

The Melting Temperature of Polymers

1. Semi-crystalline Nature of Polymers

Polymers are never 100% crystalline: even highly crystalline materials such as high-density polyethylene (HDPE) contain substantial amorphous fractions. Most engineering polymers are in fact **semi-crystalline** and consist of crystalline lamellae embedded in an amorphous matrix.

Why incomplete crystallization? Several polymer-specific factors frustrate perfect crystallization:

- **chain entanglements:** in the melt, long chains are topologically interlaced. Crystallization requires local alignment and unfolding of chain segments. Entanglements severely hinder large-scale disentanglement, thus preventing the formation of extended defect-free crystals. Instead, chains crystallize in folded conformations, yielding thin lamellae (typically ~5–30 nm thick).
- **chain ends and molar mass distribution:** chain ends differ from chain-internal repeat units and cannot be regularly incorporated into a periodic crystal lattice.
- **structural irregularities:** atactic sequences, comonomer units, or branches are incompatible with a periodic lattice and are expelled into amorphous regions.

As a result, polymer crystals are not extended three-dimensional objects but thin platelets (lamellae) embedded in amorphous material. This two-phase morphology governs both optical and mechanical behavior: scattering and refractive-index contrast make many semi-crystalline polymers opaque, while their mechanical and thermal properties result from the combined response of crystalline and amorphous regions.

2. The Thermodynamic Melting Temperature

For a perfect, infinite crystal, stability is governed by the Gibbs free energy. The crystalline phase is stable if its Gibbs free energy is lower than that of the corresponding amorphous phase. At equilibrium, the two phases coexist when

$$\Delta G = \Delta H - T\Delta S = 0 \quad , \quad (1)$$

which defines **the thermodynamic melting temperature T_{m0} :**

$$T_{m0} = \frac{\Delta H}{\Delta S} \quad . \quad (2)$$

Here, ΔH and ΔS are the enthalpy and entropy changes per unit volume (units: J m^{-3} and $\text{J m}^{-3} \text{K}^{-1}$, respectively). Consequently, a large enthalpy change ΔH (strong cohesive energy, efficient packing, or strong intermolecular interactions such as hydrogen bonding) increases T_{m0} . A small entropy change ΔS (for example, if chains are already somewhat extended in the melt) also increases T_{m0} .

Thus, as for the glass transition temperature T_g , **chain rigidity and specific interactions raise the melting point**. For polymers, however, T_{m0} is only of theoretical nature: it cannot be measured directly, since real polymer crystals are finite lamellae whose thickness is kinetically determined (see below).

3. The Melting Temperature of Lamellae

Polymer crystals grown from melts or dilute solutions are not infinite lattices but **lamellar platelets**. Their lateral dimension can reach micrometers, but their thickness l is limited to only a few to few tens of nanometers. Chains fold back at the lamella surfaces, thus creating fold planes that carry an excess free energy per unit area, the **fold surface free energy** σ_e (unit: J m^{-2}). Lateral surfaces contribute an additional surface free energy σ_l , but for thin lamellae the fold surface contribution dominates.

Consider the energetic contributions to the stability of a single lamella of surface area A and thickness l (volume: $V = A \cdot l$):

- the stabilizing **bulk free-energy gain from crystallization** is proportional to the lamella volume: $-\Delta g_v Al$, where Δg_v is the Gibbs free energy difference per unit volume between crystal and melt (unit: J m^{-3} ; positive if the crystal is favored).
- **surface free-energy penalty** from the upper and lower fold planes: $2\sigma_e A$ in total.

