

Lecture Notes: Condensed Matter Theory I (TKM1), part 2

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I. PHONONS

In our discussion of the electronic properties, we assumed that the ions are fixed, an assumption that was justified because of the large difference in the electron and ion masses. Next we will analyze the behavior of ionic vibrations. Before we perform a systematic investigation of the problem we discuss a few simple examples.

A. Linear Chain of vibrating atoms

We consider a long chain of coupled ions, where coupling only exists between nearest neighbors. We consider equal masses M and equal force constants k , respectively. In addition we assume periodic boundary condition, i.e. we consider a ring of N oscillators. The positions of the l -th ions are given as:

$$R_l = R_l^{(0)} + u_l. \quad (1)$$

The lattice "vector" (we are in one dimension) that corresponds to the equilibrium positions is

$$R_l^{(0)} = la, \quad (2)$$

where a is the distance between two neighboring equilibrium positions of the ions. u_l is the deviation of the ions from their minimum potential position and characterizes the lattice dynamics. The equation of motion follows immediately as

$$M \frac{d^2 u_l}{dt^2} = -2k u_l + k (u_{l+1} + u_{l-1}). \quad (3)$$

This equation of motion also follows from the Lagrange function

$$L = \sum_l \frac{M}{2} \left(\frac{du_l}{dt} \right)^2 - \frac{k}{2} \sum_l (u_l - u_{l-1})^2. \quad (4)$$

To solve the equation of motion we make the ansatz

$$u_l = A e^{i\omega t} e^{-i \frac{2\pi n l}{N}}. \quad (5)$$

The last equation reflects the periodic boundary condition

$$u_{l+N} = u_l, \quad (6)$$

which follows if n is an integer. The corresponding wave number is

$$q_n = \frac{2\pi}{a} \frac{n}{N} \quad (7)$$

and we can write

$$u_l = A e^{i\omega t} e^{-iR_l q_n}. \quad (8)$$

It holds immediately that

$$u_{l\pm 1} = e^{\mp i q_n a} u_l \quad (9)$$

which allows us to write the equation of motion as

$$-M\omega^2 u_l = -2k u_l (1 - e^{-i q_n a} - e^{+i q_n a}) \quad (10)$$

which yields

$$\omega(q) = \sqrt{\frac{2k}{M}} (1 - \cos(qa))^{1/2}. \quad (11)$$

It obviously holds that only solutions with $-\frac{\pi}{a} < q \leq \frac{\pi}{a}$ are physically nonequivalent. To see this one analyzes u_l for q and $q + \frac{2\pi}{a}$ and finds that they are indeed identical. The situation is exactly as we saw in case of the periodic electronic system. Only wave numbers of the first Brillouin are relevant. In the limit of large N the wave vector values q_n are dense and we don't have to worry about the integer label n of q .

In the limit of small ω , which corresponds to small q , we use $\cos x \simeq 1 - x^2/2$ and it follows

$$\omega(q) = c_s |q| \quad (12)$$

which determines the sound velocity

$$c_s = \sqrt{\frac{k}{m}} a. \quad (13)$$

1. Continuum's limit and one dimensional field theory

It is possible to determine this last result without solving the entire discrete problem explicitly. To this end we consider the so called continuum's limit, where we replace sums by integrations etc. In this case it is convenient to change the notation somewhat. We use x to label coordinates, i.e. $R_l \rightarrow x$. In the continuum limit we are not interested in what

happens at distances of order of a , but at much larger distances, i.e. we can, whenever convenient, replace

$$\sum_l \cdots \rightarrow \frac{1}{a} \int dx \cdots . \quad (14)$$

For our Lagrangian follows

$$\begin{aligned} L &= \sum_l a \frac{M}{2a} \left(\frac{du_l}{dt} \right)^2 - \frac{ka}{2} \sum_l a \left(\frac{u_l - u_{l-1}}{a} \right)^2 \\ &\rightarrow \int dx \left(\frac{m}{2a} \left(\frac{\partial u(x,t)}{\partial t} \right)^2 - \frac{ka}{2} \left(\frac{\partial u(x,t)}{\partial x} \right)^2 \right) \end{aligned} \quad (15)$$

Lets introduce

$$\mu = \frac{m}{a} \text{ and } \kappa = ka \quad (16)$$

which yields the action $S = \int dt L$ of the classical field theory

$$S = \int dt L = \int dx dt \left(\frac{\mu}{2} \left(\frac{\partial u}{\partial t} \right)^2 - \frac{\kappa}{2} \left(\frac{\partial u}{\partial x} \right)^2 \right). \quad (17)$$

It is also convenient to introduce the Lagrange density

$$\mathcal{L} = \frac{\mu}{2} \left(\frac{\partial u}{\partial t} \right)^2 - \frac{\kappa}{2} \left(\frac{\partial u}{\partial x} \right)^2 \quad (18)$$

such that

$$S = \int dx dt \mathcal{L} \quad (19)$$

In the next step we derive the equation of motion that follows from this action. We use the notation

$$\begin{aligned} u_t &\equiv \frac{\partial u}{\partial t} \\ u_x &\equiv \frac{\partial u}{\partial x} \end{aligned} \quad (20)$$

We consider a somewhat more general situation and analyze a Lagrange density that depends on u_t , u_x , as well as u . Suppose that $u(x,t)$ is the solution that minimizes the action S . This implies that all solutions

$$u(x,t,\alpha) = u(x,t) + \alpha \zeta(x,t) \quad (21)$$

will increase S and thus $\left. \frac{dS}{d\alpha} \right|_{\alpha=0} = 0$. We furthermore assume that $\zeta(x, t_{i,f}) = 0$ for $t = t_i$ and t_f (i.e. the initial and final time points). In addition we assume $\zeta(x_s, t) = 0$, where x_s are surface points of our problem.

It follows

$$\frac{dS}{d\alpha} = \int dxdt \left(\frac{\partial \mathcal{L}}{\partial u} \frac{\partial u}{\partial \alpha} + \frac{\partial \mathcal{L}}{\partial u_t} \frac{\partial u_t}{\partial \alpha} + \frac{\partial \mathcal{L}}{\partial u_x} \frac{\partial u_x}{\partial \alpha} \right) = 0 \quad (22)$$

It holds

$$\begin{aligned} \int dt \frac{\partial \mathcal{L}}{\partial u_t} \frac{\partial u_t}{\partial \alpha} &= - \int dt \frac{\partial}{\partial t} \frac{\partial \mathcal{L}}{\partial u_t} \frac{\partial u}{\partial \alpha} \\ \int dx \frac{\partial \mathcal{L}}{\partial u_x} \frac{\partial u_x}{\partial \alpha} &= - \int dx \frac{\partial}{\partial x} \frac{\partial \mathcal{L}}{\partial u_x} \frac{\partial u}{\partial \alpha} \end{aligned} \quad (23)$$

which yields

$$\frac{dS}{d\alpha} = \int dxdt \left(\frac{\partial \mathcal{L}}{\partial u} - \frac{\partial}{\partial t} \frac{\partial \mathcal{L}}{\partial u_t} - \frac{\partial}{\partial x} \frac{\partial \mathcal{L}}{\partial u_x} \right) \frac{\partial u}{\partial \alpha} = 0 \quad (24)$$

which yields for arbitrary $\frac{\partial u}{\partial \alpha} = \zeta(x, t)$ the generalized Euler-Lagrange equation

$$\frac{\partial}{\partial t} \frac{\partial \mathcal{L}}{\partial u_t} + \frac{\partial}{\partial x} \frac{\partial \mathcal{L}}{\partial u_x} - \frac{\partial \mathcal{L}}{\partial u} = 0 \quad (25)$$

We are now in a position to determine the equation of motion. It holds with

$$\mathcal{L} = \frac{\mu}{2} u_t^2 - \frac{\kappa}{2} u_x^2 \quad (26)$$

that

$$\frac{\partial \mathcal{L}}{\partial u_t} = \mu u_t \quad \text{and} \quad \frac{\partial \mathcal{L}}{\partial u_x} = -\kappa u_x \quad (27)$$

and the equation of motion is

$$\mu u_{tt} - \kappa u_{xx} = 0 \quad (28)$$

or explicitly

$$\frac{1}{c_s^2} \frac{\partial^2 u}{\partial t^2} - \frac{\partial^2 u}{\partial x^2} = 0 \quad (29)$$

with

$$c_s = \sqrt{\frac{\kappa}{\mu}} = \sqrt{\frac{k}{m}} a \quad (30)$$

as sound velocity. The last interpretation is justified as the above equation of motion is obviously a wave equation with solution

$$u(x, t) = A e^{i\omega t} e^{-iqx} \quad (31)$$

where insertion yields

$$-\frac{\omega^2}{c_s^2} + q^2 = 0 \quad (32)$$

yielding the low momentum portion of the above spectrum

$$\omega = c_s q \quad (33)$$

with same c_s . Thus, if we are only interested in the long wavelength behavior of the system, it is sufficient to perform the continuum limit at the level of the actions and Lagrangian already.

