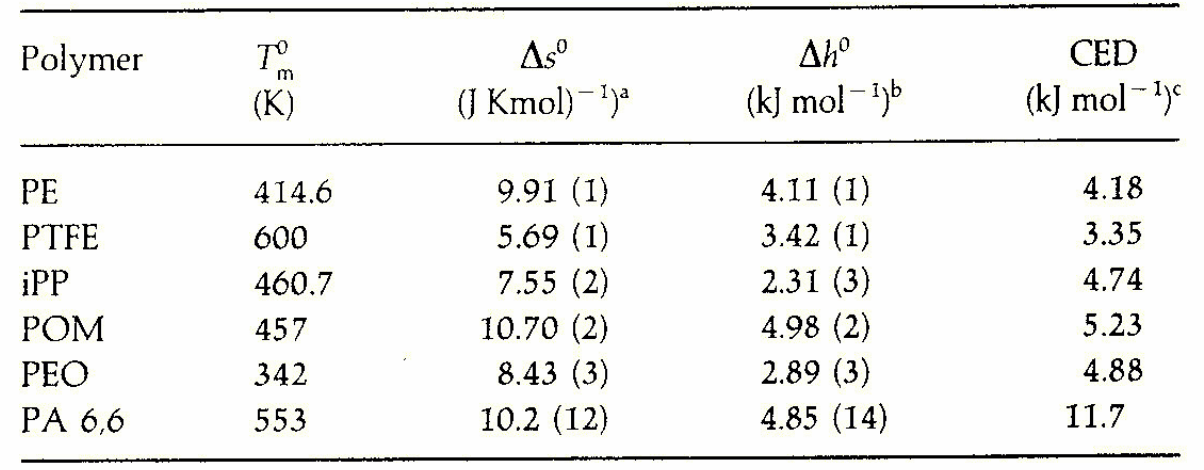
$$T_m = T_m^0\left[1 - \frac{2\sigma}{\Delta h^0 \rho_c L_c^* \beta}\right]$$

$$T_m = T_m^0\left[1 - \frac{2\sigma}{\Delta h^0 \rho_c \beta \dfrac{2\sigma T_m^0}{\Delta h^0 \rho_c (T_m^0 - T_c)}}\right]$$



- T_m^0 and structure
  - $T_m^0 = \Delta H_f^0 / \Delta S_f^0$
    - ΔH_f ~ interchain interaction
    - ΔS_f ~ chain flexibility
  - T_m^0 higher for more regular, rigid, closely-packed, and stronger interaction 🕮Table 8.1

$$T_m^0 = \frac{\Delta h^0 \cdot x}{\Delta s^0 \cdot y}$$



Polymer	T_m^0 (K)	Δs^0 (J Kmol)$^{-1}$)^a	Δh^0 (kJ mol^{-1})^b	CED (kJ mol^{-1})^c
PE	414.6	9.91 (1)	4.11 (1)	4.18
PTFE	600	5.69 (1)	3.42 (1)	3.35
iPP	460.7	7.55 (2)	2.31 (3)	4.74
POM	457	10.70 (2)	4.98 (2)	5.23
PEO	342	8.43 (3)	2.89 (3)	4.88
PA 6,6	553	10.2 (12)	4.85 (14)	11.7

- T_g and T_m are correlated.
  - $T_g = (0.5 \sim 0.8)\ T_m$ (in K)

Melting point depression

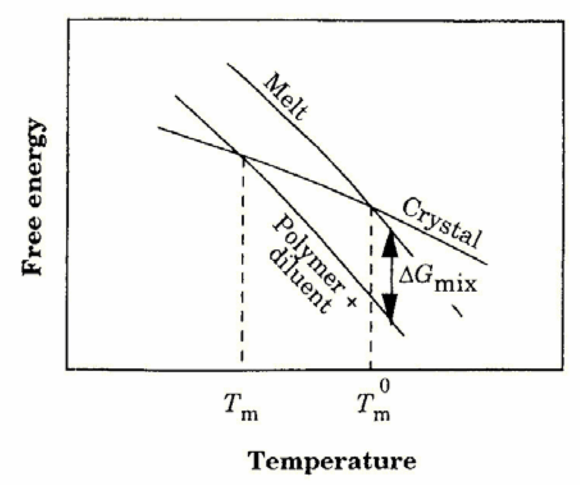
- depression by MW

$$\Delta g = \Delta h^0 - T\Delta s^0 - kT \cdot \frac{\ln(Cx)}{xv} \qquad (8.20)$$

$$T_\mathrm{m} = T_\mathrm{m}^0 \left[1 - \frac{2\sigma}{\Delta h^0 L_\mathrm{c}} - \frac{R T_\mathrm{m}^0 \ln x}{x \Delta h^0} \right] \qquad (8.21)$$

