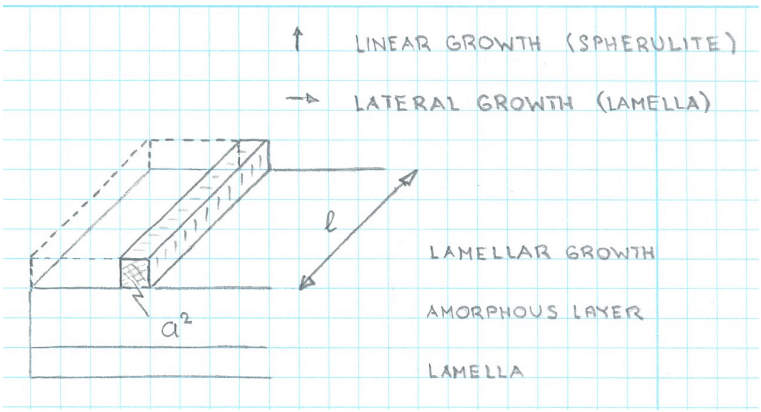
Lamellar Growth: Lateral vs Linear [pln55]

Chain-folded lamellae are not equilibrium structures.

Lamellae of width l grow laterally at temperature $T < T_\mathrm{m}(l) < T_\mathrm{m}(\infty)$,

- $T_\mathrm{m}(\infty)$: bulk melting temperature,
- $T_\mathrm{m}(l)$: threshold temperature of lateral growth,
- $\lim_{l\to\infty} T_\mathrm{m}(l) = T_\mathrm{m}(\infty)$.



Change in free energy when one stem of volume la^2 is added to lamella:

$$\Delta g = -\frac{L_\mathrm{m}}{T_\mathrm{m}(\infty)}\,(la^2)\Delta T + 2a^2\sigma_\mathrm{f}, \tag{1}$$

- L_m: latent heat of melting per unit volume,
- $\Delta T = T_\mathrm{m}(\infty) - T$: amount of undercooling,
- σ_f: interfacial energy per unit area,
- $L_\mathrm{m}/T_\mathrm{m}(\infty)$: entropy density of polymer stem in coil conformation.

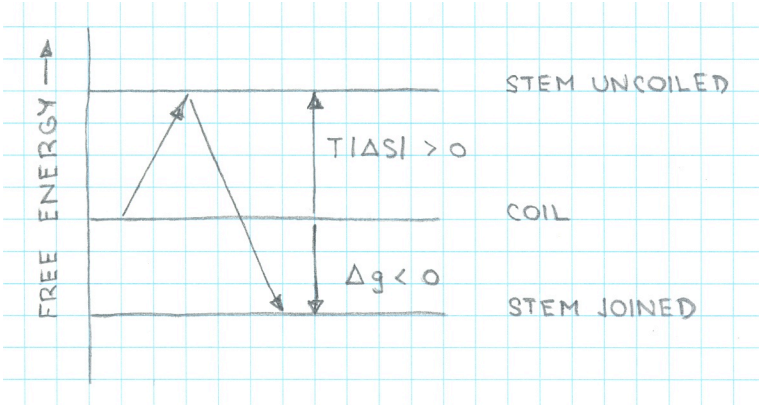
Condition for lateral growth: $\Delta g < 0$ implying $l > l_\mathrm{c}$ at given ΔT.

Threshold width $l_\mathrm{c}(\Delta T)$ or threshold temperature $T_\mathrm{m}(l)$ inferred from criterion $\Delta g = 0$ [pex37]:

$$l_\mathrm{c}(\Delta T) = \frac{2\sigma_\mathrm{f} T_\mathrm{m}(\infty)}{L_\mathrm{m}\Delta T}, \quad T_\mathrm{m}(l) = T_\mathrm{m}(\infty)\left[1 - \frac{2\sigma_\mathrm{f}}{L_\mathrm{m} l_\mathrm{c}}\right]. \tag{2}$$

Fastest lateral lamellar growth occurs at preferred width l^* (to be determined). Criterion involves a free energy barrier:

- To join the lamella, a stem of width l must straighten out; the uncoiling reduces the entropy, $\Delta S < 0$, thus raises the free energy, $T|\Delta S| > 0$.
- The joining of straightened out stem to lamella reduces the enthalpy, $\Delta H < 0$, thus lowers the free energy by the same amount.
- Net change of free energy: $\Delta g = T|\Delta S| - |\Delta H| < 0$.
- Entropy: $|\Delta S|/k_\mathrm{B} = l/l_0$ (emprirical model).



