

Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 16

**Morphology of Semicrystalline
Polymers**

February 23, 2001

Semicrystalline Polymers

Objectives

- To introduce the concept of a **unit cell** as the minimum structure necessary to replicate all of a perfect crystal through translational operations.
- To describe the relationship between the morphology of polymer **single crystals** prepared by crystallization from dilute solution and **bulk** polymers prepared by crystallization from the melt.
- To describe **spherulitic growth**, the predominant morphological feature of bulk semicrystalline polymers.
- To introduce some of the structure-property relationships for polyolefins prepared by metallocene synthetic routes.

Outline

- **Molecular Requirements for Crystallization**
 - Planar zigzag and helical chain conformations
 - Unit cell structures for polyethylene and polypropylene
- **Spherulitic Morphology**
 - Initial stages of nucleation and growth
 - Impingement of spherulites
 - Lamellar ribbons
 - Comparison of spatial scales
- **Chain Conformation**
 - Necessity for chain folding
 - Adjacent re-entry vs. switchboard models for solution
 - Chain incorporation in multiple lamellae for a melt
 - Tie chains
- **Morphology of Polyolefins from Metallocene Catalysts**

Polymer Morphology

- Morphology is the **science of form and structure**. It provides the link between the molecular structure and the bulk properties.
- As applied to polymers, morphology involves the study of the **arrangement** of polymer molecules into **crystalline and amorphous regions**.
- Polymers with **higher crystallinity** are denser, stiffer, harder, tougher and more resistant to solvents.
- **Amorphous** domains add **flexibility** and promote **ease of processing** below the melting temperature.

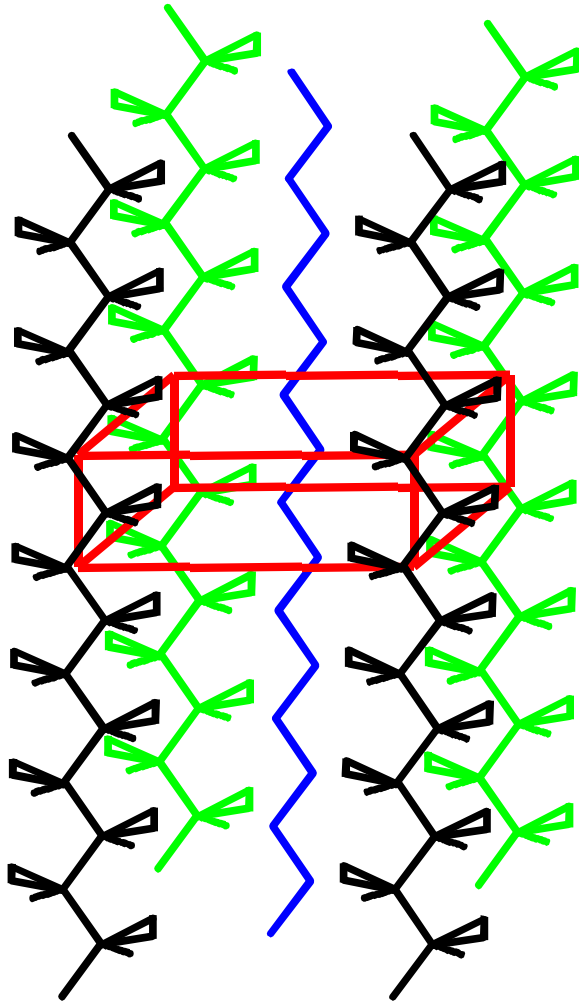
Molecular Requirements for Crystallization: Polymer Configuration

- The configuration is fixed by the chemical synthesis.
- There should be **no defects** (branches, crosslinks, and excessive end groups), which will lead to disturbances within the crystal or rejection from the crystal.
- The size and disposition of a **side group** is important.
- If the structure is **irregular**, the side groups must be **small**, e.g., poly(vinyl alcohol) and poly(vinyl fluoride).
- Side groups may be of **significant size** if they are disposed **regularly** and symmetrically, e.g., isotactic and syndiotactic vinyl polymers and regularly repeating condensation polymers.

Molecular Requirements for Crystallization: Polymer Conformation

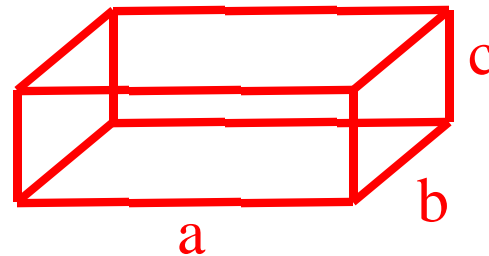
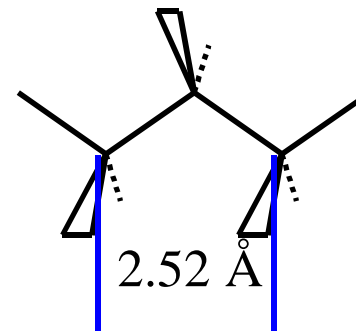
- The conformation is based on rotations about flexible backbone bonds and may be altered by annealing and/or mechanical stress.
- **Random** coil conformations occur in solution and the melt.
- **Ordered** chain conformations exist in crystals.
- **Extended chain** conformations (planar zigzag) are possible if the substituents are **small**, e.g., polyethylene, poly(vinyl alcohol), most polyamides, syndiotactic poly(vinyl chloride), syndiotactic 1,2-polybutadiene.
- **Helical** conformations result for **bulky** substituents, e.g., most isotactic and 1,1-disubstituted polymers.

Polyethylene Unit Cell



Orthorhombic unit cell

- Each polyethylene chain is in an extended **planar zigzag** conformation.
- The **c axis** is always along the **chain direction**.

