



Towards Metamaterial Superconductors: a Computer Simulation

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Towards Metamaterial Superconductors: a Computer Simulation

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Abstract

In BCS superconductors the critical temperature is dependent on the phonon dispersion relation. We want to influence - and hopefully increase - the critical temperature by varying the phonon dispersion. This can be done by altering the lattice structure of a material on the nanoscale using nanofabrication. As a proof-of-principle project we simulate these phonon structures and see whether or not higher critical temperatures come out. In this project we tested the code for mistakes and physical inaccuracies.

The code reproduced physical effects correctly, but artificial parameters which we need to put in because of numerics issues have some influence on the outcomes. However, we think this is not a big problem because in the end we calculate the ratio of critical temperatures between two systems. This means that all that is constant in the whole calculation will be divided out.

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Motivation

Already in 1911 Heike Kamerlingh Onnes discovered that certain materials become superconducting at sufficiently low temperatures [1]. Nowadays, these materials have lots of applications in both industry and research. There is one drawback though: these materials, commonly called superconductors, need to be cooled down to well below 150 Kelvin. This makes the use of superconductors quite expensive and tiresome.

Ever since the discovery of superconductors researchers have been trying to find new materials that can become superconducting. The main goal is to find materials that have a higher critical temperature (T_c): the temperature below which they become superconducting. Beside that physicists were looking for a theoretical framework that explains superconductivity. One of the biggest accomplishments in this field was the development of BCS theory: a theory that describes and explains the behaviour of superconductors.

BCS theory uses electron-phonon interaction to show that electrons form Cooper pairs. These pairs form a condensate that can move through a material with zero resistance: it becomes superconducting. The fact that electron-phonon coupling is the origin of superconductivity means that the dispersion relation of the phonons influences T_c . This is where our idea comes in: if we can find out how changing the phononic dispersion changes the T_c , then we can look for specific structures that give a higher critical temperature.

The dispersion relation of the phonons is of course highly dependent on the lattice structure of the material you work with. Already in the '80s chemists tried to alter the phonon dispersion by changing the lattice structure of materials. They made new materials by periodically replacing atoms in a lattice, which resulted in some materials that are still in use today [2]. This is a way to find out if the indicated method is any good, but not a fast one because it takes quite some time to fabricate your samples.

In 1986 this research was put on hold when there was a major breakthrough in superconductivity research: there was a material discovered that had a higher T_c than thought to be possible: the start of the field of high- T_c superconductors [3]. This is a completely different type of superconductivity, and it showed such good prospects that the research on BCS superconductors became less attractive.

Currently there is still a lot of research being done on high- T_c superconductors, but nobody has found a satisfactory theoretical description of these materials yet. More and more materials with these properties are found, but it proves to be difficult to make a lot of progress without knowing where to look. Besides this, the materials that are found are quite inconvenient: they are mostly brittle, expensive and unreliable. This makes it interesting again to have a look at the 'old' type of superconductors, which we understand much better. Since we have made a lot of progress regarding research methodology, we can pick up the research the aforementioned chemists did and do it in a different way.

The eventual goal is to fabricate new materials by altering the phonon dispersion relation. This can be done in multiple ways: in the '80s people tried to replace specific atoms, but it is also possible to change the structure of the material on the nanoscale. The idea is to make holes in a thin film of the material, which alters the phonon dispersion. This way we create a kind of 'superlattice' on a bigger scale than the atomic lattice.

Our idea is as follows: instead of experimentally making new materials we first do computer simulations of lattice structures. The electron-phonon coupling can be described mathematically, which makes it possible to calculate the T_c of a material from its phononic and electronic structure. This calculation can be cast into MATLAB code, which allows for trying out lots of different phonon dispersions much faster than previously possible. This gives us a proof-of-principle project, in which we want to show whether or not this path is a promising one. Of course this is no conclusive proof that it is possible to make BCS superconductors with much higher critical temperatures than before, but if our results show that the concept works it gives a starting point for future research.

Chapter 2

How to Calculate T_c

In the previous chapter we postulated that it is possible to calculate the critical temperature of a BCS superconductor from the electron and phonon dispersion relations. Here we will go a bit deeper into the procedure for doing this, while avoiding most of the mathematics. For a more extensive look into the mathematical procedure, we refer to the masters thesis by Oliver Ostojić which covers this quite extensively [4].

