

4 Crystalline solid state materials and defect structures

4.1 What are the prerequisites of the formation of polymer crystals? Discuss the terms **infrastructure**, **constitution**, **configuration**, and **conformation**.

A prerequisite to form a crystal out of macromolecules is the necessary symmetry with respect to constitution, configuration and conformation. Lattice planes in 3D space have to be established. Within the crystal the regular sequence of conformation leads to parallel chains of molecules. The sequence of conformation determines the crystal structure.

Electrostatic interactions are responsible for the formation of polymeric solid states, such as thermoplastics, out of (macro-) molecules. The interactive forces between the (linear) molecules result in a 3D arrangement, i.e. the crystalline lattice in polymers. These interactions are superimposed with the covalent bonds within macromolecules and networks in elastomers, if the distances are small enough.

The related energies E_B are often 2 orders of magnitude smaller than for covalent bonds. The intermolecular distances are of the order of 1 nm.

The formation of crystalline solid states out of polymers depends on the 3D arrangement (**infrastructure**) within the molecule, the **constitution**, the **configuration**, and the **conformation**.

Infrastructure is the 3D arrangement of atoms within the molecule.

Constitution describes the chemical connections. i.e. the arrangement of atoms along the chains, substitutes, and end groups, the sequence, type, and length of side groups as well as molecular weight distribution. It is usually given by the monomeric components, which could be symmetric or asymmetric.



Figure 1: Example of linear constitution (thermoplastics).



Figure 2: Example of ramified constitution (thermoplastics).



Figure 3: Example of constitution: Interconnected elastomers or duromers.

Configuration of macromolecules describes the arrangement of atoms or groups along the chains for a known constitution.

The material properties can drastically differ between different configurations, such as atactic, syndiotactic, and isotactic PVC. Terms like *cis*- (neighboring) and *trans*- (opposite) are common.

Atactic configurations prevent the lattice formation. Higher degrees of symmetry allow crystal formation. Configuration is a complex issue but can be tailored by the (organic) chemist.

Tacticity (from Greek 'taktikos': of or relating to arrangement or order) is the relative stereochemistry of adjacent chiral centers within a macromolecule.

- In isotactic macromolecules all the substituents are located on the same side of the macromolecular backbone.

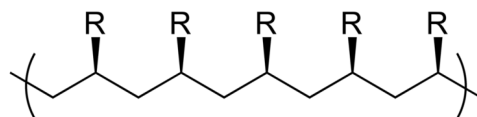


Figure 4: Example of isotactic configuration.

- In syndiotactic or syntactic macromolecules the substituents have alternate positions along the chain.

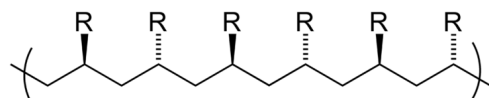


Figure 5: Example of syndiotactic configuration.

- In atactic macromolecules the substituents are placed randomly along the chain.

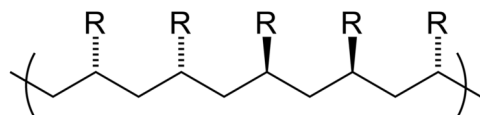


Figure 6: Example of atactic configuration.

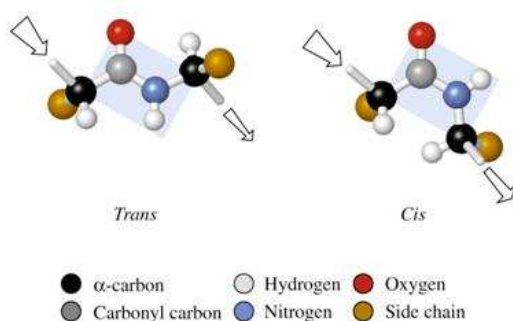


Figure 7: Cis- and trans- configuration.

Conformation of macromolecules represents the exact geometrical arrangement including binding angles and symmetries within the molecular chain of the macromolecule for the known constitution and configuration. Changes of the conformation need only small amount of energy and are reversible. Because the shape of the different conformations is characteristic,

typical terms are introduced, e.g. chair-type tt-conformation or (boat configuration) reservoir-type tg-conformation, bundle-type irregular sequence of t and g or zig-zag-type all t configuration.