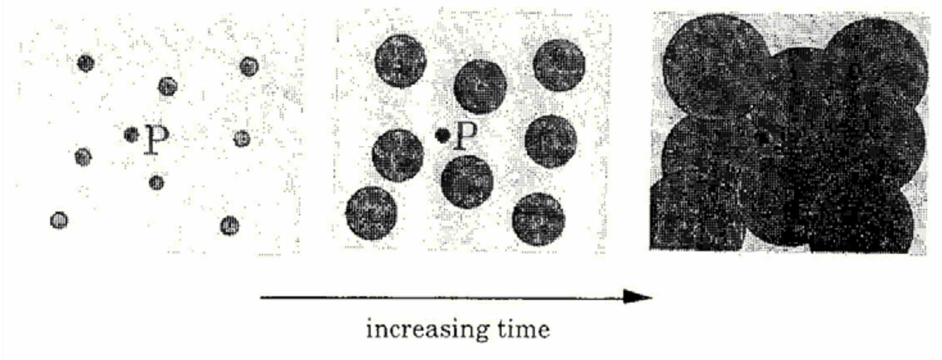
- depression by diluent (low MW or other polymer)

$$\frac{1}{T_\mathrm{m}} - \frac{1}{T_\mathrm{m}^0} = \left(\frac{R}{\Delta h_\mathrm{u}}\right)\left(\left(\frac{V_\mathrm{u}}{V_1}\right)v_1 + \frac{1}{x}\left(v_2 + \frac{1}{x - \zeta_0 + 1}\right) - \left(\frac{V_\mathrm{u}}{V_1}\right)\chi_1 v_1^2\right)$$



Avrami eqn

- describes time-crystallinity relation
  - for any crystallization ~ general
  - useful in molding simulation



- probability of P passed by c waves in t, p(c)

$$p(c) = \frac{\exp(-E)E^c}{c!}$$

E ~ avg # of passing waves for all P

$p(0) = \exp(-E) = 1 - v_c$ ~ no wave passing ~ remain molten (amorphous)

- in athermal nucleation followed by spherical growth
  - nucleation at once and start to grow at t= 0

$$E(t) = \tfrac{4}{3}\pi(\dot{r}t)^3 g$$

$$p(0) = \exp(-E) = 1 - v_c = \exp(-\tfrac{4}{3}\pi\dot{r}^3 g t^3)$$

g ~ vol conc’n of nuclei

- in thermal nucleation
  - sporadic nucleation ~ constant rate in space and time

$$\mathrm{d}E = 4\pi r^2\left(t - \frac{r}{\dot{r}}\right)I^*\,\mathrm{d}r$$

$$E = \int_0^{\dot{r}t} 4\pi r^2 I^*\left(t - \frac{r}{\dot{r}}\right)\mathrm{d}r = \frac{\pi I^* \dot{r}^3}{3}\,t^4$$

$$1 - v_c = \exp\left(-\frac{\pi I^* \dot{r}^3}{3}\,t^4\right)$$

I* ~ # of nuclei/cm^3 s

Avrami eqn

$$1 - v_c = \exp(-Kt^n)$$

- in early stage before impinging

$$v_c = Kt^n$$

~ Göler eqn

$\boxed{e^{-x} = 1 - x \text{ for small } x}$

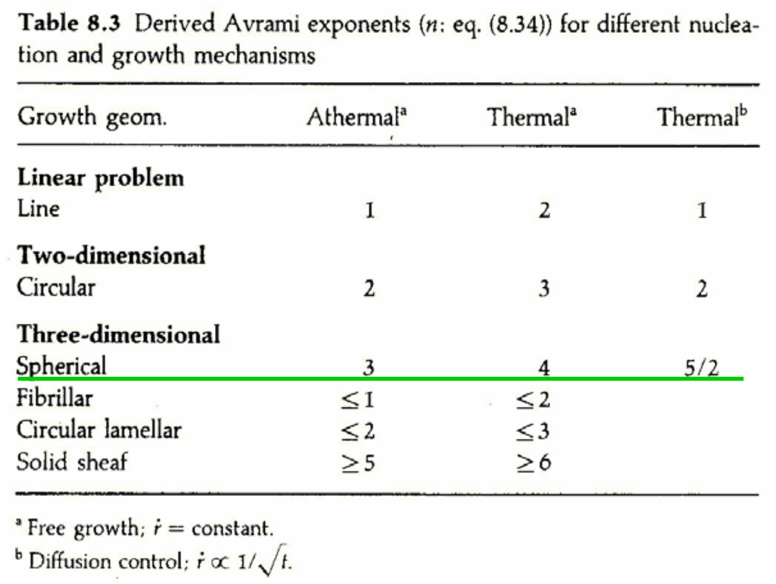


Table 8.3 Derived Avrami exponents (n: eq. (8.34)) for different nucleation and growth mechanisms