The Hamiltonian of our system should describe both the phonons and the electrons. We model the electrons using the tight binding model and the phonons as a one dimensional chain of masses with springs in between them. Thus there is only nearest neighbor interaction. The Hamiltonian of this model is as follows:

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_{\langle ij \rangle} \frac{1}{2} K (u_i - u_j)^2 - \sum_{\langle ij \rangle} (t_{ij} - \alpha(u_i - u_j))(c_i^\dagger c_j + h.c.) \quad (2.1)$$

with p_i the momentum of atom i , m_i its mass, u_i its displacement from the equilibrium position, K the spring constant between two atoms, t_{ij} the hopping term between two atoms, α the change of the hopping term when the interatomic distance varies and $c_i(c_i^\dagger)$ the annihilation(creation) operator of an electron. The observant reader probably already deduced that the i and j index the equilibrium positions of the atoms in the chain.

The first two of these terms describe the phonons. The first is the kinetic energy term, the second the potential energy term. The electron term is a bit less straightforward. Between the first brackets we see the hopping factor, but it is modulated by the displacement of the atoms. This makes a lot of sense: if the distance between two atoms gets smaller, the probability of an atom hopping over becomes bigger. Between the last set of brackets is the annihilation of an atom at position j and the creation at position i : an electron hops from position j to i . The reversed process is expressed as the Hermitian conjugate of $c_i^\dagger c_j$. Both processes occur with the same

probability.

The modulation of the hopping term by the displacement of the atoms is not in the 'normal' tight binding model, mainly because this is not a very strong effect. This modulation is the origin of the electron-phonon coupling. In BCS theory, electron-phonon coupling causes the formation of Cooper pairs: Leon Cooper showed that an arbitrarily small attractive force between electrons is sufficient to make the formation of Cooper pairs energetically favourable [5].

The next step is to go from real space to reciprocal space, because in reciprocal space the bare phonon and electron parts of the Hamiltonian become diagonal. The kinetic and potential energy terms are quite easily transformed by applying a Fourier transform*. The same goes for the standard tight binding part of the last term; the modulated part though is a bit less obvious. When transformed into reciprocal space, the easy terms are expressed in second quantisation: we use creation and annihilation operators (different ones for the phonons and the electrons). We substitute these operators into the modulated part of the Hamiltonian to transform it. This yields the following equation:

$$H = \sum_k \epsilon_k c_k^\dagger c_k + \sum_q \hbar \omega_q a_q^\dagger a_q + \frac{1}{\sqrt{N}} \sum_{kq} g(k, q) (a_q c_k c_{k+q}^\dagger + a_q^\dagger c_k^\dagger c_{k+q}) \quad (2.2)$$

Here k indexes through the electrons, q through the phonons. ϵ_k is the electron dispersion relation, c_k (c_k^\dagger) the creation (annihilation) operator for the electrons. Equivalently, ω_q is the phonon dispersion relation and a_q (a_q^\dagger) the creation (annihilation) operator for the phonons. The first two terms are the 'normal' electron and phonon energies, but the last one is the most interesting one: this is the electron-phonon coupling.

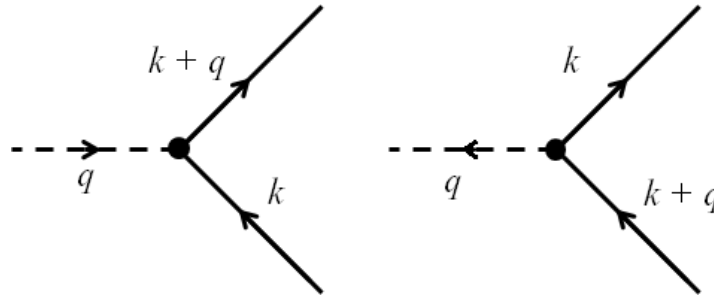


Figure 2.1: The feynmann diagrams of the two possible processes in electron-phonon coupling. The k and the $k + q$ are the quantum numbers of the electron, q that of the phonon.

In figure 2.1 we see the two possible processes that are shown mathematically in equation two. Either the phonon adds energy to the electron

*This is not exactly a Fourier transform because we do the transformation on a periodicity in the lattice, but it is formally equivalent to it.

(picture on the left) or it takes energy from it (picture on the right). These two possibilities are expressed using the creation and annihilation operators, both with the same amplitude $g(k, q)$.