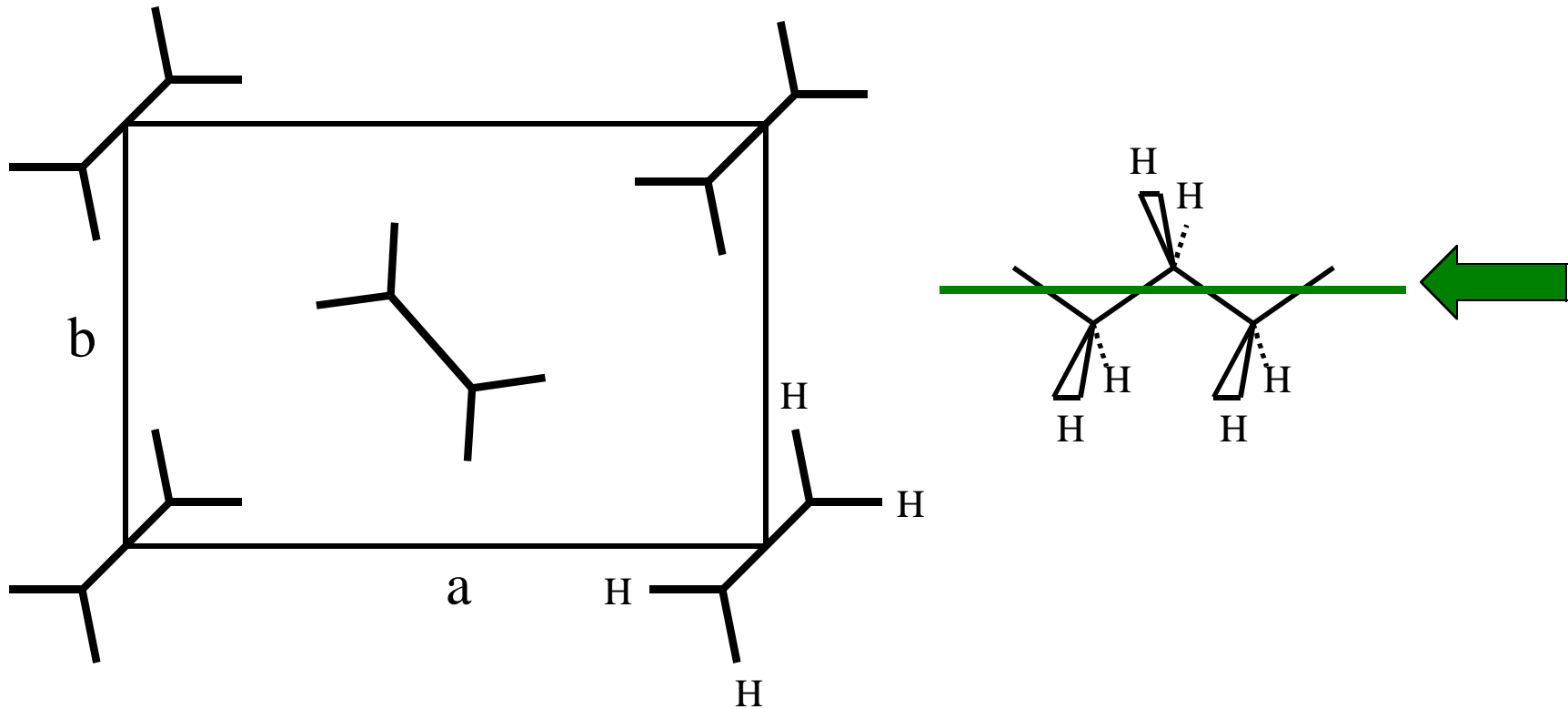


$$a = 7.41 \text{ \AA}$$

$$b = 4.94 \text{ \AA}$$

$$c = 2.55 \text{ \AA}$$

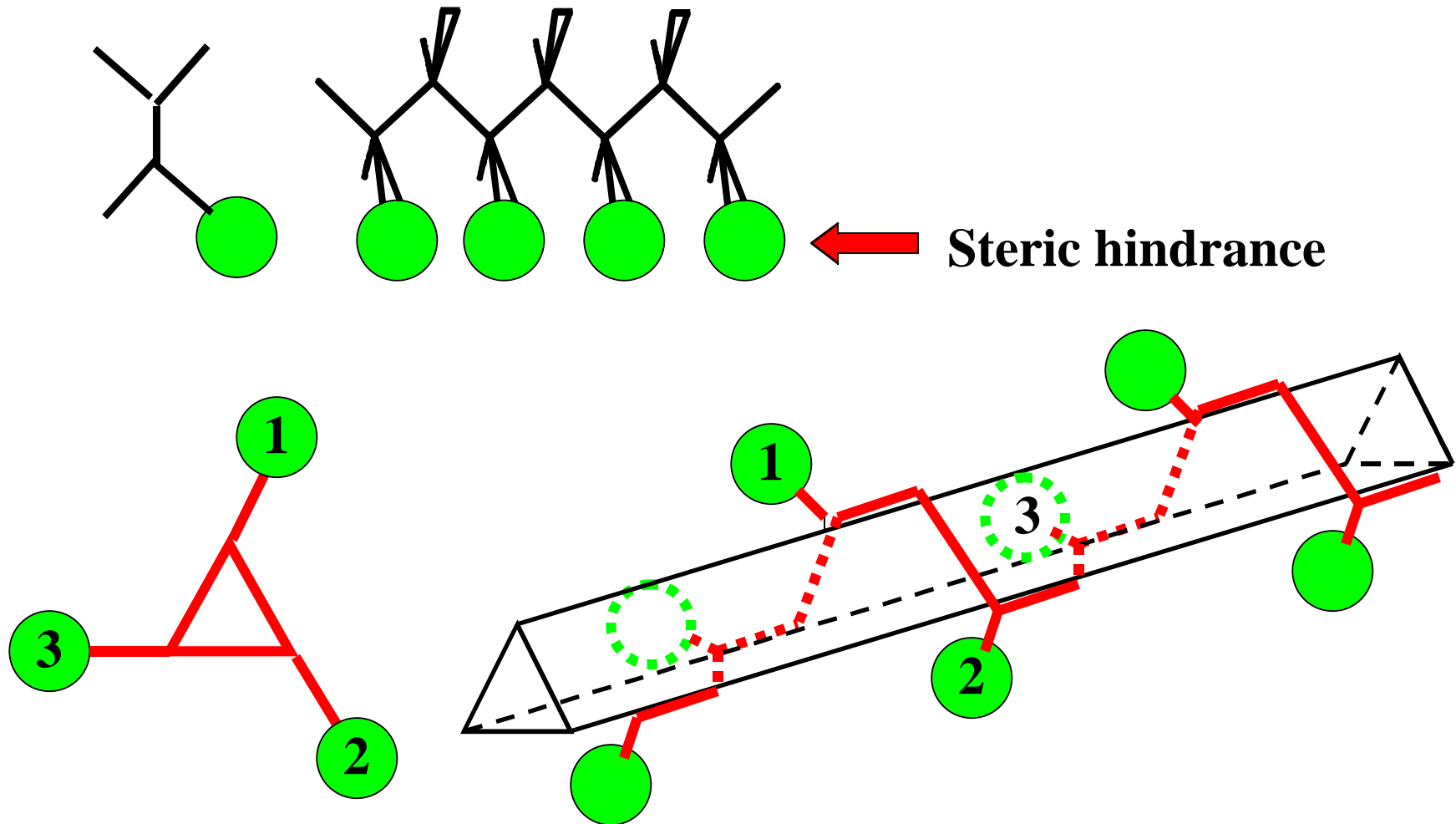
Polyethylene Unit Cell



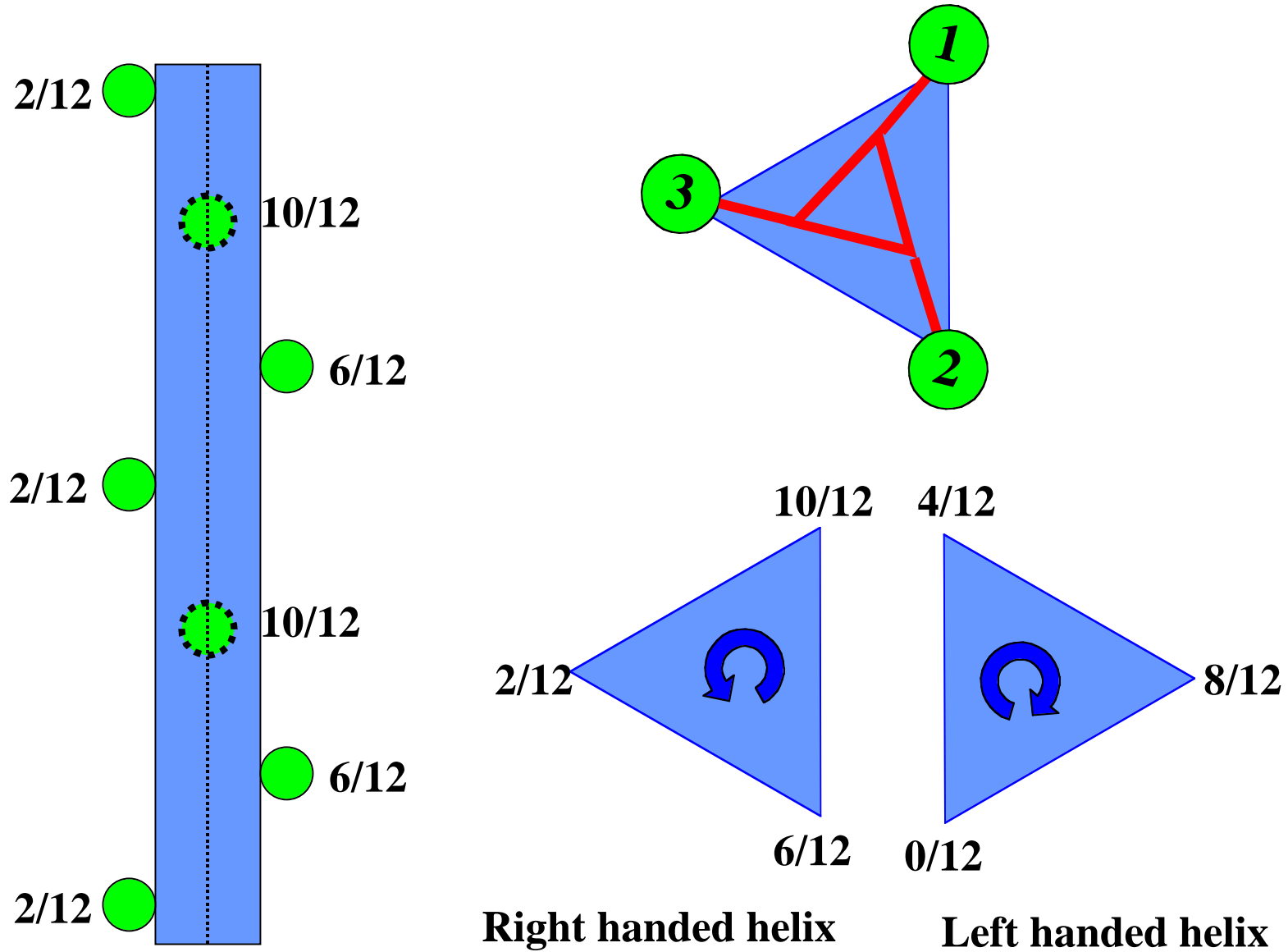
- The view is from above, looking along the chain axis.
- There are **two chains per unit cell** for polyethylene.
- The orthorhombic unit cell has high packing efficiency; 73% of space is occupied.