Growth geom.	Athermal[a]	Thermal[a]	Thermal[b]
Linear problem			
Line	1	2	1
Two-dimensional			
Circular	2	3	2
Three-dimensional			
Spherical	3	4	5/2
Fibrillar	≤ 1	≤ 2	
Circular lamellar	≤ 2	≤ 3	
Solid sheaf	≥ 5	≥ 6	

[a] Free growth; $\dot{r}$ = constant.

[b] Diffusion control; $\dot{r} \propto 1/\sqrt{t}$.

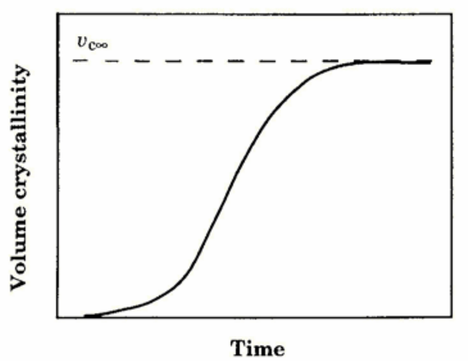
- for diffusion-controlled growth
  - diffusion of impurity
  - $(\acute{r}\ t)^3\ t \rightarrow (\acute{r}\ t^{½})^3\ t$
  - n = 2.5 for sporadic nucleation

- high n for ‘high-dimensional’ growth

- Avrami eqn for polymers
  - semicrystalline

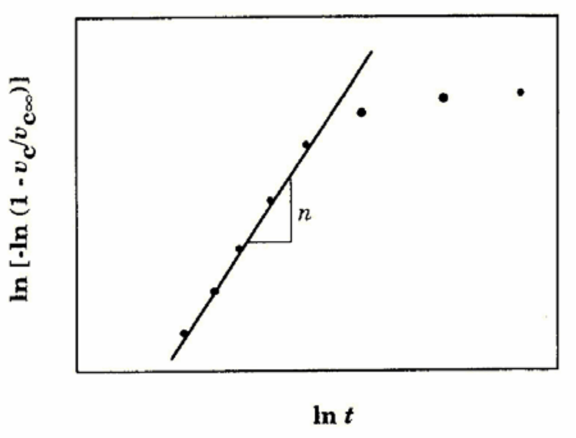
$$1 - \frac{v_c}{v_{c\infty}} = \exp(-Kt^n)$$

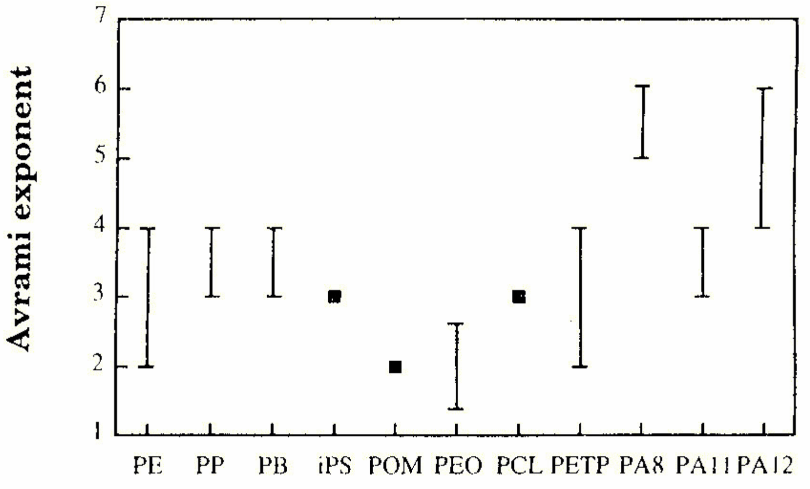
  - n betw 3 and 4
  - primary crystallization only
    - secondary (subsidiary) crystallization slow



- experiments

$$\ln\left[-\ln\left(1 - \frac{v_c}{v_{c\infty}}\right)\right] = \ln K + n \ln t$$





- PE
  - low MW (< 10000) ~ n = 4
    - axialitic growth
  - high MW (< 10^6) ~ n = 3
    - spherulitic growth
  - UHMWPE ~ n = 2
    - slow, low-dimensional growth