B. Acoustic and optic branches of the spectrum

Next we consider the situation with more than one atom per unit cell. We consider for simplicity a one dimensional system with two atoms in each unit cell. The positions of the ions are given as

$$\begin{aligned} R_l^1 &= R_l^{(0)} + u_l^1 \\ R_l^2 &= R_l^{(0)} + b + u_l^2 \end{aligned} \quad (34)$$

The lattice vector is $R_l^{(0)} = la$ (l is an integer) that corresponds to the equilibrium positions of atom 1, while atom 2 has equilibrium positions $R_l^{(0)} + b$, where $0 < b < a$. Let k_1 and k_2 be the force constants (they can be different as b must not be $a/2$) and M_1 and M_2 the corresponding masses. The equations of motion follow immediately as

$$\begin{aligned} M_1 \frac{d^2 u_l^1}{dt^2} &= -k_1 (u_l^1 - u_l^2) - k_2 (u_l^1 - u_{l-1}^2) \\ M_2 \frac{d^2 u_l^2}{dt^2} &= -k_1 (u_l^2 - u_l^1) - k_2 (u_l^2 - u_{l+1}^1) \end{aligned} \quad (35)$$

We make again the ansatz

$$u_l^k = A^k e^{i\omega t} e^{-iR_l^{(0)} q}. \quad (36)$$

and obtain

$$\begin{aligned} -\omega^2 M_1 A^1 &= -k_1 (A^1 - A^2) - k_2 (A^1 - A^2 e^{-iqa}) \\ -\omega^2 M_2 A^2 &= -k_1 (A^2 - A^1) - k_2 (A^2 - A^1 e^{iqa}) \end{aligned} \quad (37)$$

This is a homogeneous system of equations. Requiring that the determinant vanishes one obtains the frequencies

$$\omega_{\pm}^2 = \frac{1}{2} \omega_0^2 \left(1 \pm \sqrt{1 - \gamma \sin^2 (qa/2)} \right) \quad (38)$$

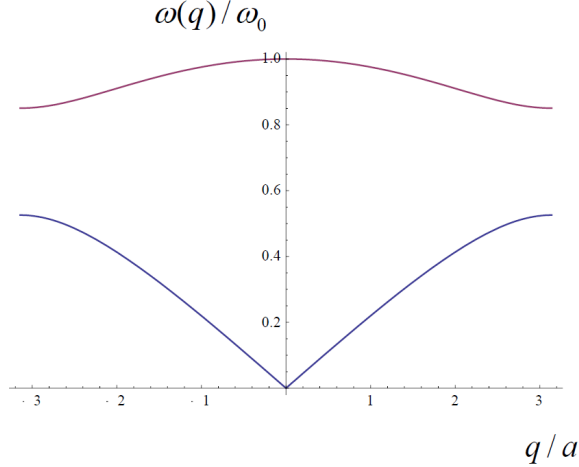


FIG. 1: Dispersion relation of a chain of atoms with two atoms per unit cell

where

$$\begin{aligned}\omega_0^2 &= \frac{k_1 + k_2}{M_1 M_2} (M_1 + M_2) \\ \gamma &= \frac{16 M_1 M_2 k_1 k_2}{(k_1 + k_2)^2 (M_1 + M_2)^2}\end{aligned}\quad (39)$$

$0 < \gamma < 1$ and takes its largest value $\gamma_{\max} = 1$ in case $M_1 = M_2$ and $k_1 = k_2$.

At small momenta holds

$$\begin{aligned}\omega_- &\simeq \sqrt{\gamma} \frac{\omega_0 a}{4} q \\ \omega_+ &\simeq \omega_0 \left(1 - \frac{\gamma}{32} (qa)^2 \right)\end{aligned}\quad (40)$$

Thus, ω_- behaves like the sound waves we discussed previously. It is called the acoustic branch. On the other hand ω_+ remains finite in the long wavelength limit and is called the optical branch. To interpret these two branches (and thus justify the nomenclature acoustic and optic branch) we determine the ratio A^1/A^2 from the above system of equations

$$\frac{A^1}{A^2} = \frac{k_1 + k_2 - M_2 \omega_{\pm}^2}{k_1 + k_2 e^{iq\omega_{\pm}}}$$

In the limit of $q = 0$ follows for ω_- that $\frac{A^1}{A^2} = 1$. Thus, both atoms move in phase. On the other hand, for ω_+ follows $\frac{A^1}{A^2} = -\frac{M_2}{M_1}$ and both atoms move against each other, hence the term optical branch as such motions easily couple to dipole excitations. The entire momentum dependence is shown in the Fig.1 We also see a gap in the spectrum between

the largest state of ω_- and the lowest state of ω_+ . The gap is given as

$$\Delta = \frac{\omega_0}{\sqrt{2}} \left(\sqrt{1 + \sqrt{1 - \gamma}} - \sqrt{1 + \sqrt{1 + \gamma}} \right)$$

which vanishes as $\gamma \rightarrow 1$. In this limit the two ions are identical and the lattice constant is in fact $\tilde{a} = a/2$. The two branches now describe the states with $0 < |q| < \frac{1}{2} \frac{\pi}{\tilde{a}}$ and $\frac{1}{2} \frac{\pi}{\tilde{a}} < |q| < \frac{\pi}{\tilde{a}}$ of the actual Brillouin zone of the system. Indeed, for $\gamma = 1$ we have $\omega_0^2 = k/M$ and

$$\omega_{\pm}^2 = \frac{1}{2} \frac{k}{M} \left(1 \pm \sqrt{1 - \sin^2(q\tilde{a})} \right) \quad (41)$$

which is equivalent to our earlier treatment of the chain with one atom per unit cell.

In the Fig.?? we show the dispersion for $\gamma = 1$ in comparison with that of a single-atom chain and lattice constant $2a$.

C. Systematic treatment of lattice vibrations

We now perform a more systematic treatment of lattice vibrations and come back to the potential energy V_{ii}^{eff} that we discussed when we analyzed the Born Oppenheimer approximation. This potential describes the interaction energy of slow ions due to their direct Coulomb repulsion

$$V_{ii} = \sum_{l,l'=1}^{N_i} \frac{e^2 Z_l Z_{l'}}{|\mathbf{R}_l - \mathbf{R}_{l'}|} \quad (42)$$

and due to the electronic ground state energy determined from the electron Schrödinger Equation $H_{el}\psi_n = E_{el,n}\psi_n$:

$$V_{ii}^{eff} = V_{ii} + E_{el,n}$$

The positions of ions are given by

$$\mathbf{R}_n^k = \mathbf{R}_n^{(0)} + \mathbf{a}_n^k + \mathbf{u}_n^k, \quad (43)$$

where $\mathbf{R}_n^{(0)}$ are the Bravais lattice vectors. The superscript k stands for the ion number k in the unit cell. \mathbf{a}_n^k refers to the classical equilibrium position of minimal potential of the ions in the crystalline solid. The deviations from this mean position are denoted by \mathbf{u}_n^k or in components by $u_{n,\alpha}^k$, where $\alpha = x, y, z$. As $u_{n,\alpha}^k = 0$ is the absolute minimum of the potential energy we can expand and obtain

$$V_{ii}(\mathbf{R}_n^k) = V_{ii}(\mathbf{R}_n^{(0)} + \mathbf{a}_n^k) + \frac{1}{2} \sum_{n,n',\alpha,\beta,k,k'} \Phi_{n,n';\alpha,\beta}^{k,k'} u_{n,\alpha}^k u_{n',\beta}^{k'} \quad (44)$$

i.e.

$$\Phi_{n,n';\alpha,\beta}^{k,k'} = \frac{\partial^2 V_{ii}}{\partial u_{n,\alpha}^k \partial u_{n',\beta}^{k'}} \quad (45)$$

The classical equation of motion is given as:

$$M_k \ddot{u}_{n,\alpha}^k = - \sum_{n',\beta,k'} \Phi_{n,n';\alpha,\beta}^{k,k'} u_{n',\beta}^{k'} \quad (46)$$

The coefficients $\Phi_{n,n';\alpha,\beta}^{k,k'}$ have certain symmetries: Since partial derivatives are symmetric, it follows

$$\Phi_{n,n';\alpha,\beta}^{k,k'} = \Phi_{n',n;\beta,\alpha}^{k',k} \quad (47)$$

Translational symmetry implies

$$\Phi_{n,n';\alpha,\beta}^{k,k'} = \Phi(\mathbf{R}_n - \mathbf{R}_{n'})_{\alpha,\beta}^{k,k'} \quad (48)$$

Finally, a homogeneous shift or rotation should not produce any force. To this end we write

$$\mathbf{u}_n^k = \delta \mathbf{u}$$

for all k and n or

$$\mathbf{u}_n^k = \delta \boldsymbol{\omega} \times \mathbf{R}_n^k,$$

The simultaneous motion of all atoms does not lead to a force, i.e. the right hand side of Newton's law, Eq.46 should vanish

$$\sum_{n',\beta,k'} \Phi_{n,n';\alpha,\beta}^{k,k'} \delta u_\beta = 0$$

which is true for arbitrary components δu_β of $\delta \mathbf{u}$, i.e.

$$\sum_{n',k'} \Phi_{n,n';\alpha,\beta}^{k,k'} = 0. \quad (49)$$

From the rotation invariance follows

$$\sum_{n',k'} \Phi_{n,n';\alpha,\beta}^{k,k'} R_{n'\beta}^{k'} = 0.$$

It is very useful to introduce amplitudes $A_{n,\alpha}^k \equiv \sqrt{M_k} u_{n,\alpha}^k$. We look for solutions of the following form

$$A_{n,\alpha}^k = A_\alpha^k(\mathbf{q}) e^{i(\mathbf{q}\mathbf{R}_n^{(0)} - \omega t)} \quad (50)$$

or equivalently

$$u_{n,\alpha}^k = \frac{A_\alpha^k(\mathbf{q})}{\sqrt{M_k}} e^{i(\mathbf{q}\mathbf{R}_n^{(0)} - \omega t)} \quad (51)$$

Inserting this ansatz, we obtain

$$-\omega^2 M_k u_{n,\alpha}^k = - \sum_{n',\beta,k'} \Phi_{n,n';\alpha,\beta}^{k,k'} u_{n',\beta}^{k'}$$

which gives

$$\omega^2 A_{n,\alpha}^k = \sum_{n',\beta,k'} \Phi_{n,n';\alpha,\beta}^{k,k'} \frac{A_{n',\beta}^{k'}}{\sqrt{M_k M_{k'}}$$

From Translation invariance follows

$$\Phi_{n,n';\alpha,\beta}^{k,k'} = \frac{\sqrt{M_k M_{k'}}}{N} \sum_{\mathbf{p}} e^{i\mathbf{p}\cdot(\mathbf{R}_n^{(0)} - \mathbf{R}_{n'}^{(0)})} D_{\alpha,\beta}^{k,k'}(\mathbf{p})$$

which leads to

$$\omega^2 A_\alpha^k(\mathbf{q}) = \frac{1}{N} \sum_{n',\beta,k'} A_\beta^{k'}(\mathbf{q}) e^{i\mathbf{q}\cdot(\mathbf{R}_{n'}^{(0)} - \mathbf{R}_n^{(0)})} \sum_{\mathbf{p}} e^{i\mathbf{p}\cdot(\mathbf{R}_n^{(0)} - \mathbf{R}_{n'}^{(0)})} D_{\alpha,\beta}^{k,k'}(\mathbf{p})$$