Helical Conformations of Isotactic Polymers

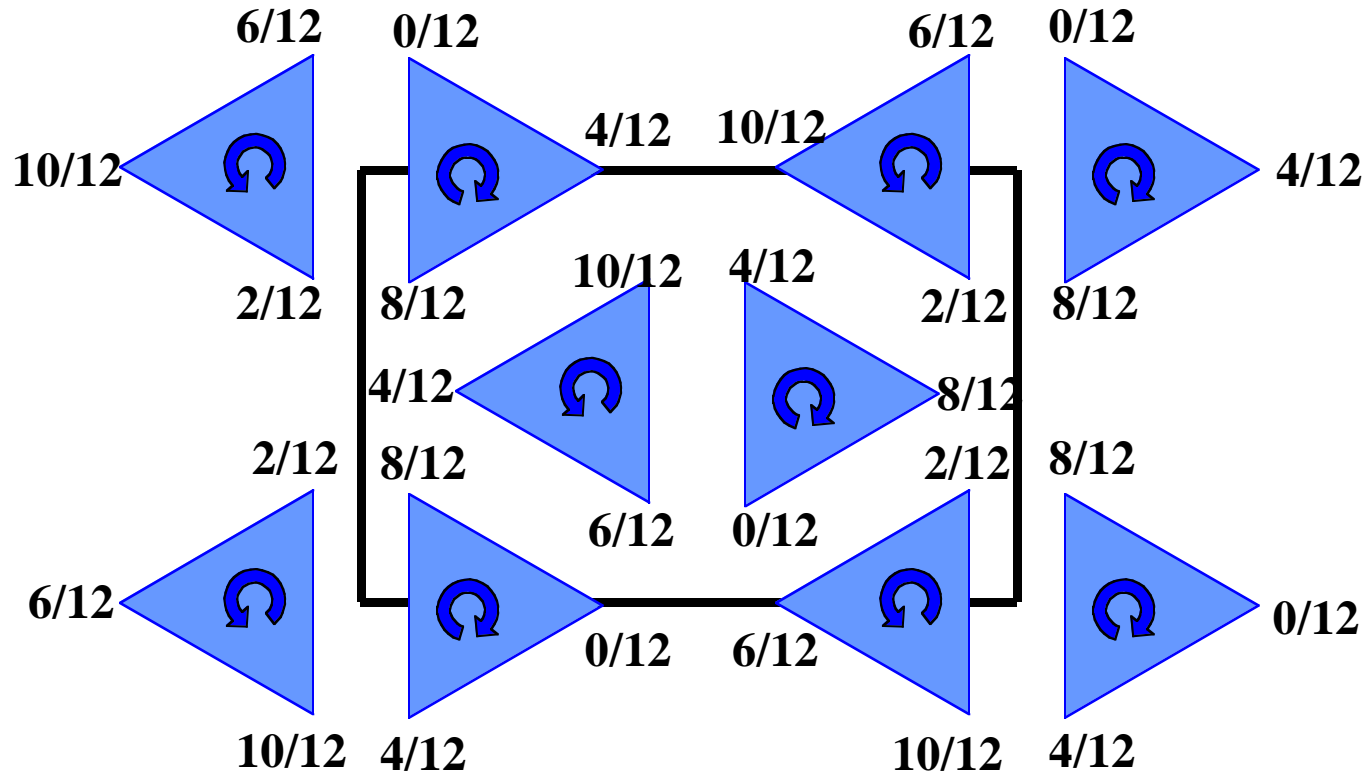
Steric hindrance between pendent groups can cause the most stable individual chain conformation to be a **helical** structure.