Theories for crystal growth

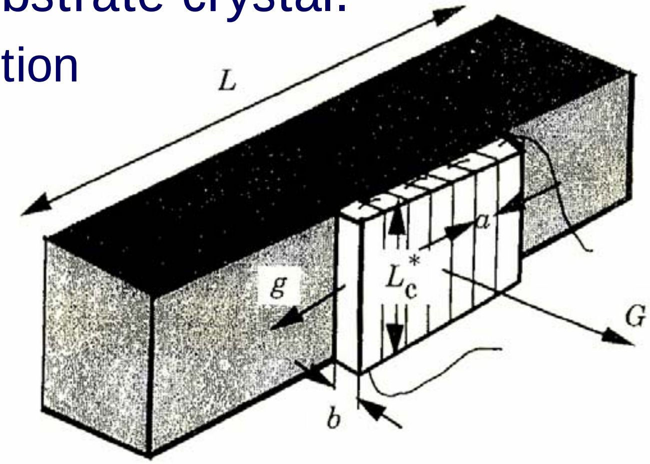
- equilibrium theories
  - Crystal thickness increases with T to a certain T.
  - does not predict the effect of supercooling
  - not popular

- kinetic theories
  - The end-state is not of the lowest possible energy.
  - Crystal growth rate is dep on L_c, which is determined by supercooling.

  - enthalpic nucleation theory ~ Lauritzen-Hoffman theory
  - entropic theory ~ Sadler-Gilmer theory

Lauritzen-Hoffman theory

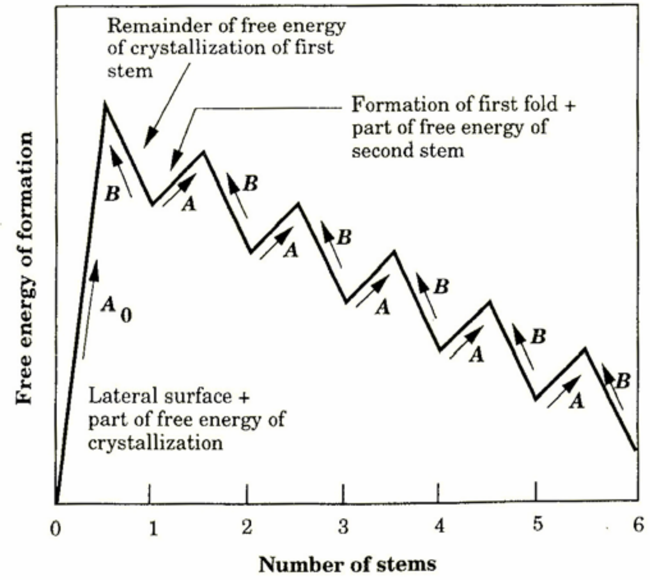
- model
  - (1) Random coil finds a flat surface of substrate crystal.
    - needs a substrate ~ secondary nucleation
  - (2) random coil → extended chain
    - segmental relaxation
  - (3) Chain folds.



- deposit of 1st stem ~ A_0/B
  - secondary ~ 2 sides (+ 2 ends)
  - $A_0 \sim 2bL_c\sigma_L - \psi abL_c\Delta g$
  - $B \sim (1-\psi)abL_c\Delta g$

Δg ~ defined > 0

- 2nd, 3rd, --- stem ~ A/B
  - fold and deposit
  - $A \sim 2ab\sigma - \psi abL_c\Delta g$
  - $B \sim (1-\psi)abL_c\Delta g$



- rate

$$A_0 = \beta \exp\left[- \frac{2bL_c\sigma_L - \psi abL_c\Delta g)}{kT_c} \right]$$

$$\beta = \frac{kT_c}{h} J_1 \exp\left[- \frac{U^*}{R(T_c - T_\infty)} \right] \quad \text{or} \quad \beta = \left(\frac{kT_c}{h}\right)\left(\frac{1}{\bar{M}_z}\right)\exp\left[- \frac{\Delta E_r}{RT_c} \right]$$

$$A = \beta \exp\left[- \frac{(2ab\sigma - \psi abL_c\Delta g)}{kT_c} \right]$$

$$B = \beta \exp\left[- \frac{((1 - \psi)abL_c\Delta g)}{kT_c} \right]$$

- flux

$$S = N_0A_0 - N_1B = N_1A - N_2B = \cdots \quad = N_vA - N_{v+1}B$$

$$N_{v+1} = \left(\frac{A}{B}\right)N_v - \frac{S}{B} \qquad N_{v+1} = \left(\frac{A}{B}\right)^2 N_{v-1} - \frac{S}{B}\left(1 + \frac{A}{B}\right)$$

$$S = N_0A_0\left(1 - \frac{B}{A}\right)$$

$$S(L_c) = N_0\beta\left[\exp\left(- \frac{(2bL_c\sigma_L - \psi abL_c\Delta g)}{kT_c} \right) \times \left[1 - \exp\left(- \frac{(2ab\sigma - abL_c\Delta g)}{kT_c} \right)\right]\right]$$