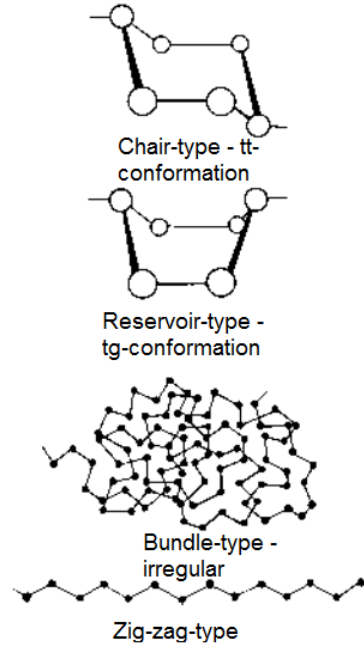


Figure 8: Conformation of macromolecules.

4.2 Draw two screw dislocations using spherical atoms and cylindrical bonds. Indicate the Burgers vector. Explain how the two dislocations can interact.

Screw dislocation:

- one-dimensional lattice defect (line defect);
- characterized by Burgers vectors parallel to the dislocation line;
- the energy of screw dislocation is proportional to b^2 :

$$E_{sd} = \frac{Gb^2}{4\pi} \ln\left(\frac{r_1}{r_0}\right),$$

where G - elastic constant (shear modulus),

r_0 -radius of dislocation nucleus,

r_1 - half mean distance of dislocation in the solid state.

\Rightarrow Small Burgers vectors are energetically favoured because e.g. $(2b)^2 > b^2 + b^2$

\Rightarrow two screw dislocations are formed

Interaction of dislocations

Dislocations can move through the crystal and interact. The interaction between dislocations is strongly dependent on the direction of Burgers vector. If two dislocations meet in the same gliding plane, they are attracted to each other, in the case where the Burgers vectors are antiparallel. If the Burgers vectors are parallel, the dislocations reject each other.

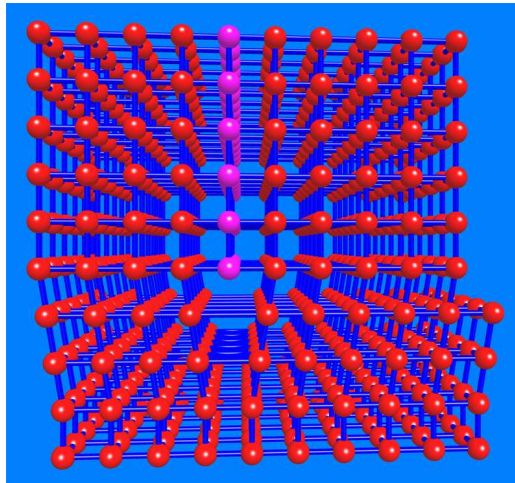


Figure 9: Screw dislocation.

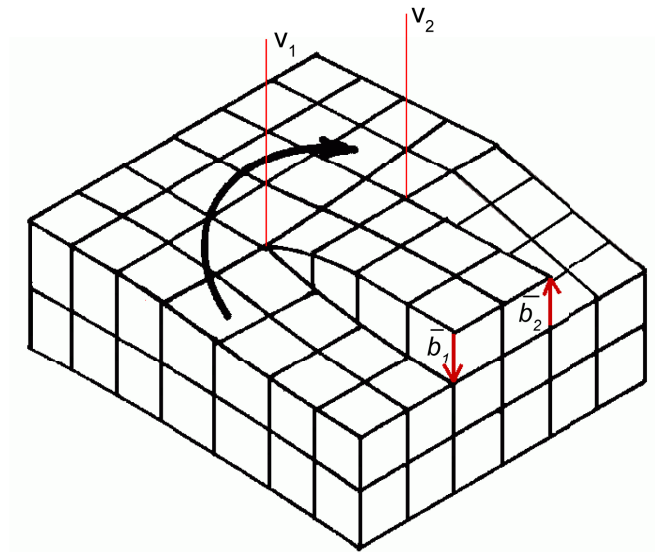


Figure 10: Screw dislocation.

4.3 It should be shown that the lines of closest packing are $\langle 110 \rangle$ for fcc structures and $\langle 111 \rangle$ in bcc structures.

Idea: We extend a sphere from the center (atom) at point $(0,0,0)$ until we meet the next atom. The line that connects the center of the sphere with the next closest atom is the line of closest packing.

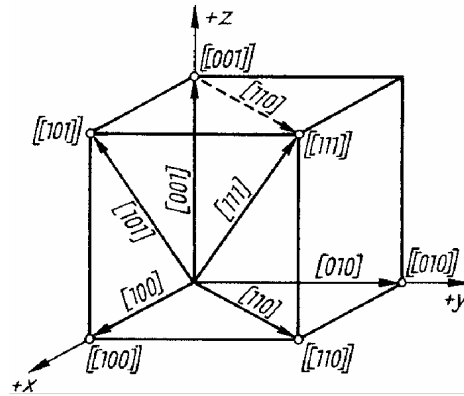


Figure 11: Description of lattice points and of the related directions.