This amplitude is used in the expression for the electron-phonon coupling strength, but first there are a few things that need fixing. First of all, if our system is not monoatomic we get different bands in the phonon dispersion relation. We need an extra index for that. Next we should make sure that we take only the actually existing phonons. When we go to a multiatomic system, our Brillouin zone gets smaller so we should re-evaluate which phonons in the old Brillouin zone are the real ones. If we take all this into account we get the multiatomic amplitude of the aforementioned processes:

$$M_{k,k+q}^{\nu} = \frac{g(k, q)}{\sqrt{2\omega_{q,\nu}}} \Gamma_{q,\nu}. \quad (2.3)$$

The index for the different bands is the ν and $\Gamma_{q,\nu}$ says for every phonon frequency what weight it carries in the calculation to prevent double counting. For a more extensive look at this Γ , see the aforementioned masters thesis by Ostojić.

Now we can go to the coupling strength, which we call λ . Here we follow a paper by Philip Allen [6]. For every electronic frequency we want to know how strongly it couples to all the phononic frequencies. For the sake of transparency we first express λ as a function of q (so we show how much each phonon frequency couples to all electronic frequencies). This gives the following formula:

$$\lambda_{q,\nu} = \frac{2}{\omega_{q,\nu} N(E_F)} \cdot \sum_k |M_{k,k+q}^{\nu}|^2 \delta(\epsilon_k) \delta(\epsilon_{k+q}) \quad (2.4)$$

We have a different lambda for every combination of q and ν , so for every phonon frequency in our system. The $\omega_{q,\nu}$ is the same phonon dispersion from earlier on and we already saw $M_{k,k+q}^{\nu}$. The deltafunctions at the end select only those electrons that are at the Fermi level. We define our Fermi energy to be at $\epsilon = 0$. The electrons with quantum numbers k and $k + q$ should be at that energy because in BCS theory only the electrons at the Fermi surface can interact with the phonons. As you can see in figure one, these are the electrons with momentum k and $k + q$.

This is the expression for the strenght of the electron-phonon coupling of one phonon. However, in the end we want to know how strong the coupling in our entire system is. This is quite easy: we can just sum over q and ν which gives the complete coupling strength. From this coupling strength we can then calculate the critical temperature T_c [7]:

$$\lambda = \sum_{q,\nu} \lambda_{q,\nu} \quad (2.5)$$

$$T_c = 1.13\omega_D e^{\frac{1}{\lambda}} \quad (2.6)$$

The sum gets the total coupling strength λ from $\lambda_{q,\nu}$ and the ω_D in formula 2.6 is the Debye-frequency. In the end, what we will calculate is not an exact critical temperature, but the ratio between the phonon dispersion we're interested in and some basis dispersion we compare it with. This avoids issues with units because you divide them all out.

Chapter 3

Sanity Checks

When you do a simulation, you almost always make use of approximations. This is partially because of numerics issues, but also due to the physical model that you choose. In our case we use for instance a model of electron-phonon coupling that is very much like BCS theory, but a bit more sophisticated. For this reason it is a good idea to check if the results we obtain from our simulation agree with reality. Unfortunately the nature of our results prevents us from examining their agreement with the real world directly. So we devised some sanity checks: tests that we can calculate with our code of which we do know the correct results. In this chapter we will go through some of these tests and their results and we will discuss what this means for the code. First we will discuss some tests we did on the phonon dispersion relation, after that on the lambdas.

3.1 The Isotope Effect on the Phonon Dispersion

Ultimately we want to vary the phonon dispersion to influence the T_c , so we should check if the phonon dispersions we get behave correctly. In

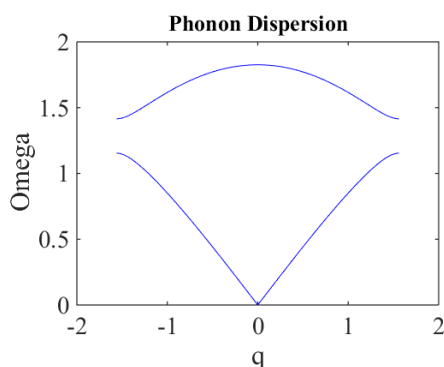


Figure 3.1: Example of a phonon dispersion. This one is of a mass unit cell with two masses in it, hence the two bands. The ratios between the masses are 1:1.2 which results in the opening of bandgaps.

figure 3.1 we see an example of a phonon dispersion that our code gives. At first sight the dispersion looks as expected. We used a mass unit cell with two masses, so the dispersion has two bands. There are bandgaps because the masses in the unit cell are slightly different.