- crystal thickness

$$L_c^* = \frac{\displaystyle\int_{L_c=2\sigma/\Delta g}^{\infty} L_c S(L_c)\,\mathrm{d}L_c}{\displaystyle\int_{L_c=2\sigma/\Delta g}^{\infty} S(L_c)\,\mathrm{d}L_c}$$

$$L_c^* = \frac{2\sigma}{\Delta g} + \frac{kT}{2b\sigma_L}\cdot\frac{\left(2+(1-2\psi)a\cdot\frac{\Delta g}{2\sigma}\right)}{\left(1-\frac{a\Delta g\psi}{2\sigma_L}\right)\cdot\left(1+\frac{a\Delta g(1-\psi)}{2\sigma_L}\right)} = \frac{2\sigma}{\Delta g} + \delta L_c$$

L_C,min when $T_c = T_m$ from Thompson-Gibbs eqn

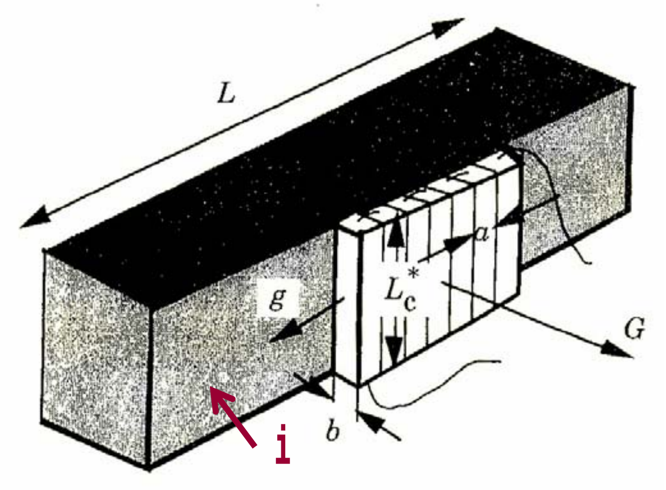
$$T_m = T_m^0\left(1 - \frac{2\sigma}{L_c\rho_c\Delta h^0}\right) \qquad (7.21)$$

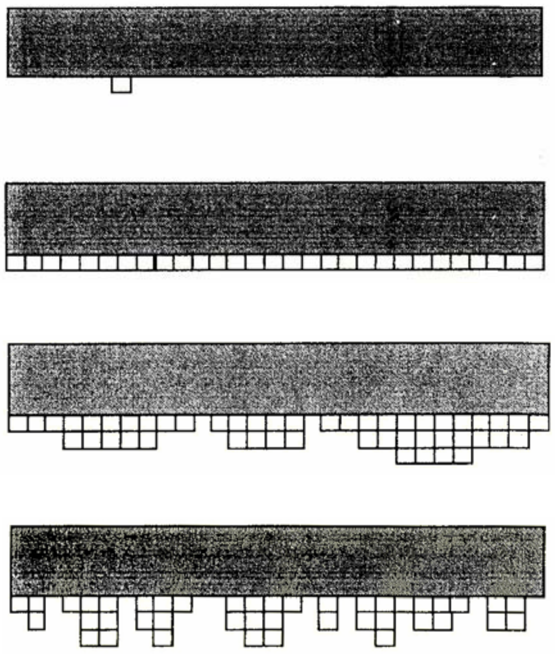
$$L_{c\min} = \frac{2\sigma}{\Delta g} = \frac{2\sigma T_m^0}{\Delta h^0\rho_c(T_m^0 - T_c)}$$

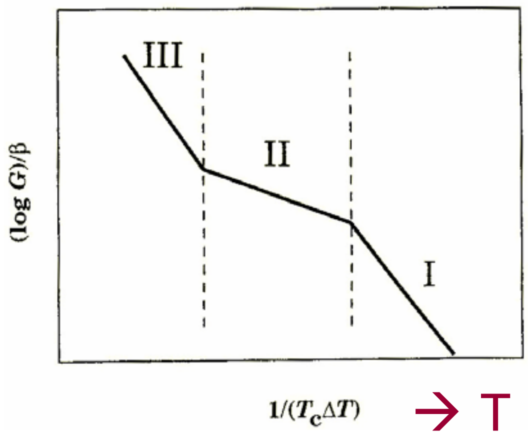
- agrees well with experimental L_c-ΔT relation