- Body-centered cubic (bcc)

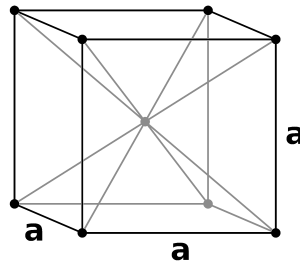


Figure 12: Body-centered cubic.

$$\begin{aligned}
 A &= (0, 0, 0)^T; \\
 B^I &= (1/2, 1/2, 1/2)^T - \text{the coordinates of the next closes atom}; \\
 B &= (1, 1, 1)^T; \\
 AB &= B - A; \\
 AB &= (1, 1, 1)^T; \\
 &\text{AB-line of closest packing.}
 \end{aligned}$$

- Faced-centered cubic (fcc)

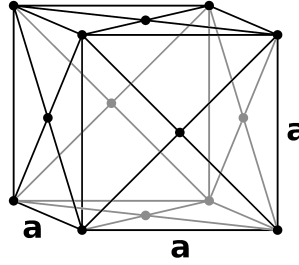


Figure 13: Faced-centered cubic.

$$\begin{aligned}
 A &= (0, 0, 0)^T; \\
 B^I &= (1/2, 1/2, 0)^T - \text{the coordinates of the next closes atom}; \\
 B &= (1, 1, 0)^T; \\
 AB &= B - A; \\
 AB &= (1, 1, 0)^T; \\
 &\text{AB-line of closest packing.}
 \end{aligned}$$

4.4 It should be quantitatively explained, why vacancies always exist, whereas the number of dislocations in a single crystal can be zero.

Vacancies always exist. Their number is related to the temperature, so they are called thermal defects. In thermal equilibrium, the free energy F is given by the sum of the inner energy U and the entropy S :

$$F = U - TS.$$

To produce a vacancy we need to break only very few bonds, related to an ion of inner energy of about 1 eV.

To produce a dislocation we need orders of magnitude more energy. For a crystal with volume $V=1 \text{ mm}^3$ to produce an edge dislocation an additional half plane must be incorporated and we sum up all bonds along plane.

Along 1 mm we have 10^7 atoms \Rightarrow energy needed to produce dislocation $E_{ed} \cong 10^7 * 1\text{eV} \cong 10\text{MeV}$

From the energetic point of view both vacancy and dislocation need some energy to be produced, but usually one gains entropy.

$F=U-TS=U - kT\ln W$, where $kT \approx 26 \text{ meV}$ at room temperature, with W the probability $\Rightarrow \ln W=\ln N=\ln 10^{21}=50$. $\Rightarrow kT\ln W=1,3 \text{ eV} \Rightarrow$ from free energy point of view vacancies are always possible, but dislocaions not.

Entropy is basically the number W of microscopic states that a system can be in, $S = k \ln(W)$, where k is the Boltzmann constant and S is called the entropy.

Suppose we have a very simple crystal, with N lattice positions, each of which either contains an atom, or not. If all the lattice positions are filled, there is only one state the system can be in, so $W = 1$. If there is one defect, it can be in N different positions, so (assuming no symmetries), $W = N$.

If there are two defects, the number of possible grids with $(N - 2)$ positions filled and 2 vacant is $W = N(N - 1)/2$. More generally, if you have n missing atoms in the grid of N , the number of ways that you can choose the n positions to put your defects is $(N \text{ choose } n)$, i.e. $W = N! / ((N - n)! n!)$.

Of course, there is a maximum here, where exactly half of the sites is filled and the other half is empty. So by entropy considerations alone, it would be most convenient to have half of the crystal empty.

However, entropy is not the whole story. Nature makes a big point not about maximizing the entropy, but rather about minimizing the free energy. The formula for this is $F = U - TS$, where U is the internal energy of the system, T is temperature and S is the entropy. From here you can see that increasing the entropy lowers the free energy. But, adding defects also has a price: it increases the total internal energy of the system (the reason being that you need to do work to take out an atom from a perfect crystal). So apart from increasing S , you also increase U . Since the target is not to make S as large, but F as small as possible, you need to find a balance between increasing F by adding internal energy, and decreasing it by adding entropy. Each empty spot that you create gives the system more microscopic states to be in, but it also adds energy to it.