Peierls Instability

If you look at the basic model of a conjugated polymer chain with delocalized π -bonds long enough, you must realize that you are simply looking at one possible embodiment of a one-dimensional free electron gas model.

- In a first approximation, we assume - as always - that the potential for the electrons along the chain is constant, and that the chain has some length **L** - here we are. For the π -electrons that we are looking at, we obtain the good old free electron gas dispersion function

$$E_{elect} = \frac{\hbar^2 \cdot k^2}{2\,m}$$

In a *second* approximation, we now throw in *some* periodic potential and consider the Fermi energy.

- This gives us Brillouin zones, changes of the dispersion function mostly on Brillouin zone boundaries, and some wave vector k_F separating occupied from unoccupied states. The dispersion function shown just above will change to something more complicated with a band gap at the Brillouin zone boundaries.
- Notice that the emphasize *here* is on *some* periodic potential. The whole apparatus mentioned above works for *any* periodic potential, not just for a periodic array of atoms or ions.

In particular, a *periodic* distortion of the bond lengths as shown below must be expected to somehow influence the behavior of the electrons in the systems - we may consider it to be a periodic potential, too.

- The picture below shows a possible elastic deformation - we shortened the double bonds by having some strain **2ε**, or alternatively, we elongated the single bonds by **2ε**
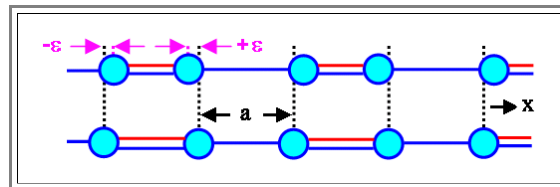
- This does *not* happen, because the double bond has an intrinsically, i.e. electronically determined shorter bond length, but only because we - in this thought experiment - put some elastic stress on the bonds.

We now have some elastic or mechanical energy E_{mech} stored in the strained bonds. The magnitude of E_{mech} for one unit volume of the chain is simply

$$E_{mech}(\epsilon) = \frac{\sigma \cdot \epsilon}{2} = \frac{Y \cdot 2\epsilon^2}{2} = Y \cdot \epsilon^2$$

- We substituted the stress σ via **σ = Y · ε** with **Y = Youngs modulus**.
- If you have some doubts about this formula - that's fine. But we only want to get the flavor of what is happening, and in principle what we are doing is correct, give or take some factor of **2** or so.

Now, after we "somehow" mechanically deformed the chain in a periodic fashion, we consider the effect on the π-electrons.

- Without the deformation, they experience a constant potential **U = 0** - that was, after all, our starting point within the free electron gas model.
- But with the deformation, they now see a periodically changing potential **U(ε)**. We changed the positions of the atoms or ions, and the only effect that can have is to induce a periodic variation of the potential energy for the electrons which will depend on ε, of course.
- We have no idea how large that effect is going to be, but the most simple formula we can use in a first approximation would be

$$U(\epsilon) = 2 \cdot A \cdot \epsilon \cdot \cos\left(\frac{\pi}{a} \cdot x\right)$$

- The proportionality constant **A** is actually of considerable interest in general terms: It can be interpreted as some kind of coupling constant between electrons and **phonons** .

- After all, a periodic displacement of atoms from their regular lattice positions *is* a phonon - even if doesn't bounce around a crystal.

▶ Now let's look at what all that means in reciprocal space. We can use one of our old pictures for this in slightly modified form
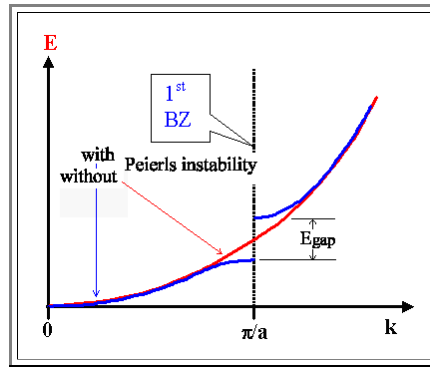
▶ We have a band gap at the Brillouin zones, of course. It's magnitude is directly given by the amplitude of the periodic potential, i.e. we have

$$E_{gap} = 2 \cdot A \cdot \epsilon$$

- The last thing we need to notice is that the available states will be occupied right up to the **1st** Brillouin zone, because we have one "free" electron per lattice constant.

▶ What we see now is that the total energy of the "free" electrons is smaller if there is a band gap. But we don't get it for free - we have to pay some elastic energy E_{mech} to get a reduction in the electronic energy.