- solution-grown crystals ~ large ΔT ~ small L_c (~10 nm)
- melt-grown crystals ~ small ΔT ~ large L_c
    - faster (1) + slower (2) → less perfect crystals

- crystallization regimes
  - regime I
    - small ΔT
    - $g >> i \rightarrow G_I = b\, iL$
    - adjacent reentry
  - regime II
    - $g \leq i \rightarrow G_{II} = b\, (ig)^{1/2}$
  - regime III
    - $g <(<<) i \rightarrow G_{III} = b\, iL$
    - switchboard





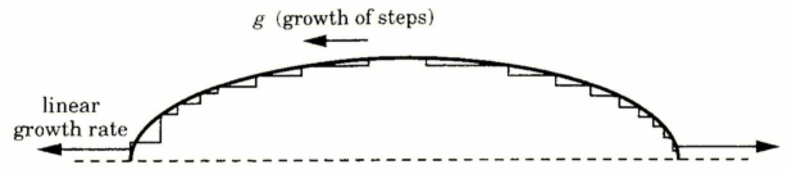


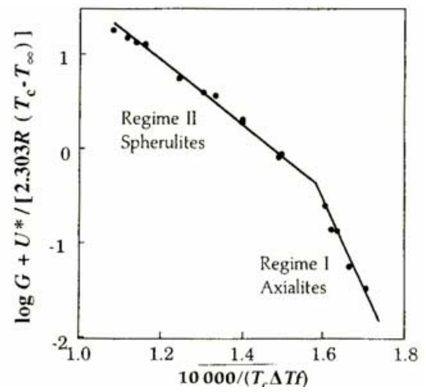
PE

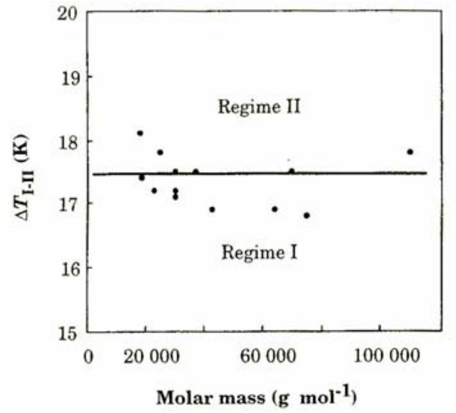
$$L_c^* = \frac{C_1}{\Delta T} + C_2 \qquad (8.76)$$

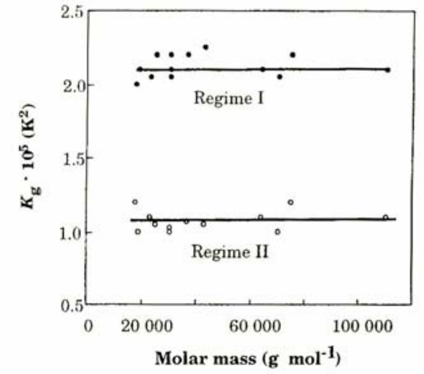
$$G = \beta \exp\left(-\frac{K_g}{T_c \Delta T f}\right) \qquad (8.77)$$

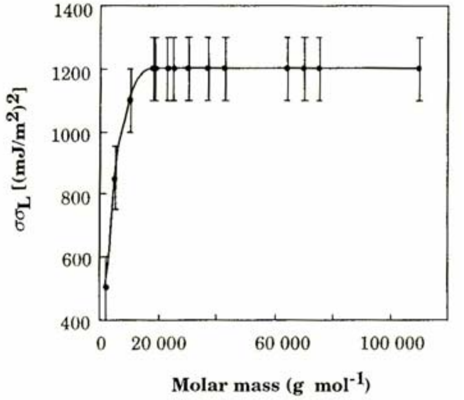
	Regime I	Regime II	Regime III
$K_g{}^a$	$\frac{4b\sigma\sigma_L T_m^0}{\Delta h^0 k}$	$\frac{2b\sigma\sigma_L T_m^0}{\Delta h^0 k}$	$\frac{4b\sigma\sigma_L T_m^0}{\Delta h^0 k}$
ΔT (K)	< 17	17–23	> 23
$\frac{g}{i}$	$\gg 1$	< 1	$\ll 1$
Supermolecular structure	axialitic	spherulitic	spherulitic