If we now vary the masses in the unit cell together (i.e. keeping the relative differences the same), the dispersion should get smaller. This is called the isotope effect: the dispersion goes with one over the square root of the masses. To test this we plotted the maximum value in the dispersion against the masses in the unit cell. We took a unit cell with only one mass in it. That means that there is only one band in the dispersion, but that makes no difference for this test. If our code works correctly we should see the values fall off with the square root of the mass.

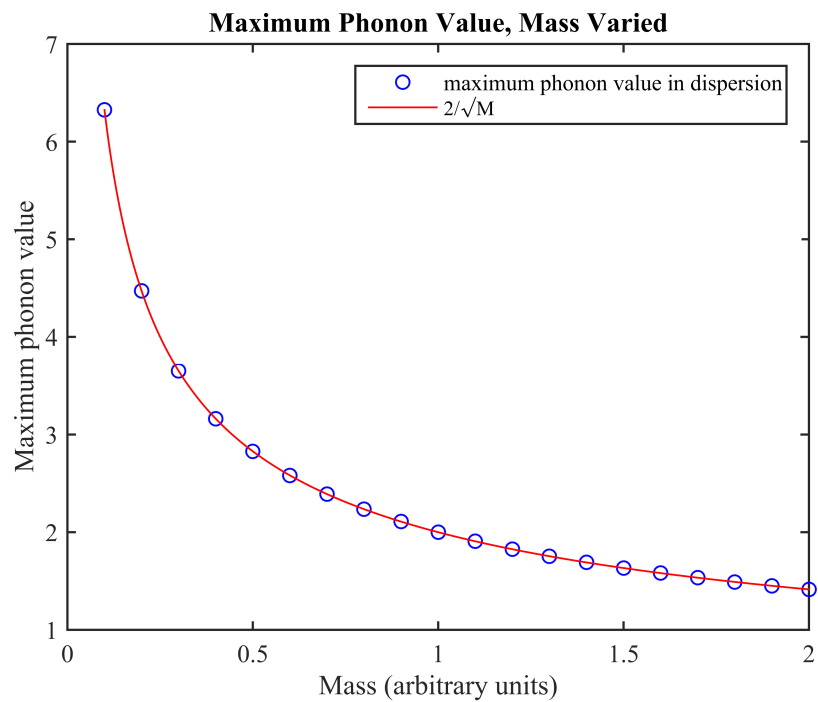


Figure 3.2: The maximum phonon value in the dispersion of a unit cell with one mass in it. This mass is varied. The red line shows a $2/\sqrt{M}$ dependence.

In figure 3.2 we see that the phonon dispersion does what we expect: the $2/\sqrt{M}$ dependence fits the values exactly. This means that our code handles the isotope effect very well.

3.2 Bandgap Size

Next we want to do some checks on the size of the bandgap in the phonon dispersion. In figure 3.3 we see a typical density of states as our code produces it. This one is of a unit cell with two masses, one twice as heavy as the other. In the middle of the graph we see a region without states: the bandgap.

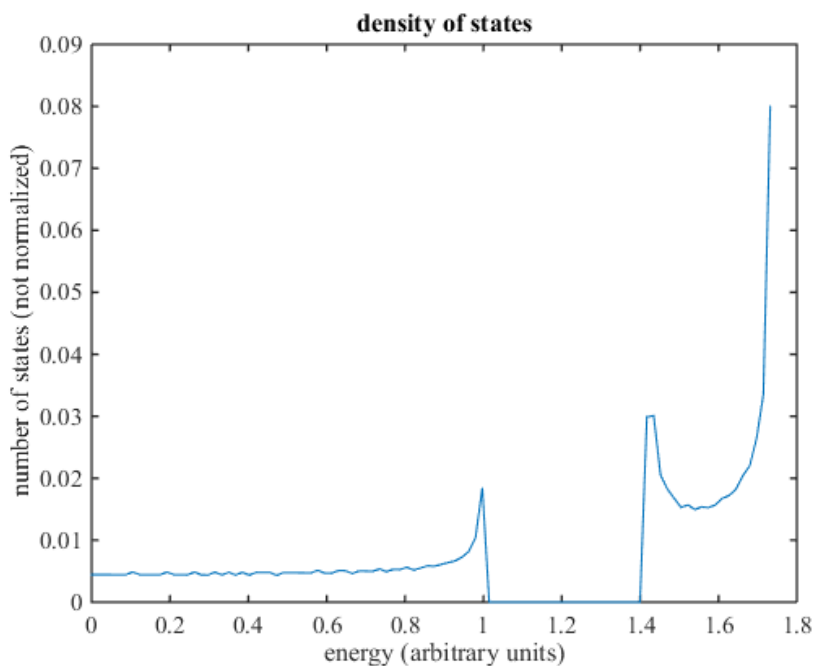


Figure 3.3: The density of states of a system with a mass unit cell with two masses in it. The second mass is twice as heavy as the first one, which results in a bandgap.