The total free-energy change for the lamella is therefore

$$\Delta G_{\text{lamella}} \approx -\Delta g_v \cdot Al + 2\sigma_e \cdot A \quad (3)$$

The volumetric Gibbs free energy Δg_v can be expressed in enthalpic and entropic terms:

$$\Delta g_v = \Delta h_v - T_m \Delta s_v \quad (4)$$

with Δh_v and Δs_v the enthalpy and entropy of crystallization per unit volume. At the apparent melting temperature T_m , the total free-energy change vanishes, i.e. $\Delta G_{\text{lamella}} = 0$. Therefore:

$$\Delta g_v = \Delta h_v - T_m \Delta s_v = \frac{2\sigma_e}{l} \quad (5)$$

Solving for the melting temperature T_m leads to

$$T_m = \frac{\Delta h_v}{\Delta s_v} - \frac{2\sigma_e}{\Delta s_v \cdot l} \quad (6)$$

Using Equation 2 to introduce T_{m0} , this can be rearranged to the **Thomson-Gibbs equation**:

$$T_m = \frac{\Delta h_v}{\Delta s_v} \left(1 - \frac{2\sigma_e}{\Delta h_v \cdot l}\right) = T_{m0} \left(1 - \frac{2\sigma_e}{\Delta h_v \cdot l}\right) \quad (7)$$

The corresponding melting point depression ΔT relative to the thermodynamic reference is inversely proportional to lamella thickness:

$$\Delta T = T_{m0} - T_m = \frac{2\sigma_e}{\Delta h_v \cdot l} . \quad (8)$$

Thus, the observed melting temperature of a lamella is always lower than the thermodynamic melting temperature. It must be kinetically controlled! Only for infinitely thick lamellae does $T_m \rightarrow T_{m0}$. Under common processing conditions, lamellae of about 10 nm thickness are typically obtained, which melt 30–50 °C below T_{m0} . This reduction reflects the balance between the stabilizing bulk free-energy gain (scaling with lamella volume) and the destabilizing surface free-energy penalty associated with the fold plane area.

4. Kinetic Selection of the Lamellar Thickness

The Thomson-Gibbs equation (Equation 7) shows that, thermodynamically, thicker lamellae melt at higher temperature and the equilibrium limit corresponds to $l \rightarrow \infty$. In practice, lamellae are thin (typically 5–20 nm) because **nucleation and crystal growth are time-dependent, kinetic processes**. The lamellar thickness observed in a sample is therefore kinetically selected according to the supercooling, transport rates, and topological constraints (entanglements). Below, we derive expressions for the critical thickness and the nucleation barrier using a simple, physically transparent model.

Given that the lamellar thickness is, however, rather small (often 5–20 nm), a significant degree of supercooling takes place before a polymer crystallizes (Equation 8). The reason is of kinetic origin: the lamellar thickness is selected by the interplay of nucleation barriers, growth rates, and the increasing viscosity of the undercooled melt.

Consider the nucleation of a lamellar crystallite consisting of n stems, each with cross-sectional area a^2 and length l . For simplicity, we approximate the arrangement of stems in the lamellar cross-section by a circular shape. This is a convenient construction since many polymers crystallize from regular conformations (e.g. zig-zag) that resemble cylinders when viewed along the chain axis. The volume and the surface areas of the nucleus are then:

$$V_{\text{nucleus}} = na^2l , A_{\text{fold}} = na^2 , A_{\text{lat}} = 2\sqrt{\pi}\sqrt{na}l . \quad (9-11)$$

Here, the lateral area is obtained as the perimeter of the circular cross-section ($2\sqrt{\pi}\sqrt{na}$) multiplied by the nucleus thickness l . The total free energy of nucleus formation is the sum of a bulk stabilization term and the two surface penalties:

$$\Delta G_{\text{nucleus}} = na^2l \cdot (-\Delta g_v) + 2na^2 \cdot \sigma_e + 2\sqrt{\pi}\sqrt{na}l \cdot \sigma_l . \quad (12)$$

The volumetric free-energy difference can be related to the degree of supercooling ΔT :

$$\Delta g_v = \Delta h_v - T\Delta s_v = \Delta h_v \left(1 - T \frac{\Delta s_v}{\Delta h_v}\right) = \Delta h_v \left(1 - \frac{T}{T_{m0}}\right) = \Delta h_v \left(\frac{T_{m0} - T}{T_{m0}}\right) = \frac{\Delta h_v \Delta T}{T_{m0}} . \quad (13)$$