Summation over n' leads with

$$\frac{1}{N} \sum_{n'} e^{i(\mathbf{q}-\mathbf{p})\mathbf{R}_{n'}^{(0)}} = \delta_{\mathbf{q},\mathbf{p}}$$

to

$$\omega^2 A_\alpha^k(\mathbf{q}) = \sum_{\beta,k'} D_{\alpha,\beta}^{k,k'}(\mathbf{q}) A_{\beta'}^{k'}(\mathbf{q}) \quad (52)$$

which is an eigenvalue equation in the space of vector components of the displacement (labelled by the index α or β) and the space labelled by the atoms per unit cell (with index k and $k' = k'$). The eigenmodes are found from

$$\det(\omega^2 \hat{1} - \hat{D}) = 0, \quad (53)$$

where the matrix \hat{D} is given by

$$\begin{aligned} D_{\alpha,\beta}^{k,k'}(\mathbf{q}) &= \sum_{n'} D_{n,n';\alpha,\beta}^{k,k'} e^{-i\mathbf{q}\cdot(\mathbf{R}_n^{(0)} - \mathbf{R}_{n'}^{(0)})} \\ &= \sum_{n'} \frac{1}{\sqrt{M_k M_{k'}}} \Phi_{n,n';\alpha,\beta}^{k,k'} e^{-i\mathbf{q}\cdot(\mathbf{R}_n^{(0)} - \mathbf{R}_{n'}^{(0)})} = \frac{1}{\sqrt{M_k M_{k'}}} \Phi(\mathbf{q})_{\alpha,\beta}^{k,k'}. \end{aligned} \quad (54)$$

It is easy to show that

$$\begin{aligned} [D_{\beta,\alpha}^{k',k}(\mathbf{q})]^* &= \sum_{n'} \frac{1}{\sqrt{M_k M_{k'}}} \Phi_{n',n';\beta,\alpha}^{k',k} e^{i\mathbf{q}\cdot(\mathbf{R}_{n'}^{(0)} - \mathbf{R}_n^{(0)})} \\ &= \sum_{n'} \frac{1}{\sqrt{M_k M_{k'}}} \Phi_{n,n';\alpha,\beta}^{k,k'} e^{-i\mathbf{q}\cdot(\mathbf{R}_n^{(0)} - \mathbf{R}_{n'}^{(0)})} = D_{\alpha,\beta}^{k,k'}(\mathbf{q}) \end{aligned}$$

This means that the matrix \hat{D} is hermitian and that $3M$ real solutions exist, where M is the number of ions in a unit cell. We denote solutions by the subscript j : $\omega_j(\mathbf{q})$ and $A_{j,\alpha}^k$.

The roots of the secular Eq.52 are all real. If the $D_{\alpha,\beta}^{k,k'}(\mathbf{q})$ are real as well it follows that the solutions $A_{\beta'}^{k'}(\mathbf{q})$ are also real. For $\mathbf{q} = \mathbf{0}$ the $D_{\alpha,\beta}^{k,k'}(\mathbf{q} = \mathbf{0})$ are clearly real. In general this is however not the case. It follows that $D_{\alpha,\beta}^{k,k'}(-\mathbf{q}) = [D_{\alpha,\beta}^{k,k'}(\mathbf{q})]^*$ which means that

$$\omega_j(-\mathbf{q}) = \omega_j(\mathbf{q}) \quad \text{and} \quad A_{j,\alpha}^k(-\mathbf{q}) = [A_{j,\alpha}^k(\mathbf{q})]^* . \quad (55)$$

Now consider the limit $\mathbf{q} \rightarrow 0$. We obtain from the equation of motion for $\mathbf{q} = 0$:

$$\omega^2(0) M_k \frac{A_{\alpha}^k(0)}{\sqrt{M_k}} = \sum_{n',\beta,k'} \Phi_{n,n';\alpha,\beta}^{k,k'} \frac{A_{\beta}^{k'}(0)}{\sqrt{M_{k'}}} . \quad (56)$$

There are solutions with

$$A_{j,\alpha}^k(0)/\sqrt{M^k} = \delta u_{\alpha} \neq 0$$

independent of α , that yield

$$\omega^2(0) M_k \delta u_{\alpha} = \sum_{\beta} \delta u_{\beta} \sum_{n',k'} \Phi_{n,n';\alpha,\beta}^{k,k'} = 0 \quad (57)$$

where we used our earlier result $\sum_{n',k'} \Phi_{n,n';\alpha,\beta}^{k,k'} = 0$. There are in total 3 independent solutions of its kind with δu_{α} , $\alpha = x, y, z$ which yields that there are 3 modes for which $\omega_j(0) = 0$. Those are the three dimensional acoustic modes, where for small q_{α} follows

$$\omega_j(q) = c_j |\mathbf{q}| + \dots$$

with three distinct velocities of sound, depending on the acoustic modes under consideration. Thus, there should be $3M - 3$ solutions with $\omega_j(0) > 0$. Those are the optic modes, that only emerge in systems with more than one atom per unit cell. Physically this is due to the fact that they correspond to a motion of different atoms in the unit cell relative to each other. To see this we analyze

$$\omega^2(0) M_k \frac{A_{\alpha}^k(0)}{\sqrt{M_k}} = \sum_{n',\beta,k'} \Phi_{n,n';\alpha,\beta}^{k,k'} \frac{A_{\beta}^{k'}(0)}{\sqrt{M_{k'}}} \quad (58)$$

and sum over k :

$$\begin{aligned}\omega^2(0) \sum_k M_k \frac{A_\alpha^k(0)}{\sqrt{M_k}} &= \sum_{n',\beta,k',k} \Phi_{n,n';\alpha,\beta}^{k,k'} \frac{A_\beta^{k'}(0)}{\sqrt{M_{k'}}} \\ &= \sum_{k'\beta} \frac{A_\beta^{k'}(0)}{\sqrt{M_{k'}}} \sum_{n,k} \Phi_{n,n';\alpha,\beta}^{k,k'} = 0\end{aligned}\quad (59)$$

Since we consider $\omega_j(0) > 0$, it must hold that

$$\sum_k M_k \frac{A_\alpha^k(0)}{\sqrt{M_k}} = \sum_k M_k u_\alpha^k(0) = 0$$

i.e. the mean displacement, averaged over all atoms per unit cell vanishes (as expected for a relative motion). In optical modes the center of mass is constant.

Finally, acoustic modes are divided into 1 longitudinal and 2 transversal, depending of whether its eigenvector $A_{j,\alpha}^k(\mathbf{q} \rightarrow \mathbf{0})$ is parallel or perpendicular to \mathbf{q} , respectively.

D. Quantization of phonon modes.

The kinetic energy of vibrations reads

$$T = \frac{1}{2} \sum_{n,k,\alpha} M_k (\dot{u}_{n,\alpha}^k)^2 = \frac{1}{2} \sum_{n,k,\alpha} (\dot{A}_{n,\alpha}^k)^2 . \quad (60)$$

The potential energy reads

$$U = \frac{1}{2} \sum_{n,n',\alpha,\beta,k,k'} \Phi_{n,n';\alpha,\beta}^{k,k'} u_{n,\alpha}^k u_{n',\beta}^{k'} = \frac{1}{2} \sum_{n,n',\alpha,\beta,k,k'} D_{n,n';\alpha,\beta}^{k,k'} A_{n,\alpha}^k A_{n',\beta}^{k'} . \quad (61)$$

The Fourier transform of the D matrix $D_{\alpha,\beta}^{k,k'}(\mathbf{q})$ is a Hermitian matrix. Thus, it has $3M$ orthonormal eigenvectors $e_{j,\alpha}^k(\mathbf{q})$ with real eigenvalues $\omega_j^2(\mathbf{q})$:

$$\sum_{\alpha,k} e_{j,\alpha}^k [e_{j',\alpha}^k]^* = \delta_{j,j'} . \quad (62)$$

Another property is

$$e_{j,\alpha}^k(-\mathbf{q}) = [e_{j,\alpha}^k(\mathbf{q})]^* \quad (63)$$

We expand the amplitudes $A_{n,\alpha}^k$ using the eigenvectors $e_{j,\alpha}^k(\mathbf{q})$

$$A_{n,\alpha}^k(t) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} A_\alpha^k(\mathbf{q}, t) e^{i\mathbf{q}\cdot\mathbf{R}_n^{(0)}} = \frac{1}{\sqrt{N}} \sum_{j,\mathbf{q}} e_{j,\alpha}^k(\mathbf{q}) Q_j(\mathbf{q}, t) e^{i\mathbf{q}\cdot\mathbf{R}_n^{(0)}} , \quad (64)$$

where N is the total number of unit cells ($N = N_1 N_2 N_3$). Since $A_{n,\alpha}^k(t)$ is real we must have $Q_j(-\mathbf{q}, t) = [Q_j(\mathbf{q}, t)]^*$.

Using orthonormality of the vectors $e_{j,\alpha}^k(\mathbf{q})$ we obtain

$$T = \frac{1}{2} \sum_{j,\mathbf{q}} \left| \dot{Q}_j(\mathbf{q}, t) \right|^2 = \frac{1}{2} \sum_{j,\mathbf{q}} \dot{Q}_j(\mathbf{q}) \dot{Q}_j(-\mathbf{q}) , \quad (65)$$

and for the potential energy we obtain

$$U = \frac{1}{2} \sum_{j,\mathbf{q}} \omega_j^2(\mathbf{q}) |Q_j(\mathbf{q}, t)|^2 = \frac{1}{2} \sum_{j,\mathbf{q}} \omega_j^2(\mathbf{q}) Q_j(\mathbf{q}) Q_j(-\mathbf{q}) . \quad (66)$$

To formulate a Lagrangian theory it would be better to have real coordinates instead of complex $Q_j(\mathbf{q})$. Alternatively one can use $Q_j(\mathbf{q})$ and $Q_j(-\mathbf{q})$ as independent variables.