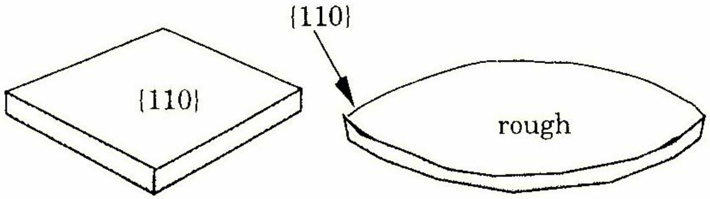






Sadler-Gilmer theory

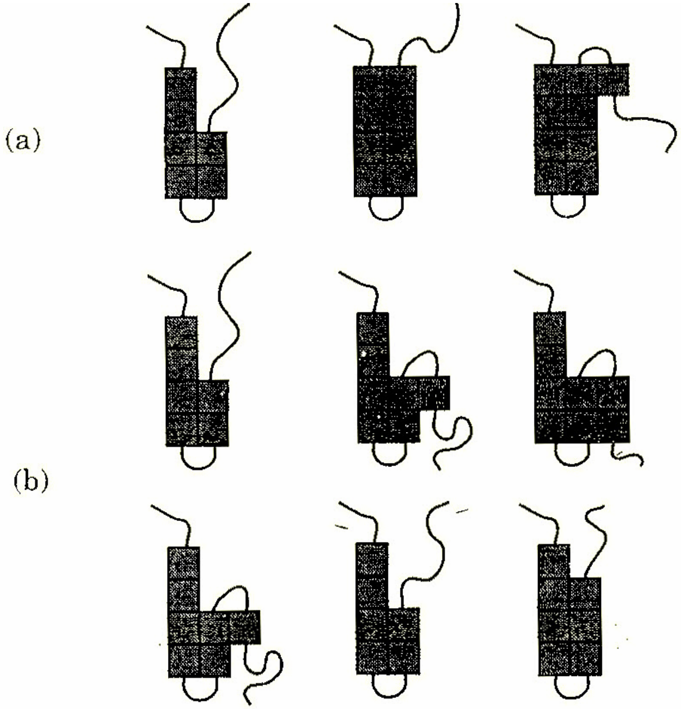
- based on Xtallization behavior of small molecules
  - at $T < T_r$ (roughening temperature)
    - growth with faceted surfaces
  - at $T > T_r$
    - macroscopically round, microscopically rough
  - $G \propto \Delta T$ and $\log G \propto 1/(T_c \Delta T)$
    - free energy barrier is presents at high T, and
    - it should be entropic ← Roughening does not require new surface.
- the same observed in polymer Xtals
  - solution-grown PE Xtals, as T increases
    - diamond → truncated → leaf
  - melt-grown PE Xtals at high T (regime I), isolated
    - rounded crystal with rough surface

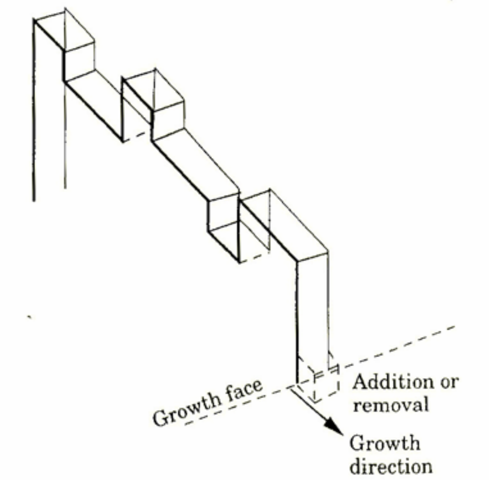


ΔT=45°C; T_c=70°C (p-xylene) ΔT=15°C; T_c=130°C (melt)

- Xtallization with ‘segment’
  - segment shorter than whole stem (L_c)
  - interaction energy betw segment and surface is small
    - for PE ~ segment of 6 repeat units with E ~ 0.6 kT
- Xtallization on a rough surface
  - Segments attached to surface randomly. ~ ‘blind attachment’
  - Stem growth limited. ~ ‘pinning’
  - Non-viable conformations sorted out. ~ ‘detachment’

  - Chain extended and parallel to neighbor participates in crystallization ~ entropic





- rate

$$\frac{k_-}{k_+} = \exp\left(\frac{2\varepsilon}{kT_m^0} - \frac{m\varepsilon}{kT_c}\right)$$