Polypropylene Helical Conformation

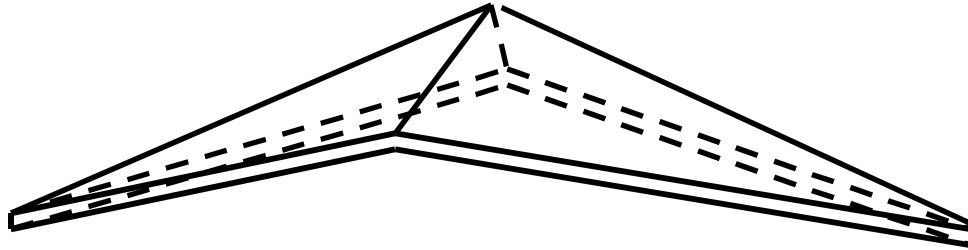


Polypropylene Monoclinic Unit Cell



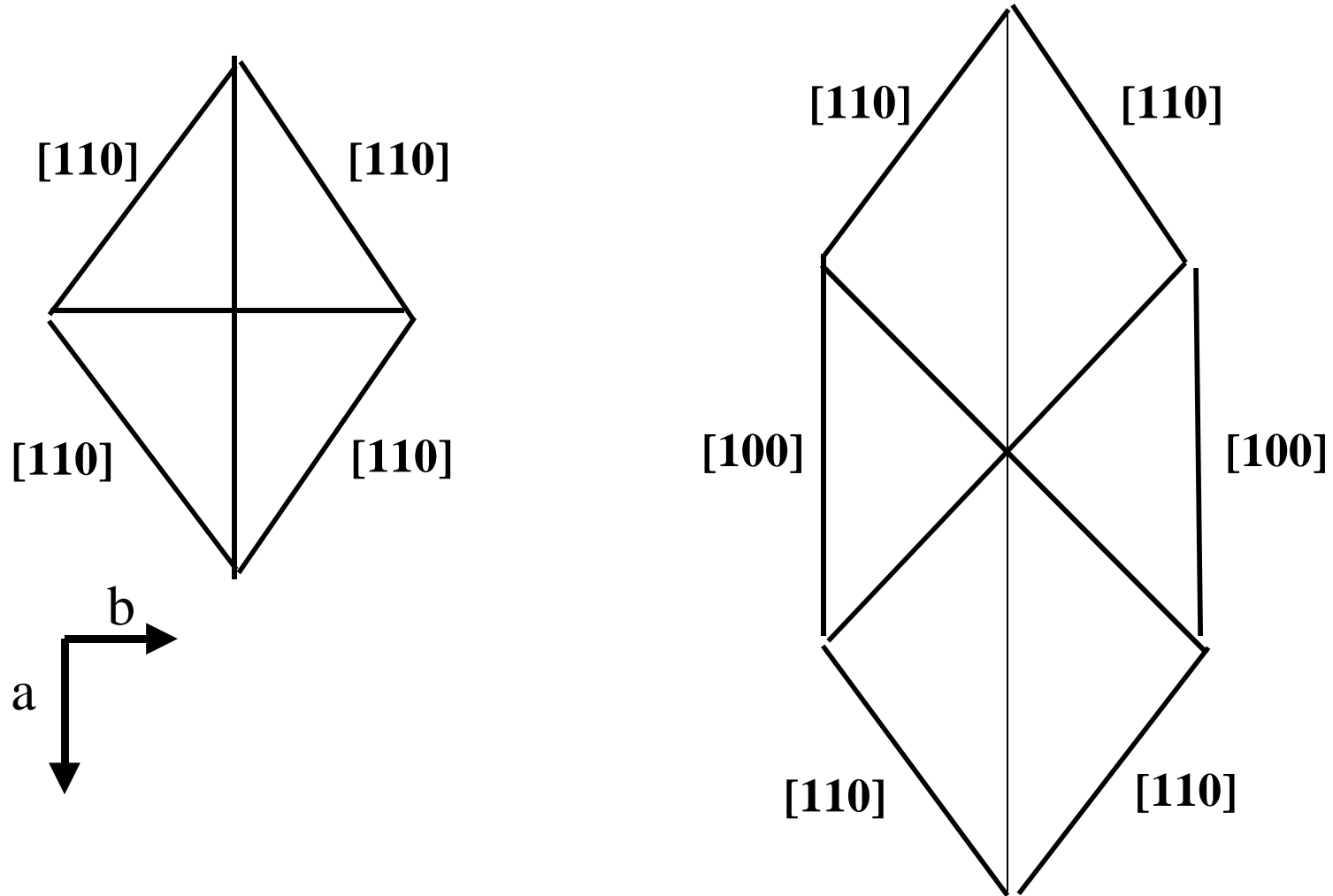
Up-down directional disorder of helical chains may also occur.

Polyethylene Single Crystals

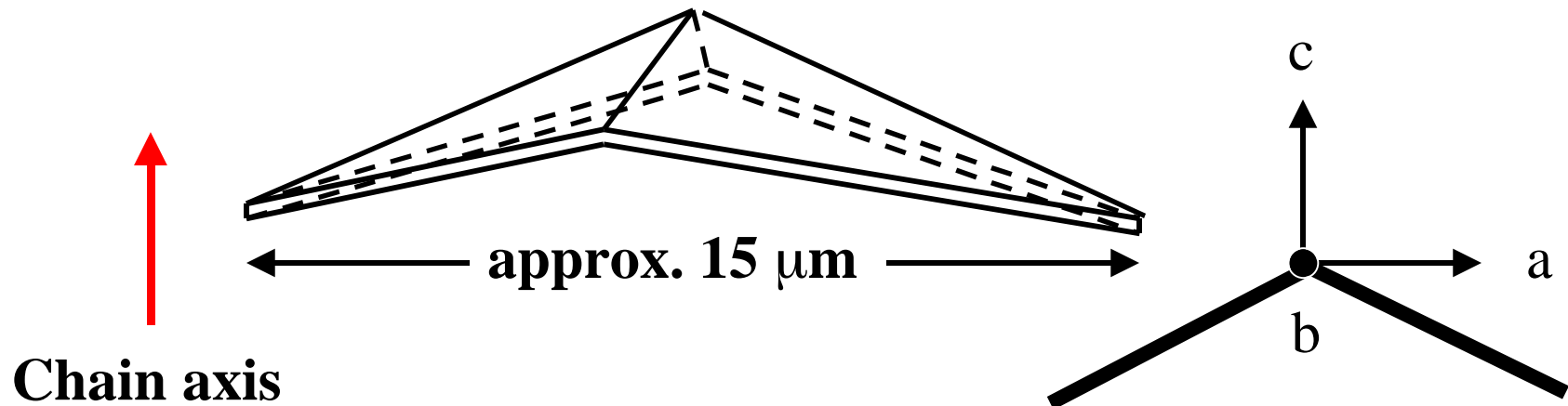


- Single crystals may be obtained by cooling a dilute solution (0.1%) from above the melting temperature. Often hollow pyramids are formed that collapse to diamond-shaped platelets upon removal of the solvent.