To simplify we will suppress the index j and use $Q_j(\mathbf{q}) = Q_{j\mathbf{q}}$.

The conjugated variables:

$$P_{j\mathbf{q}} = \frac{\partial T}{\partial \dot{Q}_{j\mathbf{q}}} = \dot{Q}_{j-\mathbf{q}} . \quad (67)$$

The Hamiltonian:

$$H = \frac{1}{2} \sum_{j,\mathbf{q}} P_{j\mathbf{q}} P_{j-\mathbf{q}} + \frac{1}{2} \sum_{j,\mathbf{q}} \omega_{j\mathbf{q}}^2 Q_{j\mathbf{q}} Q_{j-\mathbf{q}} . \quad (68)$$

We can now quantize this problem where $P_{j\mathbf{q}}$ and $Q_{j\mathbf{q}}$ become operators with canonic commutation relation $[Q_{j\mathbf{q}}, P_{j'\mathbf{q}'}] = i\hbar \delta_{\mathbf{q},\mathbf{q}'} \delta_{jj'}$

We introduce the creation and annihilation operators:

$$\begin{aligned} a_{j\mathbf{q}}^\dagger &= \frac{1}{\sqrt{2\hbar\omega_{j\mathbf{q}}}} (\omega_{j\mathbf{q}} Q_{j-\mathbf{q}} - iP_{j\mathbf{q}}) , \\ a_{j\mathbf{q}} &= \frac{1}{\sqrt{2\hbar\omega_{j\mathbf{q}}}} (\omega_{j\mathbf{q}} Q_{j\mathbf{q}} + iP_{j-\mathbf{q}}) , \end{aligned} \quad (69)$$

with bosonic commutation relation

$$\left[a_{j\mathbf{q}}, a_{j'\mathbf{q}'}^\dagger \right]_- = \delta_{\mathbf{q},\mathbf{q}'} \delta_{jj'} .$$

The inverse relations

$$\begin{aligned} Q_{j\mathbf{q}} &= \sqrt{\frac{\hbar}{2\omega_{j\mathbf{q}}}} (a_{j\mathbf{q}}^\dagger + a_{j-\mathbf{q}}) , \\ P_{j\mathbf{q}} &= i\sqrt{\frac{\hbar\omega_{j\mathbf{q}}}{2}} (a_{j\mathbf{q}}^\dagger - a_{j-\mathbf{q}}) . \end{aligned} \quad (70)$$

This gives

$$H = \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} \left(a_{\mathbf{q}}^{\dagger} a_{\mathbf{q}} + \frac{1}{2} \right) . \quad (71)$$

It is important to express the physical field $u_{n,\alpha}^k$ in terms of the $a_{j,\mathbf{q}}$ and $a_{j,\mathbf{q}}^{\dagger}$, respectively

$$\begin{aligned} u_{n,\alpha}^k &= \frac{A_{n,\alpha}^k}{\sqrt{M_k}} = \frac{1}{\sqrt{NM_k}} \sum_{j,\mathbf{q}} e_{j,\alpha}^k(\mathbf{q}) Q_j(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_n^{(0)}} \\ &= \frac{1}{2\sqrt{NM_k}} \sum_{j,\mathbf{q}} \left[Q_j(\mathbf{q}) e_{j,\alpha}^k(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_n^{(0)}} + Q_j(-\mathbf{q}) e_{j,\alpha}^k(-\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_n^{(0)}} \right] \\ &= \frac{1}{\sqrt{2NM_k}} \sum_{j,\mathbf{q}} \sqrt{\frac{\hbar}{\omega_j(\mathbf{q})}} \left[a_{j,\mathbf{q}} e_{j,\alpha}^k(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_n^{(0)}} + a_{j,\mathbf{q}}^{\dagger} [e_{j,\alpha}^k(\mathbf{q})]^* e^{-i\mathbf{q}\cdot\mathbf{R}_n^{(0)}} \right] . \end{aligned} \quad (72)$$

E. Phonon density of states

The Hamiltonian, Eq.71, describes a gas of non-interacting bosons. An important question is the value of the chemical potential of the phonons. The number of phonons varies with temperature with no phonons in the ground state and an increasing number of phonons as the temperature increases. The number of phonons is determined by the minimal value of the free energy

$$\frac{\partial F}{\partial N} = 0$$

which implies that the chemical potential $\mu = 0$. Thus, the internal energy is given as

$$U = \sum_{j,\mathbf{q}} \hbar\omega_{j\mathbf{q}} \left(n_{j\mathbf{q}} + \frac{1}{2} \right) = U_0 + \sum_{j,\mathbf{q}} \hbar\omega_{j\mathbf{q}} n_{j\mathbf{q}} . \quad (73)$$

Where U_0 is the ground state energy and

$$n_{j\mathbf{q}} = \frac{1}{e^{\beta\hbar\omega_{j\mathbf{q}}} - 1} , \quad (74)$$

the bose function. This allows for example to analyze the specific heat

$$C_V = \frac{1}{V} \left. \frac{\partial U}{\partial T} \right|_V . \quad (75)$$

In order to evaluate thermodynamic implications of a phonon spectrum we analyze the phonon density of states:

$$\begin{aligned}
D(\omega) &= \frac{1}{V} \sum_{j, \mathbf{q}} \delta(\omega - \omega_j(\mathbf{q})) \\
&= \sum_j \int \frac{d^3q}{(2\pi)^3} \delta(\omega - \omega_j(q))
\end{aligned} \tag{76}$$

If we consider acoustic phonons with

$$\omega_j(q) = c_j |\mathbf{q}|, \tag{77}$$

we obtain after performing the integration over angles:

$$\begin{aligned}
D_{\text{ac.}}(\omega) &= \sum_j \frac{1}{2\pi^2} \int_0^\infty dq q^2 \delta(\omega - c_j q) \\
&= \sum_j \frac{\omega^2}{2\pi^2 c_j^3} \equiv 3 \left\langle \frac{1}{c_s^3} \right\rangle \frac{\omega^2}{2\pi^2}
\end{aligned} \tag{78}$$

However, one has to be careful, as $D(\omega)$ is obviously normalized.

$$\int_0^\infty D_{\text{ac.}}(\omega) d\omega = \frac{3}{V} \sum_{\mathbf{q}} = 3 \frac{N}{V}. \tag{79}$$

This implies that the parabolic density of states cannot continue forever. The origin of this behavior is of course that the linear sound dispersion relation is only valid for small momenta and should not be extended up to the BZ boundary. However, there is a simple trick to deal with this issue that captures important aspects qualitatively correct. One introduces an upper cut off ω_D (the Debye frequency) such that

$$3 \frac{N}{V} = 3 \int_0^{\omega_D} \left\langle \frac{1}{c_s^3} \right\rangle \frac{\omega^2}{2\pi^2} d\omega \tag{80}$$

which yields

$$3 \frac{N}{V} = \left\langle \frac{1}{c_s^3} \right\rangle \frac{\omega_D^3}{2\pi^2} \tag{81}$$

Often one uses a temperature scale, the Debye temperature,

$$k_B \theta_D = \hbar \omega_D \tag{82}$$

to characterize the upper cut off. Typical values for θ_D are several hundred Kelvin.

First we consider the specific heat at high temperatures $k_B T \gg \hbar \omega_D$ (only for acoustic phonons) and expand the Bose function

$$\frac{1}{e^x - 1} = \frac{1}{x} \left(1 - \frac{x}{2} + \frac{x^2}{12} + \dots \right) , \quad x \ll 1 . \quad (83)$$

This yields

$$\begin{aligned} C_V &= \frac{1}{V} \frac{\partial}{\partial T} \sum_{s,\mathbf{q}} \hbar\omega_{s,\mathbf{q}} \frac{k_B T}{\hbar\omega_{s,\mathbf{q}}} \left(1 - \frac{1}{2} \frac{\hbar\omega_{s,\mathbf{q}}}{k_B T} + \frac{1}{12} \left(\frac{\hbar\omega_{s,\mathbf{q}}}{k_B T} \right)^2 + \dots \right) \\ &= 3k_B \frac{N}{V} \left(1 - \frac{1}{12} \frac{\hbar^2 \langle \omega_{s,\mathbf{q}}^2 \rangle}{(k_B T)^2} + \dots \right) , \end{aligned} \quad (84)$$

where $\langle \omega_{s,\mathbf{q}}^2 \rangle = \frac{1}{3N} \sum_{s,\mathbf{q}} \omega_{s,\mathbf{q}}^2$. The first term is Dulong-Petit law. If the temperature is also higher than the maximum frequency of the optical phonons, then $3 \rightarrow 3M$ as all phonons contribute to the sum.

In the low temperature limit $k_B T \ll \hbar\omega_D$ holds that only acoustic phonons are relevant.

$$\begin{aligned} C_V &= \frac{1}{V} \frac{\partial}{\partial T} \sum_{j,\mathbf{q}} \hbar\omega_{j,\mathbf{q}} n_{j,\mathbf{q}} = \frac{\partial}{\partial T} \int_0^{\omega_D} d\omega D(\omega) \hbar\omega \frac{1}{e^{\beta\hbar\omega} - 1} \\ &= \frac{3}{2\pi^2} \left\langle \frac{1}{c_s^3} \right\rangle \frac{\partial}{\partial T} \int_0^{\omega_D} d\omega \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1} = \frac{3}{2\pi^2} \left\langle \frac{1}{c_s^3} \right\rangle \frac{\partial}{\partial T} \frac{1}{\hbar^3 \beta^4} \int_0^{\beta\hbar\omega_D} dx \frac{x^3}{e^x - 1} \\ &\simeq \frac{3}{2\pi^2} \left\langle \frac{1}{c_s^3} \right\rangle \frac{4k_B^4 T^3}{\hbar^3} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{3}{2\pi^2} \left\langle \frac{1}{c_s^3} \right\rangle \frac{4k_B^4 T^3}{\hbar^3} \frac{\pi^4}{15} . \\ &= \alpha T^3 \end{aligned} \quad (85)$$

where

$$\alpha = \frac{3}{2\pi^2} \left\langle \frac{1}{c_s^3} \right\rangle \frac{4k_B^4}{\hbar^3} \frac{\pi^4}{15} = \frac{36}{5} \pi^4 \frac{k_B}{\theta_D^3} \frac{N}{V}$$

In this analysis we used that at low temperatures the upper cut off can be set to infinity. This is obviously not allowed at high temperatures. If we consider for example a metallic solid, with electronic heat capacity contribution and lattice contribution one obtains the total heat capacity

$$C_V^{\text{el+ph.}} = \gamma T + \alpha T^3 .$$

A convenient way to check for this result is to plot $\frac{C_V}{T}$ versus T^2 which should give rise to a straight line with intersection γ and slope α . For temperatures below $\simeq \theta_D \sqrt{\theta_D/T_F}$ will the electronic contribution dominate over the lattice contribution.