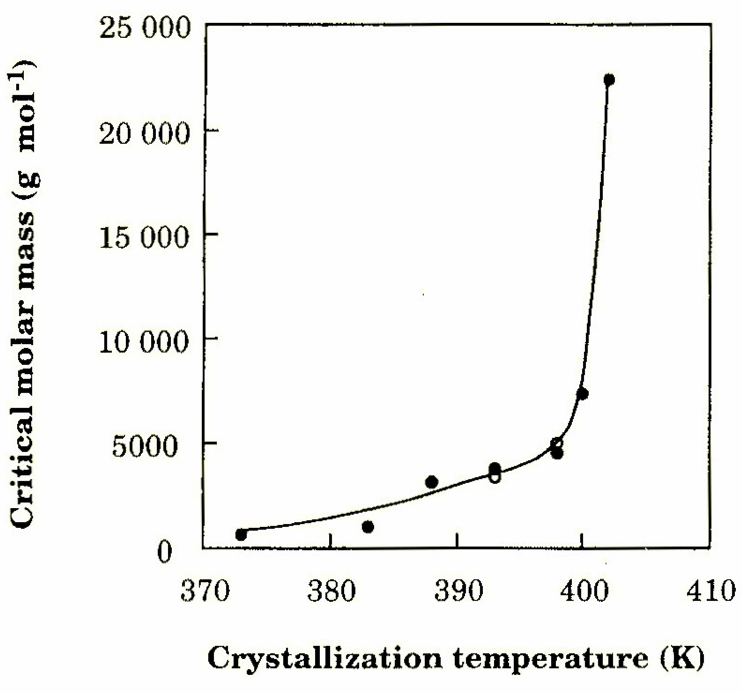
- results

$$G \propto \exp\left(-\frac{K_g}{T_c \Delta T}\right)$$

$$L_c^* = \frac{C}{\Delta T} + \delta L_c$$

Molecular fractionation

- separate Xtallization of different species
    - structure
    - molecular weight
        - Chains with M > M_{crit} only can crystallize.
        - Shorter chains crystallize at a low Temp. ~ subsidiary Xtallization
- dynamic equilibrium
    - betw fully extended-chain crystal and melt
    - Species increasing free energy are rejected.



$$\frac{1}{T_m} - \frac{1}{T_m^0(M)} = \frac{R}{\Delta H} \times [-\ln v_p + (\bar{x} - 1)(1 - v_p) - \bar{x}\chi(1 - v_p)^2]$$

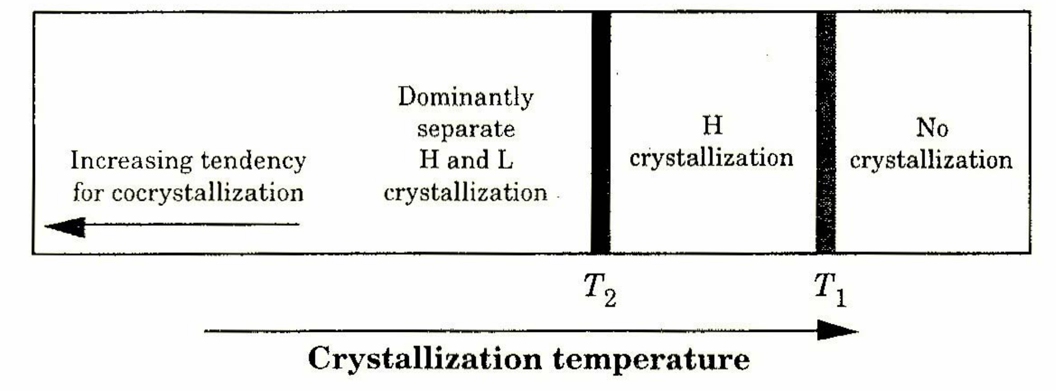
- molecular nucleation
  - At high T, theory and expt agrees.
  - At low T, M_{crit}(calc) < M_{crit}(expt)
    - molecular nucleation before molecular crystallization

$$\Delta G = vabL_c\Delta g + 2bL_c\sigma_L + 2vab\sigma + 2ab\sigma_{ce}$$

      - σ_{ce} ~ free energy associated with chain end, due to entropy reduction of cilia

$$L_{crit} = \frac{4\sigma\sigma_L b(T_m^0)^2}{(\Delta h^0)^2\Delta T^2} + \frac{2\sigma_{ce}T_m^0}{\Delta h^0\Delta T} + \frac{2kT_c T_m^0}{ab\Delta h^0\Delta T}$$

- blends of high- and low-MW polymers



- blends of linear and branched polymers
  - as T_c decreases, L only → L and B separately → L/B cocrystallize

Crystallization and property

- degree of crystallinity
  - modulus, yield strength
- spherulite size
  - clarity, toughness
- structure in spherulite
  - toughness
  - Keith-Padden theory
    - $\delta = D/G$
      - D ~ diffusion of impurity
      - G ~ radial growth rate
      - d ~ coarseness of lamellae