For a nucleus to be stable against dissolution, the free-energy change must be negative. For a given thickness l , the lamella may or may not develop into a crystal depending on whether the bulk stabilization compensates the fold-surface penalty. The critical value for l at which crystallization becomes thermodynamically possible can be determined by analyzing the limit $n \rightarrow \infty$ (since the final crystal dimension will be macroscopically large in n). In this limit, the lateral surface term ($\propto \sqrt{n}$) is negligible compared to the bulk and fold terms (both $\propto n$), and the sign of $\Delta G_{\text{nucleus}}$ only depends on the choice of l . Thus, stability requires

$$na^2l \cdot \Delta g_v \geq 2na^2 \cdot \sigma_e \quad , \quad (14)$$

which defines the **critical lamellar thickness l^*** :

$$l \geq l^* = \frac{2\sigma_e}{\Delta g_v} = \frac{2\sigma_e T_{m0}}{\Delta h_v \Delta T} \quad . \quad (15)$$

Below this thickness, nuclei are unstable and re-dissolve. **The critical thickness decreases with increasing supercooling ΔT : the deeper the melt is undercooled, the thinner the lamellae that can form.** Physically, this reflects the competition between the bulk driving force (favoring crystallization) and the fold-surface penalty (destabilizing thin lamellae).

Equation 15 therefore defines the minimum lamellar thickness required for stability in the limit of infinite lateral extension. However, real nuclei do not appear with infinite lateral size but they begin as small clusters with finite n , where the lateral surface penalty cannot be ignored. In this finite- n regime, Equation 15 is necessary but not sufficient. Although $l > l^*$ allows stability in principle, a nucleus must reach a **critical lateral size n^*** in order to overcome the perimeter penalty.

Stability is therefore a two-dimensional problem in the (l, n) plane: the lamellar thickness l sets the thermodynamic possibility for stability, while the lateral size n determines whether this stability can actually be realized. The **nucleation barrier ΔG^*** arises from this interplay.

Mathematically, this means that for a fixed lamellar thickness l , we must analyze the dependence of $\Delta G_{\text{nucleus}}(l, n)$ on n . The critical lateral size n^* is then found by extremizing $\Delta G_{\text{nucleus}}$ with respect to n :

$$\frac{\partial \Delta G_{\text{nucleus}}}{\partial n} = -\Delta g_v \cdot a^2 l + 2\sigma_e \cdot a^2 + 2\sqrt{\pi} a l \cdot \sigma_l \frac{1}{2\sqrt{n}} = 0 \quad . \quad (16)$$

Rearranging gives the **critical lateral size**:

$$n^* = \frac{\pi \sigma_l^2 l^2}{(l \Delta g_v - 2\sigma_e)^2 a^2} \quad . \quad (17)$$

Substituting Equation 17 into Equation 12 (see Equations A1–A3 in the Appendix) yields the **nucleation barrier ΔG^*** :

$$\Delta G^* = \frac{\pi \sigma_l^2 l^2}{l \Delta g_v - 2\sigma_e} \quad . \quad (18)$$

Equation 18 is only defined if $l\Delta g_v - 2\sigma_e > 0$, i.e. $l > l^*$. Otherwise, no finite n exists and the nucleus is thermodynamically unstable. At the boundaries $l \rightarrow l^*$ and $l \rightarrow \infty$, ΔG^* diverges to infinity.

- As $l \rightarrow l^*$, the driving force is only marginally sufficient to overcome the fold penalty, so an extremely large lateral size would be required, leading to an effectively infinite barrier.
- As $l \rightarrow \infty$, the numerator of Equation 18 ($\propto l^2$) dominates over the denominator ($\propto l$), and the barrier again diverges.

Thus, ΔG^* possesses a finite minimum at an intermediate lamellar thickness. This minimum corresponds to the kinetically selected (most probable) lamellar thickness observed in practice.