To describe the intermediate temperature behavior we consider a finite upper cut off and have

$$\begin{aligned}
C_V &= \frac{\partial}{\partial T} \int_0^\infty d\omega D(\omega) \hbar\omega \frac{1}{e^{\beta\hbar\omega} - 1} \\
&= k_B \int_0^\infty d\omega D(\omega) \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \\
&= \frac{3k_B}{2\pi^2} \left\langle \frac{1}{c_s^3} \right\rangle \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\beta\hbar\omega_D} d\omega x^2 \frac{x^4 e^x}{(e^x - 1)^2}
\end{aligned} \tag{86}$$

We use

$$\left\langle \frac{1}{c_s^3} \right\rangle = \frac{3\hbar^3}{(k_B \theta_D)^3} 2\pi^2 \frac{N}{V} \tag{87}$$

and obtain

$$\begin{aligned}
C_V &= 3k_B \frac{N}{V} \left(\frac{T}{\theta_D} \right)^3 \int_0^{\beta\hbar\omega_D} d\omega x^2 \frac{x^4 e^x}{(e^x - 1)^2} \\
&= 3k_B \frac{N}{V} \left(\frac{T}{\theta_D} \right)^3 f(T/\theta_D)
\end{aligned} \tag{88}$$

with Debye function

$$f(y) = \int_0^{1/y} dx \frac{x^4 e^x}{(e^x - 1)^2} . \tag{89}$$

As expected, it holds

$$f(y=0) = \frac{4}{15} \pi^4 \tag{90}$$

while for large y holds

$$f(y) \simeq \int_0^{1/y} dx \frac{x^4}{x^2} = \frac{1}{3y^3} \tag{91}$$

This allows for a natural interpolation between the low and high temperature behavior.

Optical phonons are frequently treated within the Einstein model where we neglect the momentum dependence of the frequency.

$$\omega(\mathbf{q}) = \omega_0 . \tag{92}$$

In this case holds

$$U = U_0 + (3M - 3)N \frac{\hbar\omega_0}{e^{\frac{\hbar\omega_0}{k_B T}} - 1} . \quad (93)$$

and it follows for the heat capacity.

$$C_V = \frac{1}{V} \frac{\partial U}{\partial T} = (3M - 3) \frac{N}{V} k_B \frac{\left(\frac{\hbar\omega_0}{k_B T}\right)^2 e^{\frac{\hbar\omega_0}{k_B T}}}{\left(e^{\frac{\hbar\omega_0}{k_B T}} - 1\right)^2} . \quad (94)$$

At low temperatures this yields an exponentially small heat capacity. Therefore, the low temperature heat capacity is dominated by acoustic phonons. The model of acoustic phonons with quadratic density of states and upper cut off ω_D is called Debye model, while the scenarion wit momentum independent frequency is called the Einstein model.

F. Thermal expansion of solids

Within the harmonic theory developed so far, thermal excitations of the solit will not change with temperatue as the expectation value $\langle \mathbf{u}_n^k \rangle = 0$. To obtan a qualitative understanding we include in the expansion of the energy with respect to the lattice constant higher order terms. We consider for simplicity one atom per unit cell and analyze $u = |\mathbf{R} - \mathbf{R}_0|$, the deviation of the atom positions from their ground state values and expand the potential

$$V(\xi) = V_0 + \frac{1}{2} \frac{\partial^2 V}{\partial u^2} u^2 + \frac{1}{6} \frac{\partial^3 V}{\partial u^3} u^3 + \dots \quad (95)$$

This yields for the force

$$F = -ku + gu^2 \quad (96)$$

where $k = \frac{\partial^2 V}{\partial u^2}$ and $g = -\frac{1}{2} \frac{\partial^3 V}{\partial u^3}$. If we now consider the mean force, it holds:

$$\overline{F} = -k\overline{u} + g\overline{u^2} . \quad (97)$$

In equilibrium this mean force is expected to vanish and we obtain

$$\overline{u} = \frac{g}{k} \overline{u^2} \quad (98)$$

If we now consider this analysis as a perturbation theory in g we can evaluate $\overline{u^2}$ within the harmonic theory, where $\frac{k}{2} \overline{u^2}$ is the averaged potential enegy. If we consider the Harmonic

oscillator

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{k}{2} x^2 \\ &= \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right)\end{aligned}\quad (99)$$

with $\omega = \sqrt{k/m}$, it is easy to express the expectation values of the kinetic and potential energy in terms of expectation values of the creation and annihilation operators using

$$\begin{aligned}\hat{x} &= \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}^\dagger + \hat{a}) \\ \hat{p} &= i\sqrt{\frac{m\hbar\omega}{2}} (\hat{a}^\dagger - \hat{a}),\end{aligned}\quad (100)$$

which yields

$$\begin{aligned}\frac{1}{2m} \langle \hat{p}^2 \rangle &= \frac{\hbar\omega}{2} \left(\langle \hat{a}^\dagger \hat{a} \rangle + \frac{1}{2} \right) \\ \frac{k}{2} \langle \hat{x}^2 \rangle &= \frac{\hbar\omega}{2} \left(\langle \hat{a}^\dagger \hat{a} \rangle + \frac{1}{2} \right)\end{aligned}\quad (101)$$

Thus, it holds

$$\langle V - V_0 \rangle = \frac{1}{2} \langle H \rangle = \frac{1}{2} U \quad (102)$$

where U is the internal energy. This yields

$$\bar{u} = \frac{g}{k^2} \frac{U}{N} \quad (103)$$

The thermal expansion coefficient is

$$\beta = \frac{1}{V} \frac{\partial V}{\partial T} \quad (104)$$

where L is the sample length, i.e. $V = N(a_0 + \bar{u})^3$, which yields

$$\begin{aligned}\beta &= 3 \frac{Na_0^2}{V} \frac{\partial \bar{u}}{\partial T} = 3 \frac{Na_0^2}{V} \frac{g}{k^2} \frac{1}{N} \frac{\partial U}{\partial T} \\ &= 3a_0^2 \frac{g}{k^2} C_V\end{aligned}\quad (105)$$

Thus, weak thermal expansions can be understood in terms of this simple theory where the temperature dependence of the thermal expansion is determined by the heat capacity. Often this is expressed in terms of the Grüneisen parameter:

$$\Gamma = \frac{\beta}{C_V}.$$

Once Γ deviated from being a constant, it is an interesting hint that the lattice anharmonicity is more complex than this simple theory suggests.

II. ELECTRON-ELECTRON INTERACTION IN THE PRESENCE OF PHONONS

The exchange of phonons gives rise to an effective interaction between electrons. Before we perform a quantum mechanic investigation of this effect, we show that the main results can alternatively be understood in terms of a system of coupled charges.

A. Plasma oscillations and Thomas Fermi approximation:

In our investigation of the effective interaction between electrons that is mediated by the crystalline lattice, we follow Bardeen and Pines and investigate a so called jellium model, where the ions are described in terms of a structureless positive background of fluctuating charge densities. We consider an external charge $\rho_{\text{external}}(\mathbf{r}, t)$ that leads to induced screening charges $\rho(\mathbf{r}, t)$ in the system. The Maxwell equation that determines the electric field that results from a charge redistribution is:

$$\begin{aligned}\nabla \cdot \mathbf{E} &= 4\pi(\rho + \rho_{\text{external}}) \cdot \\ \nabla \cdot \mathbf{D} &= 4\pi\rho_{\text{external}}\end{aligned}\tag{106}$$

where we introduced the displacement field

$$\mathbf{D} = \varepsilon\mathbf{E} = \mathbf{E} + 4\pi\mathbf{P}\tag{107}$$

i.e.

$$\nabla \cdot \mathbf{P} = -\rho_{\text{external}}.\tag{108}$$

In Fourier space follows

$$\begin{aligned}i\mathbf{q} \cdot \mathbf{D}(\mathbf{q}, \omega) &= i\mathbf{q} \cdot \mathbf{E}(\mathbf{q}, \omega)\varepsilon(\mathbf{q}, \omega) \\ &= 4\pi\rho_{\text{external}}(\mathbf{q}, \omega).\end{aligned}\tag{109}$$

and

$$i\mathbf{q} \cdot \mathbf{E}(\mathbf{q}, \omega) = 4\pi(\rho(\mathbf{q}, \omega) + \rho_{\text{external}}(\mathbf{q}, \omega))\tag{110}$$

Thus, the total charge $\rho + \delta\rho$ is related to the external charge $\delta\rho$ via

$$\rho(\mathbf{q}, \omega) + \rho_{\text{external}}(\mathbf{q}, \omega) = \frac{1}{\varepsilon(\mathbf{q}, \omega)}\rho_{\text{external}}(\mathbf{q}, \omega)\tag{111}$$

We first consider the classical motion of a charge density governed by Newton's law:

$$m \frac{d^2 \mathbf{r}}{dt^2} = e \mathbf{E} \quad (112)$$

and express the velocity of the carriers in terms of the charge current

$$\mathbf{j} = en_0 \frac{d\mathbf{r}}{dt} \quad (113)$$

where n_0 is the particle density of charge e . It follows

$$m \frac{d\mathbf{j}}{dt} = e^2 n_0 \mathbf{E} \quad (114)$$

The current is related to the charge density via the continuity equation

$$\partial_t \rho + \nabla \cdot \mathbf{j} = 0, \quad (115)$$

which yields (assuming $\frac{\partial \mathbf{j}}{\partial t} = \frac{d\mathbf{j}}{dt}$ which is correct at linear response to the external electric field):

$$\begin{aligned} \frac{\partial^2 \rho}{\partial t^2} &= -\nabla \cdot \frac{\partial \mathbf{j}}{\partial t} = -\frac{e^2 n_0}{m} \nabla \cdot \mathbf{E} \\ &= -\frac{4\pi e^2 n_0}{m} (\rho + \rho_{\text{external}}) \end{aligned} \quad (116)$$

This is the equation of a forced oscillator with resonance frequency

$$\omega_p = \sqrt{\frac{4\pi e^2 n_0}{m}}.$$

This is the plasma frequency of a system of movable charges. Such plasma oscillations do indeed occur in metals where the plasma frequency corresponds to several electrons volts, depending obviously on the electron density. In Fourier space the above result becomes

$$\rho = \frac{\omega_p^2}{\omega^2} (\rho + \rho_{\text{external}}) \quad (117)$$

which leads to the dielectric constant

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}. \quad (118)$$

A vanishing dielectric constant implies an infinite response to an arbitrarily small external charge density, confirming our expectation that ω_p is a resonance frequency of the charge density. A natural question arises: Do ions also undergo plasma oscillations? If so it seems

to be in conflict with the emergence of acoustic sound modes where the frequency vanishes in the long wavelength limit.