When we now vary the difference between the two masses, the density of states changes. We can investigate the size of the bandgap for these different situations. We know for sure that the bandgap should be closed when the masses are equal and that the bandgap should grow bigger if we increase the difference between the masses. Also the curve should be smooth.

In figure 3.4 we plotted this difference. The second mass is varied between 0.1 and 2 times the other mass. We see that at $M = 1$, i.e. two equal masses, the bandgap is indeed 0. When the second mass becomes very small, the bandgap gets asymptotically bigger. This is as expected, because the ratio between the two masses goes to infinity. When we increase the second mass the difference also gets bigger, but a lot slower. This is because it also grows with the ratio between the biggest mass and the smallest mass this way. So we can conclude that the size of the bandgap behaves correctly.

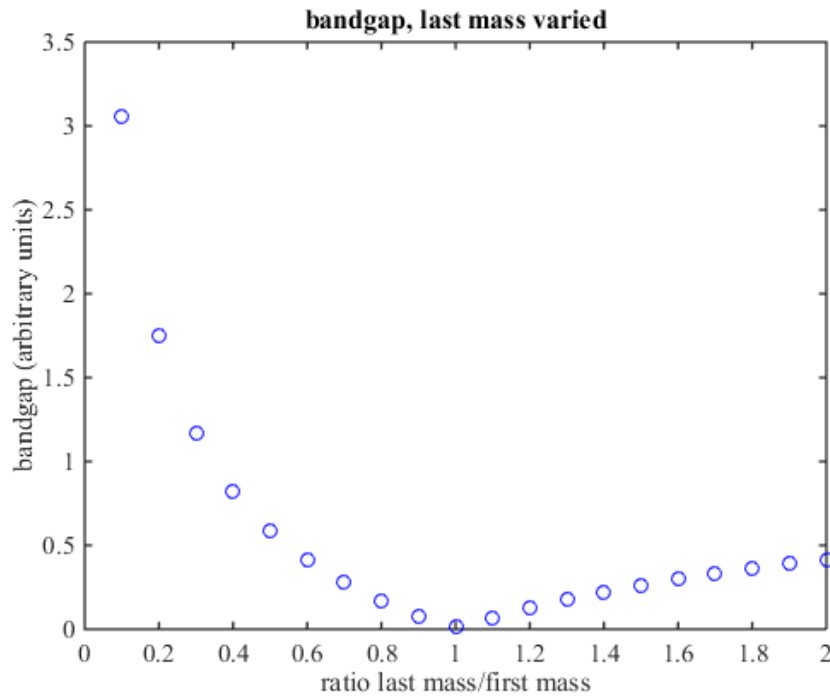


Figure 3.4: The size of the bandgap in a system with two masses. One of the masses is constant, the other one is varied between 0.1 and 2 times the original mass. The y-axis is in arbitrary units

3.3 Chemical Potential vs. the Lambdas

Next we did tests on the lambdas themselves. To remind you about what they are: the $\lambda_{q,\nu}$ indicates how strongly the phonon with quantum numbers q and ν couples to the electrons in the system. The sum of these $\lambda_{q,\nu}$ s, which we will just call lambda after this, is the thing that tells us how strong the total electron-phonon coupling is in the end.

There is much less theory about these lambdas than about the phonon dispersions, which makes it more difficult to design a test for them. One of the things we can do is look at how the lambdas react on changing the Fermi energy.

Earlier on we stated that only the electrons at the Fermi surface can take part in the electron-phonon interaction. This means that changing the Fermi energy (and with that the shape of the Fermi surface) changes the lambdas. To explain what the expected effect is, we will first show how the Fermi surface changes.

The tight binding electron model gives the following dispersion:

$$\epsilon_k = \mu - 2t(\cos(k_x a) + \cos(k_y a)) \quad (3.1)$$

with μ the chemical potential (for now we take this as zero), t the hopping parameter, k_x and k_y the momentum number of the electrons in the x and the y direction and a the lattice constant. When we now take a cross section of the surface that is defined by equation 3.1 at a certain energy level, we get the set of k -values that corresponds to that energy. That energy is the Fermi energy, so that set of k -values forms the Fermi surface.