We find the optimal thickness l_{opt} by minimizing Equation 18 with respect to l (see Equations A4–A6 in the Appendix):

$$\frac{d\Delta G^*}{dl} = \pi\sigma_l^2 \frac{2l(l\Delta g_v - 2\sigma_e) - l^2\Delta g_v}{(l\Delta g_v - 2\sigma_e)^2} = 0 \quad . \quad (19)$$

The numerator vanishes when

$$2(l\Delta g_v - 2\sigma_e) - l\Delta g_v = 0 \quad \rightarrow \quad l\Delta g_v = 4\sigma_e \quad . \quad (20)$$

Thus,

$$l_{\text{opt}} = \frac{4\sigma_e}{\Delta g_v} = 2l^* \quad . \quad (21)$$

Reinserting into Equation 18 gives the **minimum nucleation barrier**:

$$\Delta G_{\text{min}}^* = \frac{\pi\sigma_l^2 \left(\frac{4\sigma_e}{\Delta g_v}\right)^2}{\frac{4\sigma_e}{\Delta g_v} \Delta g_v - 2\sigma_e} = \frac{8\pi\sigma_l^2\sigma_e}{\Delta g_v} \quad . \quad (22)$$

This is exact within our model. The numerical prefactor 8π depends on the assumed geometry. Other choices (different packing, shapes) change the prefactor but not the scaling. The robust feature is the dependence on supercooling, obtained Equation 13:

$$\Delta G_{\text{min}}^* \propto \frac{\sigma_l^2\sigma_e}{\Delta g_v^2} = \frac{\sigma_l^2\sigma_e T_{\text{m0}}^2}{(\Delta h_v \Delta T)^2} \quad . \quad (23)$$

The energetic barrier therefore decreases rapidly with increasing ΔT . This explains why lamellar thicknesses in the range 5–20 nm are observed in practice: they correspond to values near $2l^*$, where the barrier is minimized and nucleation occurs most readily.

While an infinitely thick lamella would be most stable thermodynamically (at T_{m0}), its barrier is infinite, and such lamellae cannot form by nucleation within any finite timescale.

Appendix

To derive Equation 18, it is useful to individually evaluate the terms of Equation 12 at the critical lateral size n^* . From the terms linear in n :

$$n^* a^2 \cdot (-\Delta g_v l + \sigma_e) = a^2 (-\Delta g_v l + \sigma_e) \frac{\pi \sigma_l^2 l^2}{(l \Delta g_v - 2 \sigma_e)^2 a^2} = -\frac{\pi \sigma_l^2 l^2}{l \Delta g_v - 2 \sigma_e} . \quad (\text{A1})$$

From the perimeter term proportional to \sqrt{n} :

$$\sqrt{n^*} \cdot 2\sqrt{\pi} a l \cdot \sigma_l = 2\sqrt{\pi} a l \cdot \sigma_l \frac{\sqrt{\pi} \sigma_l l}{(l \Delta g_v - 2 \sigma_e) a} = \frac{2\pi \sigma_l^2 l^2}{l \Delta g_v - 2 \sigma_e} . \quad (\text{A2})$$

Summing both contributions yields Equation 18:

$$\Delta G^* = -\frac{\pi \sigma_l^2 l^2}{l \Delta g_v - 2 \sigma_e} + \frac{2\pi \sigma_l^2 l^2}{l \Delta g_v - 2 \sigma_e} = \frac{\pi \sigma_l^2 l^2}{l \Delta g_v - 2 \sigma_e} . \quad (\text{A3})$$

To locate the extremum of ΔG^* with respect to l , we differentiate Equation 18 using the quotation rule:

$$\frac{d}{dl} \left(\frac{u(l)}{v(l)} \right) = \frac{u'(l)v(l) - u(l)v'(l)}{(v(l))^2} \quad \text{with} \quad u(l) = \pi \sigma_l^2 l^2 \quad \text{and} \quad v(l) = l \Delta g_v - 2 \sigma_e . \quad (\text{A4})$$

The derivatives are:

$$u'(l) = 2\pi \sigma_l^2 l \quad \text{and} \quad v'(l) = \Delta g_v . \quad (\text{A5})$$

Substitution gives Equation 19 of the main text:

$$\frac{d\Delta G^*}{dl} = \frac{(2\pi \sigma_l^2 l)(l \Delta g_v - 2 \sigma_e) - (\pi \sigma_l^2 l^2) \Delta g_v}{(l \Delta g_v - 2 \sigma_e)^2} = \pi \sigma_l^2 \frac{2l(l \Delta g_v - 2 \sigma_e) - l^2 \Delta g_v}{(l \Delta g_v - 2 \sigma_e)^2} . \quad (\text{A6})$$