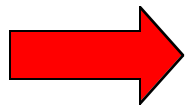
Polyethylene Single Crystal Sectorization



Solution Crystallization: Chain Folding

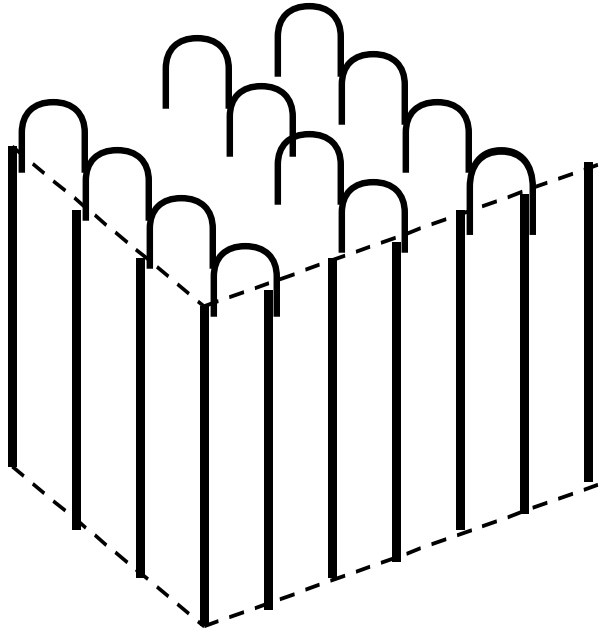


- For a polyethylene chain of molecular weight 280,000, there will be 10,000 repeat units and a contour length of 25,000 Å.
- The platelets are thin (100 - 200 Å) with electron diffraction showing that the polymer chain axis is generally **perpendicular** to the crystal basal plane.

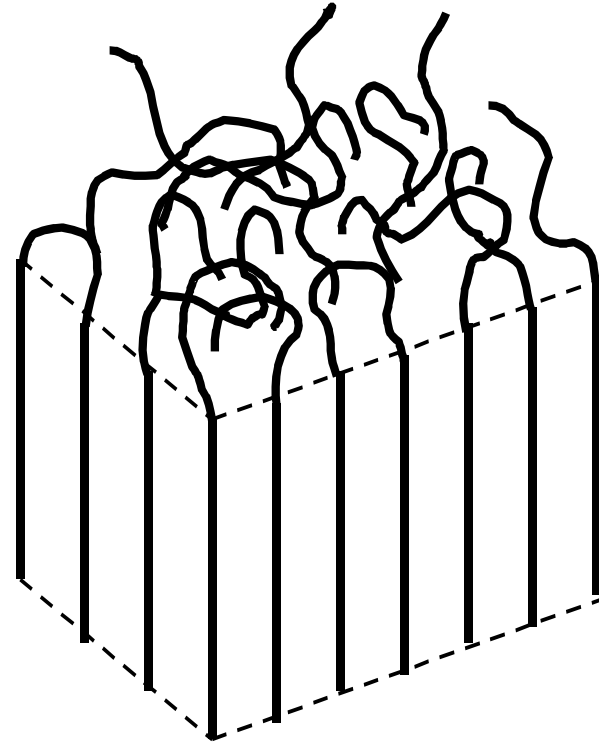


Chain folding must occur, but how?

Solution Crystallization: Chain Folding



Adjacent Re-entry Model



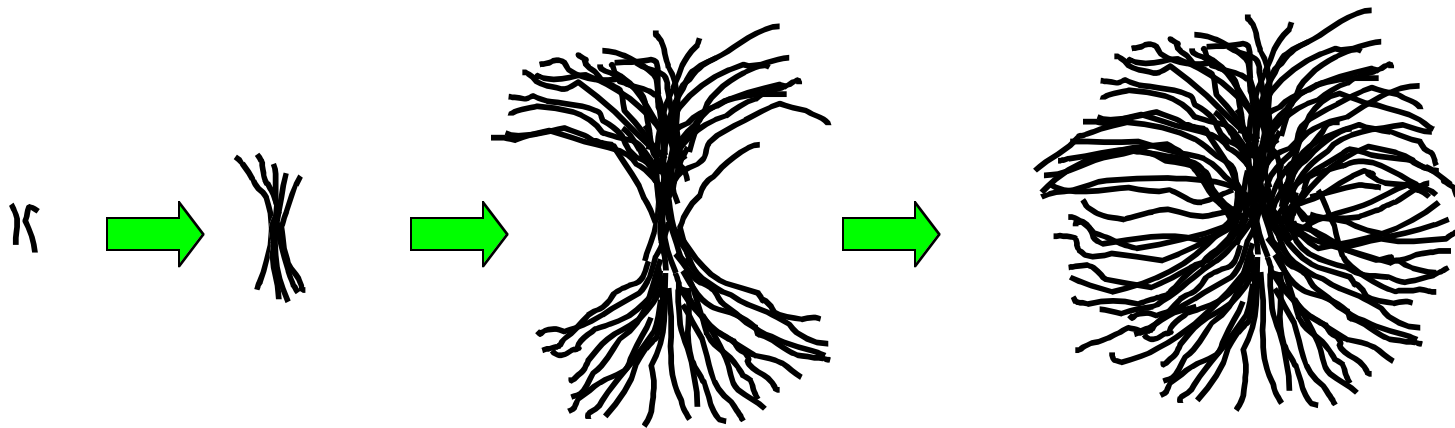
Switchboard Model

- Early models of chain folding in single crystals were highly controversial. The currently accepted model is intermediate between the adjacent reentry and switchboard models.

Comparison of Solution and Melt Crystallization

- In both cases, the driving force for the chain to uncoil from a high entropy conformation is a lowering of the enthalpy due to the formation of favorable **secondary interactions**.
- The significant difference is that, in contrast to the dilute solution case, **chain entanglement** in the melt may lead to restricted growth and crystalline imperfections.