To this end we consider a system that consists of electrons and ions. We write the total induced charge as sum of the charge densitied of both components

$$\rho(\mathbf{q},\omega) = \rho_e(\mathbf{q},\omega) + \rho_i(\mathbf{q},\omega). \quad (119)$$

If we treat the ion dynamics as classical, we use Newton's law

$$M \frac{d^2 \mathbf{r}}{dt^2} = e \mathbf{E} \quad (120)$$

and express the veocity of the carriers in terms of the ion-charge current

$$\mathbf{j} = e Z n_0 \frac{d\mathbf{r}}{dt} \quad (121)$$

which yields

$$M \frac{d\mathbf{j}_i}{dt} = e^2 Z n_0 \mathbf{E} \quad (122)$$

From the continuity equation of the ion charge and current densities

$$\partial_t \rho_i + \nabla \cdot \mathbf{j}_i = 0 \quad (123)$$

follows in analogy to our earlier calculation

$$\begin{aligned} \frac{\partial^2 \rho_i}{\partial t^2} &= -\nabla \cdot \frac{\partial \mathbf{j}_i}{\partial t} = -\frac{e^2 Z n_0}{M} \nabla \cdot \mathbf{E} \\ &= -\frac{4\pi Z e^2 n_0}{M} (\rho_i + \rho_e + \rho_{\text{external}}) \end{aligned} \quad (124)$$

In Fourier space this corresponds to

$$\rho_i = \frac{\omega_i^2}{\omega^2} (\rho_i + \rho_e + \rho_{\text{external}}) \quad (125)$$

with the ion-plasma frequency

$$\omega_i = \sqrt{\frac{4\pi Z e^2 n_0}{M}}. \quad (126)$$

The key difference to the case of a single component plasma is that now the dynamic electron charge plays the role of an addition "external" charge. Thus, ω_i is not necessarily the resonance frequency of the charge distribution.

To address this issue we need to develop a model for the induced electron density. To solve this issue we take advantage of the fact that the on the time scale of the ionic motion,

electrons react almost instantaneously. Suppose there is a potential $\phi(\mathbf{r})$, caused by the total electric field $\mathbf{E} = -\nabla\phi$. If this potential varies slowly in space we can assume that it only modified locally the chemical potential

$$E_F \rightarrow E_F + e\phi. \quad (127)$$

We know that the electron concentration without potential is related to the Fermi energy according to

$$n_e(E_F) = CE_F^{3/2} \quad (128)$$

with constant C . The induced electron charge is then

$$\begin{aligned} \rho_e &= -(en_e(E_F + e\phi) - en_e(E_F)) \\ &\simeq -\frac{3}{2}CE_F^{1/2}e^2\phi = -\frac{3}{2}n_e e \frac{e\phi}{E_F}. \end{aligned} \quad (129)$$

Since

$$\nabla^2\phi = -4\pi(\rho_e + \rho_i + \rho_{\text{external}}) \quad (130)$$

which yields

$$\nabla^2\rho_e = \frac{6\pi n_e e^2}{E_F} (\rho_e + \rho_i + \rho_{\text{external}}) \quad (131)$$

In Fourier space follows

$$\rho_e = -\frac{k_{TF}^2}{q^2} (\rho_e + \rho_i + \rho_{\text{external}}) \quad (132)$$

where we introduced the Thomas Fermi screening wave number

$$k_{TF}^2 = \frac{6\pi n_e e^2}{E_F}. \quad (133)$$

If we ignore the ion charge, it follows $\rho = \rho_e = -\frac{k_{TF}^2}{q^2} (\rho + \rho_{\text{external}})$ which leads to the dielectric constant

$$\varepsilon(q) = \frac{\rho_{\text{external}}}{\rho + \rho_{\text{external}}} = \frac{k_{TF}^2 + q^2}{q^2} \quad (134)$$

The potential energy of a point charge is affected by this dielectric constant

$$V(r) = \frac{e^2}{r} \rightarrow V_{\text{eff}}(r) = \frac{1}{\varepsilon(r)} \frac{e^2}{r} \quad (135)$$

In Fourier space this corresponds to

$$V(q) = \frac{4\pi e^2}{q^2} \rightarrow V_{\text{eff}}(q) = \frac{1}{\varepsilon(q)} \frac{4\pi e^2}{q^2} \quad (136)$$

Now we can insert our result for the dielectric constant and obtain

$$V_{eff}(q) = \frac{4\pi e^2}{q^2 + k_{TF}^2} \quad (137)$$

which yields after Fourier transformation

$$V_{eff}(r) = \frac{e^2}{r} \exp(-k_{TF}r) \quad (138)$$

Thus, the induced charge density as response to a test charge will effectively weaken the Coulom interaction at long distances. This electrostatic screening effect leads to an effective short range interaction between charges.

The above analysis ignored the inclusion of the ion charge dynamics. However, combining Eq.132 and 124 leads to an dielectric constant

$$\varepsilon(q, \omega) = \frac{\omega^2 (k_{TF}^2 + q^2) - \omega_i^2 q^2}{\omega^2 q^2} \quad (139)$$

This result combines the static screening of the electron interaction with Thomas Fermi screening length in the limit $\omega_i = 0$ (frozen ions) with the plasma edge resonance of ions in the limit $k_{TF} = 0$ (no electrons). However the actual resonance frequency of the combined system results from $\varepsilon(q, \omega) = 0$ and yields

$$\omega_{phon}(q) = \frac{\omega_i}{\sqrt{k_{TF}^2 + q^2}} q \quad (140)$$

which does indeed reproduce the behavior of an acoustic vibration as $q \rightarrow 0$. Thus, in case of the coupled ion-electron systems, the ion plasma frequency is strongly modified by screening due to electrons, leading to acoustic sound.

Finally we can analyze the effective interaction between electrons coupled to dynamic charge distributions

$$\begin{aligned} V_{eff}(q, \omega) &= \frac{1}{\varepsilon(q, \omega)} \frac{4\pi e^2}{q^2} \\ &= \frac{4\pi e^2}{k_{TF}^2 + q^2} \frac{\omega^2}{\omega^2 - \omega_{phon}^2(q)} \end{aligned} \quad (141)$$

The crucial aspect of this result is that $V_{eff}(q, \omega)$ changes its sign for $\omega < \omega_{phon}(q)$, i.e. the interaction between equally charged point charges with frequencies below the phonon frequencies is attractive. This is the attractive interaction between electrons that is mediated by phonons.

III. SUPERCONDUCTIVITY

Superconductivity was discovered in 1911 by Heike Kammerling Onnes. Below $T_c = 4.2\text{K}$ mercury passed into a state with no measurable resistance. It soon became clear that this new state of matter is in thermodynamic equilibrium where the electronic contribution to the heat capacity $C_{ns} = \gamma T$ of the normal state is being replaced by

$$C_{sc} \propto \exp\left(-\frac{\Delta}{k_B T}\right) \quad (142)$$

which can easily be interpreted as due to the opening of a gap of order Δ in the density of states. It also holds that the transition temperature of a given material and Δ is approximately constant among different superconductors, i.e. $2\Delta/(k_B T_c) \simeq 3.5$. Another crucial experiment goes back to Meissner and Ochsenfeld, who found that the magnetic flux density \mathbf{B} inside a superconductor vanishes regardless of its past, i.e. regardless of whether it was cooled down from a normal state at finite external magnetic field or whether the field was switched on only below T_c . It holds

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} = (1 + 4\pi\chi)\mathbf{H} \quad (143)$$

where the magnetic field \mathbf{H} coincides for ellipsoidal geometries with the external field. Here $\chi = \partial\mathbf{M}/\partial\mathbf{H}$ is the magnetic susceptibility. $\mathbf{B} = \mathbf{0}$ then corresponds to

$$\chi = -\frac{1}{4\pi} \quad (144)$$

i.e. a superconductor is, according to Meissner and Ochsenfeld's measurements, a perfect diamagnet.