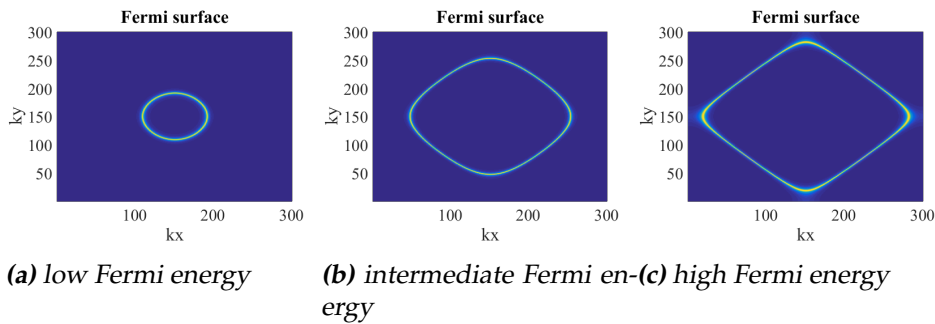


Figure 3.5: Fermi surfaces at different Fermi energies

Figure 3.5 shows three different situations. Firstly, in 3.5a a low Fermi energy. In this case, the Fermi surface is almost circular and quite small. When the Fermi energy becomes higher, the surface becomes wider and more square (figures 3.5b and 3.5c).

The question is what this means for the lambdas. In equation 2.4 we see that $\delta(\epsilon_k)\delta(\epsilon_{k+q})$ selects the correct k -values. This means that both the original electron with momentum number k , but also the resulting electron with momentum number $k + q$, should be on the Fermi surface. In other words, the momentum vector q should connect two points on the Fermi surface.

This means that when the Fermi surface gets wider, there will be a larger phonon momentum vector that connects two sides of the the Fermi surface nicely. However, we are not interested in which q vectors connect nicely. We are interested in the total coupling, the sum over the q vectors. This sum should not be affected too much by the size of the Fermi surface. We only expect problems when the Fermi surface either gets very small and becomes a filled circle, or gets very big and gets a spread at the corners (in figure 3.5c you can already see the start of this). In those cases the total lambda should grow because there are more k -values to sum over, as the sum in the formula for the lambdas only goes over the k -values on the Fermi surface.

In figure 3.6 we see that the lambdas indeed behave as expected. For both high and low values of the chemical potential the lambdas rise sharply,

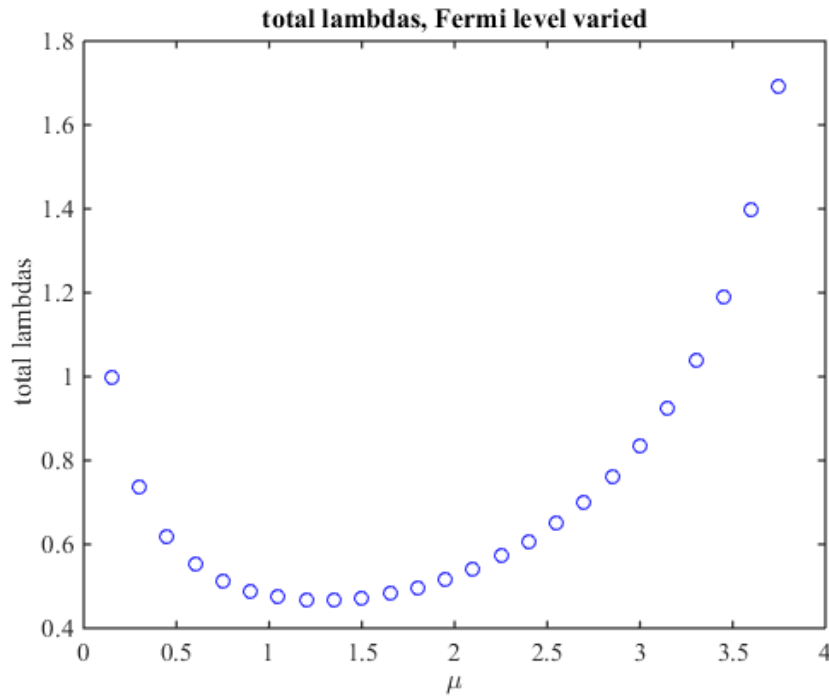


Figure 3.6: The total lambda for different Fermi energies. A higher value for μ actually means that the Fermi energy gets lower, see equation 3.1 and the subsequent explanation of the deltafunctions from equation 2.4. All values are normed to the first value of total lambda.

but in the middle there is a nice and calm region. As long as we stay between approximately $\mu = 1$ and $\mu = 2$ we have a beautiful Fermi surface.