Initial Stages of Spherulite Growth

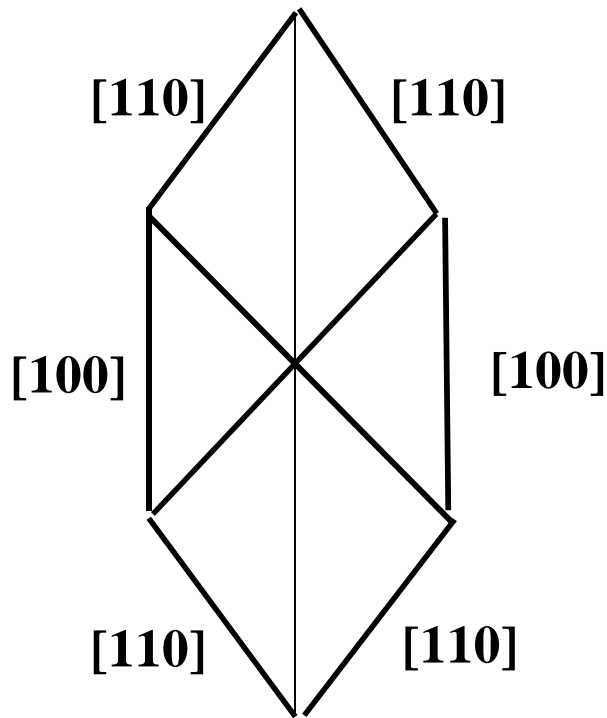


Homogeneous nucleation: Chance collisional encounters of chain segments of suitable orientation lead to a cluster from which growth proceeds. For polyethylene, this is effective only for supercooling of 50 to 80 K.

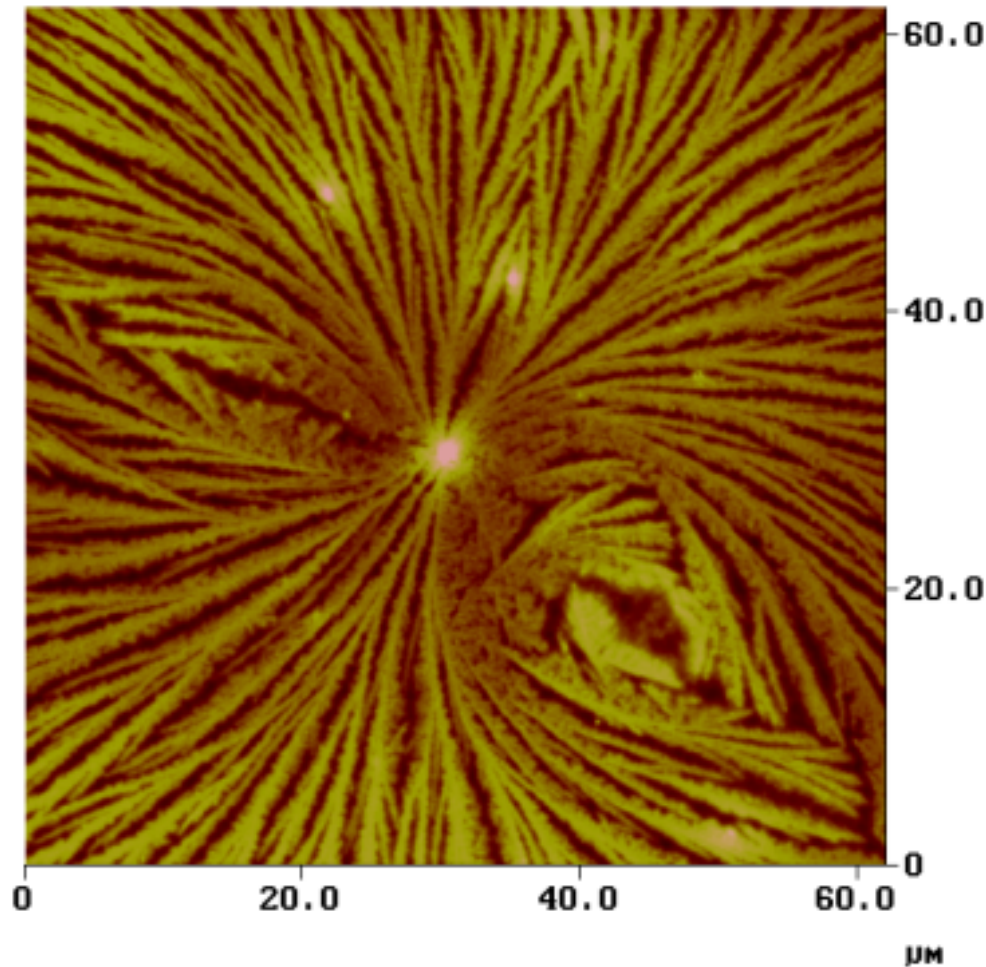
Heterogeneous nucleation: Adventitious impurities, residual crystalline polymer that has not completely melted, finely dispersed solids (carbon black, silica, talc) or the container wall may serve as nucleating agents. For polyethylene, this is effective for supercooling of 20 to 25 K.

Spherulite Growth: Extended Lamellae

- Elongated crystals are formed into **twisted ribbons** that radiate out from the nucleation center of the spherulite.
- These ribbons are related to single crystals in their general crystallographic structures, but are significantly more **disordered**.