- In order to find out out if "pays" to invest some elastic energy E_{mech} with respect top the return of electronic energy, we have to look eat the total energy $E_{total}(\epsilon) = E_{mech}(\epsilon) + E_{elec}(\epsilon)$ and see if it has a minimum , and if yes, for what kind of elastic deformation .

- Doing that is not exactly easy - even for our rather simple minded approximations used so far.

- But it is not so difficult either, so that we cannot understand the gist of the argumentation here

▶ So let's not go onto details, but just discuss what needs to be done.

- First, we need some formula for the dispersion curve for the case with a band gap. Whatever this formula will be, it depends on the magnitude of the band gap, i.e. on the amount of strain ϵ and on the constant A , which describes how much an elastic deformation influences electrons.

- This formula, as always, also defines the available states for the electrons in $\underline{\textbf{\textit{k}}}$-space.

- The total electronic energy of the system then is simply the integral over this curve up to the last occupied states, i.e. up to the Fermi wave vector or Fermi energy.

- To this integral we add the elastic energy that we have to invest to produce the periodic potential in the first place. This gives us the total energy

$$E_{total}(\epsilon) = E_{elec}(\epsilon) + E_{mech}(\epsilon)$$

- Then we find the minimum of that total energy by differentiating it with respect to the strain ϵ and setting the resulting differential quotient to zero, i.e. we do

$$\frac{\partial E_{total}(\epsilon)}{\partial \epsilon} = \frac{\partial}{\partial \epsilon}\left(\int_0^{k_F} E(k, \epsilon, A) + Y \cdot \epsilon^2 \right) = 0$$

▶ This will be our master equation. It looks pretty formidable even for the most simple model and approximation we can chose. We can easily make it more complicated by looking at more sophisticated models, but it always will have always *one* basic property: It either has a solution or it doesn't.

- If it has a solution, it means that a Peierls instability does occur because it is energetically favorable. An inherent symmetry will be broken by some elastic deformation, and a band gap in electronic states will open up. This gap might be so small that at room temperature it will not be noticed, but it will be there nonetheless.

- If it does *not* have a solution, it means that there is no Peierls instability - bond lengths are the same, the band structure does not have a gap, and the (model) material is a conductor.

As it turns out, for out problem the master equation does have a solution, and that is also true if you use more sophisticated models or math.

In the most simple form, one obtains for the strain ϵ that minimizes the total energy something like

$$\epsilon = \frac{\hbar^2 \cdot k_F^2}{m \cdot A} \cdot \frac{1}{\sinh - (\hbar^2 \cdot k_F \cdot \pi \cdot Y / 4 \cdot m \cdot A^2)}$$

It's not so obvious, what this means. Look up the hyperbolic sinus here if you are unsure what it looks like .

Playing around with numbers a bit (which means making some educated guesses about the range of possible values for A), one realizes that the argument of the hyperbolic sinus tends to be **>>1**, which means we can approximate the equation from above by

$$\epsilon \approx \frac{2 \cdot \hbar^2 \cdot k_F^2}{m \cdot A} \cdot \exp - \frac{\hbar^2 \cdot k_F \cdot \pi \cdot Y}{4 \cdot m \cdot A^2}$$

That is an interesting equation, because it comes up in similar form for various problems, most noteworthy, perhaps, for **superconductivity** , which also owns its existence to some kind of Peierls instability

Looking back, we now can draw some more conclusions:

For conjugated carbon chains, the Peierls instability has a large effect. For the most simple real conjugated polymer which is poly ..... , it causes the transition from a one-dimensional metal to a semiconductor with a rather large band gap of $\approx$ **1.6 eV**.

But *any* periodic arrangement of atoms, ions or whatever, might undergo some kind of Peierls instability. It might be so small, however, that it is not noticeable at finite temperatures.

The effect is *not* limited to one-dimensional chains. As long as we can consider the *x*-, *y*- and *z*-dimension of the electronic energy separately, as we do in the free electron gas model, we will have a Peierls instability in three dimensions, too.

However, let's not get too general at this point. The Peierls instability results from the coupling of phonons and electrons, and this is but a first step into a complicated world of collective phenomae in solids.

It may happen, and if energetically favorable, it *will* happen, causing large effects on occasion, as for conjugated polymer chains. But other effects might happen, too, and it would be too simple minded to invoke the Peierls instability for everything out there not yet understood by us.