3.4 Fermi Surface Smearing vs. the Lambdas

We are not done with the Fermi surface yet. As you can see in figure 3.5, the Fermi surface we use is not a simple line. It is a bit smeared around the theoretical position because the k-space is not continuous but has discrete values (although it approaches continuity when the number of points in the Brillouin zone goes to infinity). The smearing of the Fermi surface makes sure that there are enough points in the surface to make the calculation work. The size of this smearing should not influence our final results as it is an artificial parameter. To test this we varied this smear parameter while leaving the rest of the parameters the same. At first this was not constant at all. That is not desirable, but not that weird due to the way we calculate the lambdas. As a solution we tried to divide out the influence of the smear parameter. This gave the plot you see in figure 3.7.

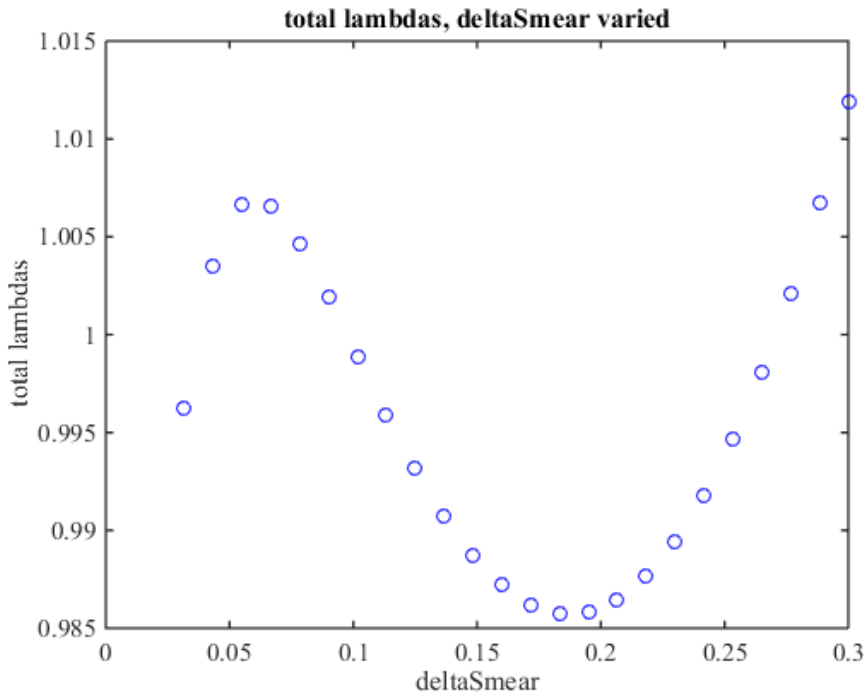


Figure 3.7: The influence of the smear parameter after we tried to divide it out. All values are normed.

As you can see, the influence is not completely gone. This is obviously not good, the smear parameter should not influence the lambdas because it is an artificial parameter.

At the time of writing, we decided not to focus on getting the last smear dependency out. We have some ideas where it could come from, but probably it is quite a lot of work to find out exactly how it enters. Besides that, in the end we want to calculate the ratio between the total lambda of two different systems as explained in chapter 2. This means that we will divide out everything that is equal in the two systems, so as long as we do not vary the smear parameter in this process we will be all right.

3.5 Phonon Dispersion Offset vs. the Lambdas

In equation 2.4 you can see that there is a prefactor of $\frac{1}{\omega_{q,\nu}}$ in front. This becomes problematic at points where $\omega_{q,\nu} = 0$.

Theoretically this will not be a problem: the $\frac{1}{\omega_{q,\nu}}$ diverges at $q = 0$ but the matrix element goes to 0 and in the end they will balance each other out. In practice we still have a problem at $q = 0$ though, because MATLAB does not handle these divergences very well. For that reason we added a

very small number to the phonon dispersion, an offset.

This offset is also an artificial parameter, so it should not influence the total lambda. To check if this is the case we plotted the total lambda as a function of the offset, see figure 3.8.