Initially it was popular to argue that superconductivity can be described phenomenologically in terms of a divergent conductivity, i.e. a superconductor was considered a perfect conductor. In this case, Ohm's law

$$\mathbf{j} = \sigma\mathbf{E} \quad (145)$$

with conductivity σ becomes the acceleration equation

$$\frac{\partial\mathbf{j}}{\partial t} = \nu\mathbf{E} \quad (146)$$

with $\nu = \frac{ne^2}{m}$. Using Faraday's law $\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}$ it follows

$$\nabla \times \frac{\partial\mathbf{j}}{\partial t} = -\frac{\nu}{c}\frac{\partial\mathbf{B}}{\partial t} \quad (147)$$

Neglecting the displacement current it follows from Ampere's law, that $\nabla \times \mathbf{B} = \frac{4\pi}{c} \mathbf{j}$ and it follows

$$\nabla \times \nabla \times \frac{\partial \mathbf{B}}{\partial t} = -\frac{4\pi\nu}{c^2} \frac{\partial \mathbf{B}}{\partial t} \quad (148)$$

If we further use that $\nabla \cdot \mathbf{B} = \mathbf{0}$, we obtain

$$\nabla^2 \frac{\partial \mathbf{B}}{\partial t} = \frac{4\pi\nu}{c^2} \frac{\partial \mathbf{B}}{\partial t}. \quad (149)$$

Integrating on both sides with respect to t yields

$$\nabla^2 (\mathbf{B} - \mathbf{B}_0) = \frac{4\pi\nu}{c^2} (\mathbf{B} - \mathbf{B}_0) \quad (150)$$

This immediately implies that $\mathbf{B} - \mathbf{B}_0$ decays with length scale λ where

$$\lambda^{-2} = \frac{4\pi\nu}{c^2} = \frac{4\pi n e^2}{m c^2}. \quad (151)$$

This is almost in agreement with the Meissner effect. The problem is that \mathbf{B} doesn't decay to zero but instead to its initial value in the past. This is in obvious conflict with the fact that superconductors are in thermodynamic equilibrium and of course does not agree with the Meissner effect. Heinz and Fritz London proposed in 1934 that instead of starting from the acceleration equation one should simply drop the time derivatives in Eq.148 i.e.

$$\nabla \times \nabla \times \mathbf{B} = -\frac{4\pi\nu}{c^2} \mathbf{B} \quad (152)$$

which is equivalent to

$$\nabla \times \mathbf{j} = -\frac{n e^2}{m c} \mathbf{B} \quad (153)$$

This is a new relation that replaces Ohm's law and the acceleration equation for the superconductor. At this point it is clearly only a phenomenological ansatz. Yet, it naturally leads to

$$\nabla^2 \mathbf{B} = \frac{4\pi n e^2}{m c^2} \mathbf{B} \quad (154)$$

which implies that the field decays on the length scale λ to zero in agreement with the Meissner effect. The length λ is called London penetration depth or often simply penetration depth. The challenge is now to develop a microscopic theory from which the London equation follows. Below we will see that the BCS theory of superconductivity indeed leads to the London equation. In case of $\nabla \cdot \mathbf{j} = \mathbf{0}$ (using the continuity equation this corresponds to time independent charge distributions $\partial\rho/\partial t = 0$) and in the Coulomb gauge $\nabla \cdot \mathbf{A} = \mathbf{0}$ it follows with $\mathbf{B} = \nabla \times \mathbf{A}$ that the London equation takes the form

$$\mathbf{j} = -\frac{n e^2}{m c} \mathbf{A}. \quad (155)$$

A. The Cooper instability

We consider two particles that interact via an attractive potential $V(\mathbf{r}_1 - \mathbf{r}_2)$ with Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_1}^2 - \frac{\hbar^2}{2m} \nabla_{\mathbf{r}_2}^2 + V(\mathbf{r}_1 - \mathbf{r}_2) \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) = E \Psi(\mathbf{r}_1, \mathbf{r}_2) \quad (156)$$

We consider relative and center of gravity coordinates

$$\begin{aligned} \mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2 \\ \mathbf{R} &= \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \end{aligned} \quad (157)$$

which yields

$$\left(-\frac{\hbar^2}{2m^*} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right) \Psi(\mathbf{R}, \mathbf{r}) = E \Psi(\mathbf{R}, \mathbf{r}) \quad (158)$$

where $m^* = 2m$ is the total mass and $\mu = m/2$ the reduced mass. The center of gravity motion is unaffected by the potential leading to the ansatz

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}) e^{i\mathbf{K}\cdot\mathbf{R}} \quad (159)$$

which yields

$$\left(-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right) \psi(\mathbf{r}) = \tilde{E} \psi(\mathbf{r}) \quad (160)$$

where $E = \tilde{E} + \frac{\hbar^2 \mathbf{K}^2}{2m^*}$. Obviously the lowest energy corresponds to the center of gravity momentum $\mathbf{K} = \mathbf{0}$, i.e. the individual momenta of the two particle that scatter are opposite. In what follows we first consider $\mathbf{K} = \mathbf{0}$, leading to $E = \tilde{E}$. Since $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ is the spatial part of the wave function it will be even in case the spin part of the wave function is a singlet and odd in case of a triplet, i.e. $\psi(\mathbf{r}) = \pm \psi(-\mathbf{r})$.

It is useful to Fourier transform this equation with $\psi(\mathbf{k}) = \int d^3r \psi(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}$ which yields

$$\int V(\mathbf{k} - \mathbf{k}') \psi(\mathbf{k}') \frac{d^d k}{(2\pi)^d} = (E - 2\varepsilon_{\mathbf{k}}) \psi(\mathbf{k}), \quad (161)$$

where $\varepsilon_{\mathbf{k}} = \frac{\hbar^2}{2m} \mathbf{k}^2$ is the energy of a single free electron. This yields with $\Delta(\mathbf{k}) = (E - 2\varepsilon_{\mathbf{k}}) \psi(\mathbf{k})$ the equation

$$\Delta(\mathbf{k}) = - \int \frac{V(\mathbf{k} - \mathbf{k}')}{2\varepsilon_{\mathbf{k}'} - E} \Delta(\mathbf{k}') \frac{d^d k}{(2\pi)^d} \quad (162)$$

A bound state would naturally correspond to $E < 2\varepsilon_{\mathbf{k}'}$, i.e. for bound states follows $2\varepsilon_{\mathbf{k}'} - E > 0$.

Eq.160 and therefore the equivalent Eq.162 are identical to the Schrödinger equation of a single particle with potential $V(\mathbf{r})$. Suppose we have an attractive potential $V(\mathbf{r}) = -V_0$ for $|\mathbf{r}| < a$. It is known that for $d = 3$ the amplitude V_0 of the attractive potential must exceed the energy $V_0^c = \hbar^2 \pi^2 / (8ma^2)$. A slightly different model would be

$$V(\mathbf{k} - \mathbf{k}') = \begin{cases} -V_0 & \varepsilon_{\mathbf{k}}, \varepsilon_{\mathbf{k}'} < \omega_D \\ 0 & \text{otherwise} \end{cases} \quad (163)$$

where we need to keep in mind that V_0 has dimension energy per volume (due to the Fourier transform), i.e. it cannot be compared with the earlier V_0 . It follows in case of a constant $\Delta(\mathbf{k}) = \Delta$ (necessarily implying singlet pairing) that (we use $\rho(\varepsilon) = A\sqrt{\varepsilon}$ with $A = \frac{2\pi(2m)^{3/2}}{h^3}$):

$$\begin{aligned} \Delta &= V_0 A \Delta \int_0^{\omega_D} \frac{\sqrt{\varepsilon}}{2\varepsilon - E} d\varepsilon \\ &= V_0 A \Delta \left(\sqrt{\omega_D} - \sqrt{\frac{-E}{2}} \arctan \left(\sqrt{\frac{2\omega_D}{-E}} \right) \right). \end{aligned}$$

We used the density of states of a three dimensional system:

$$\begin{aligned} \rho(\varepsilon) &= \int \frac{d^3k}{(2\pi)^3} \delta\left(\varepsilon - \frac{\hbar^2}{2m} k^2\right) = \int \frac{k^2 dk}{2\pi^2} \delta\left(\varepsilon - \frac{\hbar^2}{2m} k^2\right) \\ &= \frac{2\pi(2m)^{3/2}}{h^3} \omega^{1/2} \theta(\varepsilon - \omega), \end{aligned}$$

and we obtain a critical value for the potential

$$V_0^c = \frac{1}{A\sqrt{\omega_D}}.$$

Again, bound states only form for sufficiently strong attractive potentials .

In case of a many fermion system, states with momenta below the Fermi energy are all occupied and the integration over momenta starts with a magnitude $|\mathbf{k}| = k_F$ instead of $|\mathbf{k}| = 0$. This is the key distinction between electrons in free space and a many body system. Assuming for example that

$$V(\mathbf{k} - \mathbf{k}') = \begin{cases} -V_0 & |\varepsilon_{\mathbf{k}} - \varepsilon_F|, |\varepsilon_{\mathbf{k}'} - \varepsilon_F| < \omega_D \\ 0 & \text{otherwise} \end{cases} \quad (164)$$

it follows in case of a constant $\Delta(\mathbf{k}) = \Delta$ (necessarily implying singlet pairing) that

$$\begin{aligned}\Delta &= \Delta V_0 \rho_F \int_{\varepsilon_F}^{\varepsilon_F + \omega_D} \frac{d\varepsilon'}{2\varepsilon' - E} \\ &= \Delta \frac{V_0 \rho_F}{2} \log \left(\frac{2\varepsilon_F - E}{2(\varepsilon_F + \omega_D) - E} \right).\end{aligned}\quad (165)$$

In the limit of small $\lambda = V_0 \rho_F$ where E must be close to $2\varepsilon_F$, the solution is

$$E = 2\varepsilon_F - 2\omega_D e^{-\frac{2}{\lambda}}, \quad (166)$$

which yields the binding energy

$$\varepsilon_b = 2\omega_D e^{-\frac{2}{\lambda}}. \quad (167)$$

To stress the distinction between the bound state formation in free space and with filled Fermi-see once more, we go back to Eq.162 and vary the chemical potential:

$$\Delta = \Delta V_0 \int_{\varepsilon_F}^{\varepsilon_F + \omega_0} \frac{\rho(\varepsilon)}{2\varepsilon - E} d\varepsilon \quad (168)$$

If $\varepsilon_F \rightarrow 0$ it is indeed not anymore allowed to approximate the density of states $\rho(\varepsilon)$ by a constant value at the Fermi level. One has to include the variation $\rho(\varepsilon) = A\sqrt{\varepsilon}$ near the band edge. In case of an empty Fermi see with $\varepsilon_F = 0$ we have

$$\Delta = \Delta V_0 A \int_0^{\omega_0} \frac{\sqrt{\varepsilon}}{2\varepsilon + \varepsilon_b} d\varepsilon. \quad (169)$$

As the integral is no longer divergent for small ε and $\varepsilon_b \rightarrow 0$, we are back to the original result that one needs to have a threshold strength for the potential V_0 to form a bound state. We conclude that the Cooper instability for infinitesimal interaction V_0 is a consequence of the fact that the number of low energy states is enhanced in case of a Fermi surface.