Transition rates:

- melt $\to$ crystal: $u_\mathrm{MC} = \dfrac{1}{\tau}\exp\left(-\dfrac{T|\Delta S|}{k_\mathrm{B}T}\right)$,
- crystal $\to$ melt: $u_\mathrm{CM} = \dfrac{1}{\tau}\exp\left(-\dfrac{T|\Delta S| - \Delta g}{k_\mathrm{B}T}\right)$.

Empirical model for reference time scale borrowed from [pln24]: Vogel-Fulcher relaxation time near glass transition:

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right). \tag{3}$$

Rate of crystal growth:

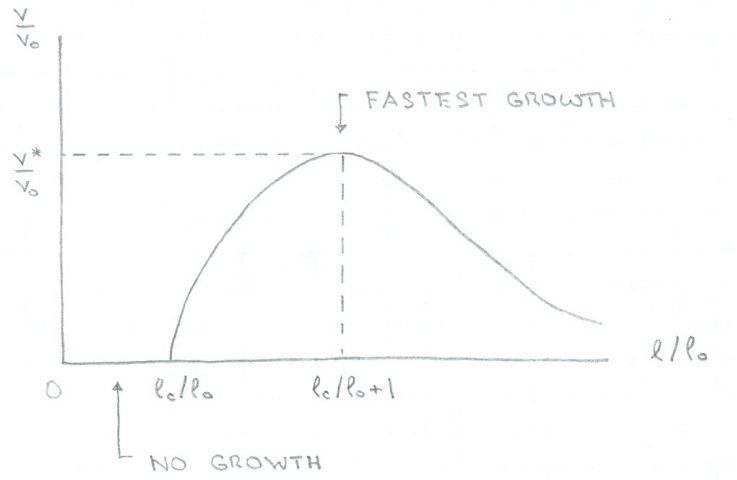
$$\begin{aligned} u \doteq u_\mathrm{MC} - u_\mathrm{CM} &= \frac{1}{\tau}\exp\left(-\frac{T|\Delta S|}{k_\mathrm{B}T}\right)\left[1 - \exp\left(\frac{\Delta g}{k_\mathrm{B}T}\right)\right] \\ &\overset{|\Delta g| \ll k_\mathrm{B}T}{\rightsquigarrow} -\frac{1}{\tau}\exp\left(-\frac{|\Delta S|}{k_\mathrm{B}}\right)\frac{\Delta g}{k_\mathrm{B}T}. \end{aligned} \tag{4}$$

Velocity of crystal growth, $v \doteq ua$, at given T using (1) and (4) [pex37]:

$$v(l) = v_0 e^{-l/l_0} \left[\frac{l}{l_c} - 1 \right], \quad v_0 = \frac{2\sigma_f a^3}{\tau k_B T}. \tag{5}$$

Fastest growth from $(dv/dl)_{l^*} = 0$ [pex37]:

$$\Rightarrow \; l^* = l_\mathrm{c} + l_0, \quad \frac{v(l^*)}{v_0} = \frac{l_0}{l_\mathrm{c}} e^{-1-l_\mathrm{c}/l_0}. \tag{6}$$



With deeper quench, meaning larger undercooling ΔT, the lamellar width l^* of fastest growth becomes thinner.

Evaluate fastest-growth velocity (5) using (3) [pex37]:

$$v(l^*) = \frac{l_0 a^3 L_\mathrm{m} e^{-1}}{k_\mathrm{B} T \tau_0 T_\mathrm{m}(\infty)} \underbrace{\exp\left(\frac{-B}{T - T_0}\right)}_{(i)} \underbrace{\Big[T_\mathrm{m}(\infty) - T\Big] \exp\left(-\frac{2\sigma_\mathrm{f} T_\mathrm{m}(\infty)}{l_0 L_\mathrm{m}[T_\mathrm{m}(\infty) - T]}\right)}_{(ii)}.$$

(i) factor controlling mobility of polymer in melt,

(ii) factor controlling thermodyanmic driving fore.

The final morphology is far from equilibrium. In practice, the morphology with the lowest free energy not really attainable.

[extracted in part from Jones 2002]