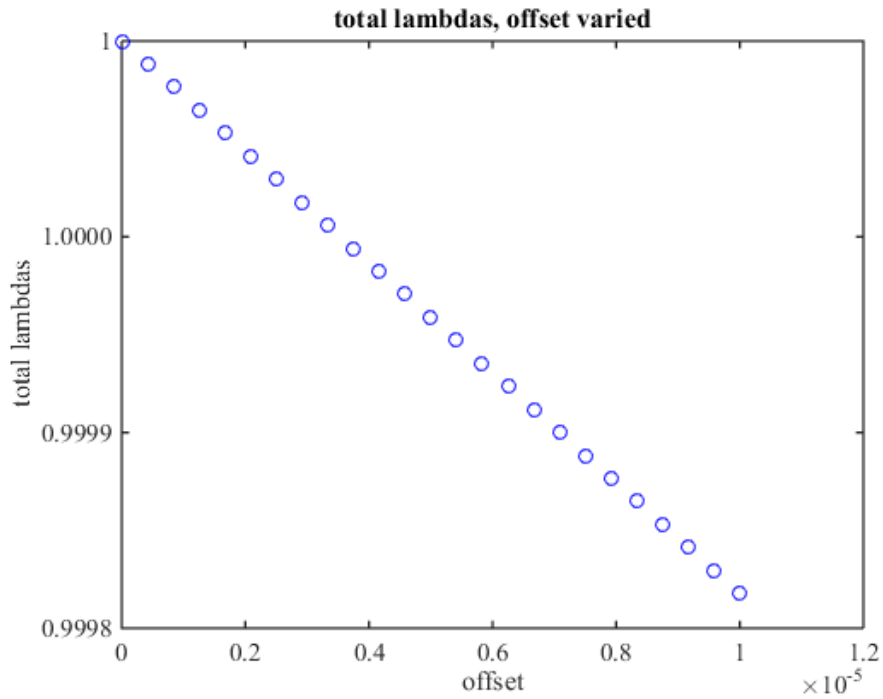


Figure 3.8: The offset parameter for the phonon dispersion vs. the total lambdas. Note that the values on the x-axis are times 10^{-5} . Values on the y-axis are normed to the first value of total lambda.

There seems to be a linear dependence on the offset parameter, but only in the order of 10^{-4} . This is quite a small effect, and the same argument as for the smear parameter can be used here: the offset parameter will not be varied during our experiments. We can conclude that the offset will not be a problem in running the code.

Chapter 4

Outlook

In the previous chapter we discussed the different tests we conducted on the code. All the tests on physically 'real' parameters - the Fermi energy, the size of the bandgap and the isotope effect - turned out well. They showed that our code does correctly calculate the lambdas. On the other hand, some work still can be done on the artificial parameters. The results we got on those parameters do not form a big problem though. There still is a dependency on the artificial parameters, but we can divide this dependency out in the final results because we calculate the ratio between two different structures in the end.

In conclusion we see that the code we made is reliable and should give good results. This does not mean that there is nothing left to be done. Some things we can do ourselves, other things should be left to other groups that want to follow up on this research.

4.1 Simulations

The obvious thing to do is to explore parameter space. That was the goal of this project, and we still want to do it. Unfortunately it falls just outside the scope of this thesis, but we should certainly finish the project. We are currently writing code that can iterate through a lot of different lattice structures, such that we can give it a list of these structures that it can calculate through. This can also be a basis to judge whether or not there are more possibilities in this field.

4.2 Nanofabrication

If the simulations show that there possibly are structures that yield a higher T_c , the next step is to try to reproduce them experimentally. One way to do

this is by making thin films in which we make holes.

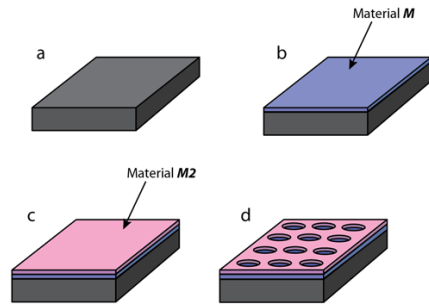


Figure 4.1: The process for making a thin film with holes. The holes or not on scale. Material M2 is the material whose phonon dispersion we are changing, material M is to ensure that the electron dispersion does not change.

The holes alter the phonon dispersion of the material, which influences the critical temperature of the material. These holes will be about 10 nanometers in size. Beneath that there is a layer to ensure that the electron dispersion relation is not changed by the holes. When we now cool this thin film with holes down and measure the temperature at which it becomes superconducting, we can see if the critical temperature indeed changes.

This experiment is something that we will not do; if our simulations show that this is actually a working idea then we can publish it and let other groups do further experimental research.

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