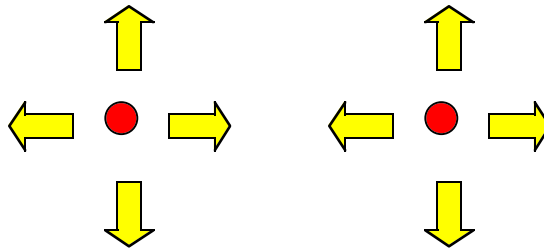
- Lamellar outlines sometimes follow low index crystallographic directions.
- $\{110\}$ directions are close packed, whereas $\{100\}$ directions are more open.



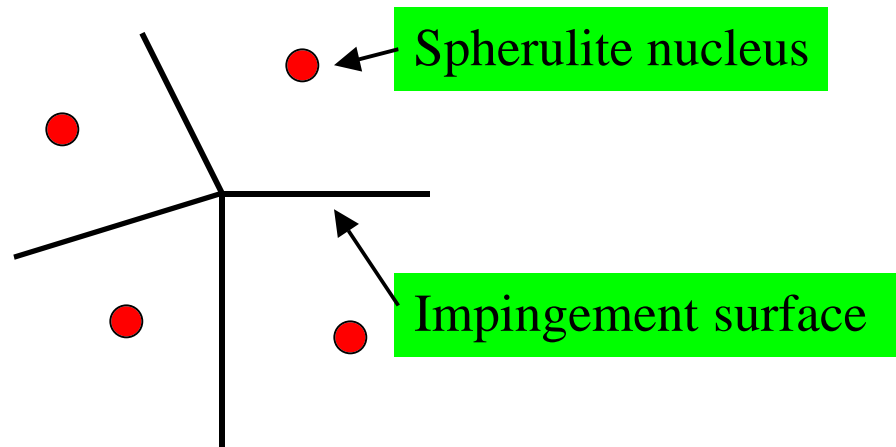
Tapping Mode Atomic Force Microscopy: Height image of **elastomeric polypropylene** crystallized isothermally at 130°C in a 200 nm thin film on Si (z scale from dark to bright 200 nm).

Spherulite Growth: Impingement

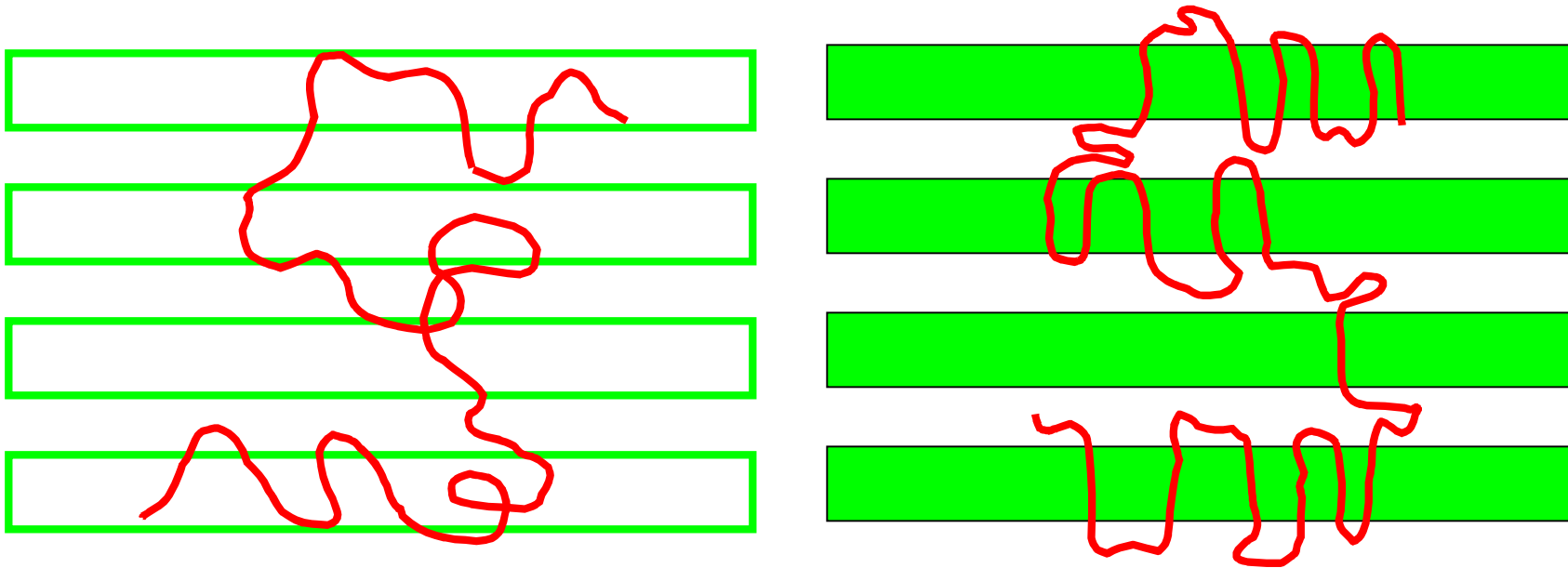
If crystallization is halted due to quenching before spherulite growth is complete, the bulk morphology consists of crystalline spherulites embedded in an amorphous matrix.



Normal spherulite growth in the bulk proceeds until impingement with another spherulite occurs.



Crystallization from the Melt: Single Chain Conformation



Diffusional limitations in the entangled melt retard center-of-mass diffusion during rapid cooling. Stem segment incorporation into multiple lamellar ribbons is easy, however.

Crystallization from the Melt: Tie Chains

- For high nucleation rates, slow diffusion in the melt, and high molecular weight, a single chain can be incorporated into two widely separated crystalline domains.
- As crystallization proceeds, the chain molecule will become a stretched “tie chain” and act as a template for condensation of other melt molecules, thus forming macroscopic fibrils.

