10.4 Semiconducting Polymers

10.4.1 Basics

The Language Barrier

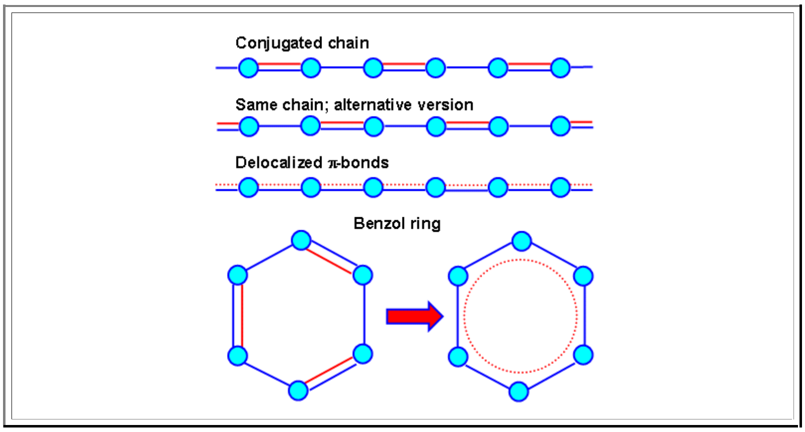
- When we look into the rapidly increasing field of semiconducting polymers, we look into something rather new and rather exciting. We also look at some problems!
  - Knowing a lot of solid state physics in general, and semiconductor physics in particular, as we do if we made it this far in the course, will not be sufficient to understand semiconducting polymers. You will now be biased to consider *all* semiconductors in terms of electrons and holes, which move more or less freely in three more or less equal directions. Their movement happens either in a conduction or in valence band, which have some density of states and exist because of a three-dimensional periodic potential. The overruling parameter is the Fermi energy of the system.
- There is nothing wrong with this particular way of modeling crystalline semiconductors - in terms of equations and in terms of thinking about them. There would be nothing wrong by trying to fit semiconducting polymers into this mold either - except that they do not fit into that mold all that well, and that practically nobody out there, who is working with semiconducting polymers, is doing it.
  - Instead, the language used is heavily biased from chemistry ("oxidation state", ,), and merrily interlaced with terms describing quasi particles ("soliton", polaron, or bi-polaron") that originally were toys from the arsenal of theoretical physicists.
  - Of course, we will also find some semiconductor terms like "holes", "doping", or "recombination", too.
  - This seems to be bad enough. But it is even worse: All those terms may not imply what *you* might think they imply, but something a bit or a lot different.
- We have neither the time, nor the prerequisite knowledge (in this statement I include myself), to delve deeply into the subject. We will just scratch the surface and look at some major points with respect to semiconducting polymers and their applications.
  - In time some more depth might be added to this via advanced modules, and some basic modules may provide more background.
  - At present, however, you may want to look at the polymer modules of other scripts or a short vocabulary of special terms:
    - Einführung in die Materialwissenschaft I
    - Polymers II
    - Vocabulary for Semiconducting Polymer
  - The last link refers to a basic module contained within this Hyperscript offering a short (and not yet complete) vocabulary of the essential terms.

Conducting , Semiconducting, and Insulating Polymers

- When we use the word "polymer" from now on, we only consider so-called **conjugated polymers**. Only these single-bond - double-bond chains are at the heart of conducting and semicondcuting polymers as we will see shortly.
- First, however, we ask ourselves a simple question that is, however, not all that easy to answer:

Why are conjugated polymers not always one-dimensional conductors?

  - Why did we all just "know" that polymers are insulators? Why a Nobel prize for the discovery of *conduction polymers*?
- You probably never thought about it. Nor was this question raised in the more basic polymer stuff you may have learned. What you learned was that polymers are insulators since there are no free electrons. Period.
  - But now we are more advanced and realize, if our nose is rubbed into the matter, that the double bonds along a conjugated chain should not be localized - they should occur to the left or to the right of any given atom with the same probability.
  - In other words, things in conjugated chain *should* be like shown below; in other words exactly as we know it to be in a benzol molecule which is shown with the same symbolism.



- In crystal physics terminology, the π-electrons all overlap and thus must form a band. This band has twice as many states as we have electrons (one for the electron on the left, one for the electron on the right of any chain atom)
  - We thus *should* have (one-dimensional) metallic conductivity along the chain!
- Well, we don't. And the reason for that is a universal pricnciple in physics, called "**symmetry breaking** " at its most general form, and "**Peierls transition**" or "**Peierls instability**" in a more specialized version.
  - A special feature of he picture above, that only emerges because we have a *long chain* , is that the bond length would be the *same* for single and double bonds on average, because the double bond is not localized. For localized double bonds, of course; as we have then in small molecules, we do not expect equal bond lengths for single-, double-, and triple bonds.
  - Equal bond lengths in a chain are thus an expression of a particular symmetry in long chains: Every carbon - carbon pair is equally likely to have the double bond (= have the π-electron) at any given time. But that particular kind of symmetry is *not* a required property of the chain. Symmetries, as we know from many examples, can be broken if we gain some (free) enthalpy by doing it.
  - Bond lengths *could* be different in long chains. Even if there is no directly evident electronic reasons for this breaking of symmetry, all "we" have to do to achieve this effect, is to invest some *elastic energy* that will change the bond lengths via some elastic strain.
  - In a thought experiment, we can easily make the bond lengths alternatingly somewhat shorter and somewhat longer, producing the simple-minded picture of localized (short) double bonds in a comjugated chain. The only question now is if we would be rewarded for doing this. Or in other words: Will we get more energy back by breaking the symmetry than we have to invest for the elastic deformation.
- For a benzol molecule, the answer clearly is *no*! The π-bonds are delocalized (as proven by measurements); there is no symmetry breaking. How about a long conjugated chain?
  - Well - the answer must be *yes* - we *must* have symmetry breaking. Simply because the "experiment" of every day experience tells us that a conjugated polymer chain is an *insulator* and not a conductor, as it would be if the π-electrons could move freely along the chain.
  - The question than is why do we have this **Peierls instability** of conjugated polymer chains - and of many other systems including, e.g. superconductors?
  - Obvioulsy because we get more electronic energy back than we have to invest in elastic energy; there can be no other reason.
- That is not only true, but it is relatively easy to understand in principle what goes on - provided you understood chapter 2 of this lecture course.
  - Here we just note that the simple-minded picture of a conjugated polymer chain with *localized* π-bonds that do *not* allow easy electron movement along the chain is actually rather correct, but for rather involved reasons, which we will consider in more detail in an advanced module
  - Conjugated polymer chains are not conductors, but insulators, or, to be more specific, *semiconductors* with a band gap sufficiently large not to show any intrinsic conductivity at **300 K** or any temperature that does not destroy the molecule anyway.