Finally we comment on the impact of a finite center of gravity momentum \mathbf{K} , that is naturally associated with a finite current density

$$j = \frac{n_e e \hbar}{m} |\mathbf{K}|, \quad (170)$$

where n_e is the electron density and $\hbar |\mathbf{K}| / m$ the velocity of the pair. Repeating the above analysis for finite \mathbf{K} , it follows for the total energy

$$E = 2\varepsilon_F - \varepsilon_b + \frac{\hbar^2 \mathbf{K}^2}{2m^*} \quad (171)$$

with ε_b of Eq.167. To get a bound state at finite current, it must hold that $E < 2\varepsilon_F$, which leads to the appearance of a critical current

$$j_c = 2n_e e \sqrt{\frac{\varepsilon_b}{m}} \quad (172)$$

which is of the same order of magnitude as the result that follows from, BCS theory.

B. BCS theory of superconductivity

The BCS theory gives an answer to the open question that emerges as consequence of the Cooper instability: What happens with an entire Fermi-sea of attractively interacting electrons. Based on the insight that the leading instability occurs at zero center of mass momentum we modl the attractive interaction between electrons, mediated by phonons via he BCS or pairing Hamiltonian:

$$H_{\text{BCS}} = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} - \frac{V_0}{N} \sum_{\mathbf{k},\mathbf{k}'} \gamma_{\mathbf{k},\mathbf{k}'} c_{\mathbf{k}',\uparrow}^\dagger c_{-\mathbf{k}',\downarrow}^\dagger c_{-\mathbf{k},\downarrow} c_{\mathbf{k},\uparrow}$$

It consists of the usual kinetic energy with band dispersion (it is easy to generalize the approach to different dispersions as we will see):

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} - \mu.$$

The sign in front of the interaction V_0 was chosen such that $V_0 > 0$ corresponds to an attractive coupling.

$$\gamma_{\mathbf{k},\mathbf{k}'} = \begin{cases} 1 & |\varepsilon_{\mathbf{k}}|, |\varepsilon_{\mathbf{k}'}| < \hbar\omega_D \\ 0 & \text{otherwise} \end{cases}$$

takes into account that only fermionic states that have energies relative to the Fermi energy below the phonon frequency interact. To find an approximate solution of this problem we perform the Hartree-Fock decoupling

$$AB = (A - \langle A \rangle)(B - \langle B \rangle) + A \langle B \rangle + B \langle A \rangle - \langle A \rangle \langle B \rangle$$

with

$$\begin{aligned} A &= c_{\mathbf{k}',\uparrow}^\dagger c_{-\mathbf{k}',\downarrow}^\dagger \\ B &= c_{-\mathbf{k},\downarrow} c_{\mathbf{k},\uparrow} \end{aligned}$$

This choice for A and B is motivated by the hope, that $\langle A \rangle \neq 0$ and $\langle B \rangle \neq 0$ amount to pairing of electrons. Whether this turns out to be the case remains to be analyzed. It is also clear that an expectation value $\langle c_{\mathbf{k}',\uparrow}^\dagger c_{-\mathbf{k}',\downarrow}^\dagger \rangle \neq 0$ makes no sense for a system with fixed particle number. Thus, this new mean field theory seems to violate charge conservation, an

issue that we need to address as we proceed. Performing the mean field decoupling yields:

$$\begin{aligned}
H_{\text{BCS}}^{\text{MF}} &= \sum_{\mathbf{k}, \sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \frac{V_0}{N} \sum_{\mathbf{k}, \mathbf{k}'} \gamma_{\mathbf{k}, \mathbf{k}'} \langle c_{\mathbf{k}', \uparrow}^\dagger c_{-\mathbf{k}', \downarrow}^\dagger \rangle \langle c_{-\mathbf{k}, \downarrow} c_{\mathbf{k}, \uparrow} \rangle \\
&\quad - \frac{V_0}{N} \sum_{\mathbf{k}, \mathbf{k}'} \gamma_{\mathbf{k}, \mathbf{k}'} \langle c_{\mathbf{k}', \uparrow}^\dagger c_{-\mathbf{k}', \downarrow}^\dagger \rangle c_{-\mathbf{k}, \downarrow} c_{\mathbf{k}, \uparrow} - \frac{V_0}{N} \sum_{\mathbf{k}, \mathbf{k}'} \gamma_{\mathbf{k}, \mathbf{k}'} c_{\mathbf{k}', \uparrow}^\dagger c_{-\mathbf{k}', \downarrow}^\dagger \langle c_{-\mathbf{k}, \downarrow} c_{\mathbf{k}, \uparrow} \rangle
\end{aligned}$$

If we introduce

$$\Delta_{\mathbf{k}} = -\frac{V_0}{N} \sum_{\mathbf{k}} \gamma_{\mathbf{k}, \mathbf{k}'} \langle c_{-\mathbf{k}, \downarrow} c_{\mathbf{k}, \uparrow} \rangle$$

this mean field Hamiltonian simplified to:

$$H_{\text{BCS}}^{\text{MF}} = \sum_{\mathbf{k}, \sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}} \left(\Delta_{\mathbf{k}}^* c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow} + \Delta_{\mathbf{k}} c_{-\mathbf{k}\downarrow}^\dagger c_{\mathbf{k}\uparrow}^\dagger \right) + \sum_{\mathbf{k}} \frac{\Delta_{\mathbf{k}}^2}{V_0}.$$

The form of this Hamiltonian is similar to an effective free electron problem in the sense that it only contains terms with two operators $c_{\mathbf{k}\sigma}^\dagger$ or $c_{\mathbf{k}\sigma}$, respectively. However, the appearance terms like $\Delta_{\mathbf{k}}^* c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow}$ and $\Delta_{\mathbf{k}} c_{-\mathbf{k}\downarrow}^\dagger c_{\mathbf{k}\uparrow}^\dagger$ has no analog in the free electron limit. Those terms are obviously the ones that explicitly violate charge conservation at the mean field level. In order to bring this Hamiltonian into the desired form, we introduce the Nambu spinor

$$c_{\mathbf{k}} = \begin{pmatrix} c_{\mathbf{k}\uparrow} \\ c_{-\mathbf{k}\downarrow}^\dagger \end{pmatrix}. \quad (173)$$

which allows us to express $H_{\text{BCS}}^{\text{MF}}$ in a form that resembles a more the usual free fermion problem.

where

$$H_{\text{BCS}}^{\text{MF}} = \sum_{\mathbf{k}} c_{\mathbf{k}}^\dagger \begin{pmatrix} \varepsilon_{\mathbf{k}} & -\Delta_{\mathbf{k}} \\ -\Delta_{\mathbf{k}}^* & -\varepsilon_{\mathbf{k}} \end{pmatrix} c_{\mathbf{k}} + \sum_{\mathbf{k}} \left(\varepsilon_{\mathbf{k}} + \frac{\Delta_{\mathbf{k}}^2}{V_0} \right).$$

The 2×2 -matrix has eigenvalues determined by

$$(E - \varepsilon_{\mathbf{k}})(E + \varepsilon_{\mathbf{k}}) - |\Delta_{\mathbf{k}}|^2 = 0$$

which yields

$$E_{\mathbf{k}\pm} = \pm E_{\mathbf{k}}$$

with

$$E_{\mathbf{k}} = \sqrt{\varepsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2} > 0.$$

It is diagonalized by the unitary transformation $U_{\mathbf{k}}$, that is determined by the eigenvectors.

Suppose one eigenvector is $\begin{pmatrix} u_{\mathbf{k}} \\ v_{\mathbf{k}} \end{pmatrix}$ and it corresponds to the eigenvalue $+E_{\mathbf{k}}$. It holds

$$\begin{pmatrix} \varepsilon_{\mathbf{k}} & -\Delta_{\mathbf{k}} \\ -\Delta_{\mathbf{k}}^* & -\varepsilon_{\mathbf{k}} \end{pmatrix} \begin{pmatrix} u_{\mathbf{k}} \\ v_{\mathbf{k}} \end{pmatrix} = E_{\mathbf{k}} \begin{pmatrix} u_{\mathbf{k}} \\ v_{\mathbf{k}} \end{pmatrix}$$

which yields explicitly

$$\begin{aligned} \varepsilon_{\mathbf{k}}u_{\mathbf{k}} - \Delta_{\mathbf{k}}v_{\mathbf{k}} &= E_{\mathbf{k}}u_{\mathbf{k}} \\ -\Delta_{\mathbf{k}}^*u_{\mathbf{k}} - \varepsilon_{\mathbf{k}}v_{\mathbf{k}} &= E_{\mathbf{k}}v_{\mathbf{k}}. \end{aligned}$$

This implies that $\begin{pmatrix} -v_{\mathbf{k}}^* \\ u_{\mathbf{k}}^* \end{pmatrix}$ is also an eigenvector but with eigenvalue $-E_{\mathbf{k}}$. The check for this, we evaluate

$$\begin{pmatrix} \varepsilon_{\mathbf{k}} & -\Delta_{\mathbf{k}} \\ -\Delta_{\mathbf{k}}^* & -\varepsilon_{\mathbf{k}} \end{pmatrix} \begin{pmatrix} -v_{\mathbf{k}}^* \\ u_{\mathbf{k}}^* \end{pmatrix} = -E_{\mathbf{k}} \begin{pmatrix} -v_{\mathbf{k}}^* \\ u_{\mathbf{k}}^* \end{pmatrix}$$

which leads to

$$\begin{aligned} -\varepsilon_{\mathbf{k}}v_{\mathbf{k}}^* - \Delta_{\mathbf{k}}u_{\mathbf{k}}^* &= E_{\mathbf{k}}v_{\mathbf{k}}^* \\ \Delta_{\mathbf{k}}^*v_{\mathbf{k}}^* - \varepsilon_{\mathbf{k}}u_{\mathbf{k}}^* &= -E_{\mathbf{k}}u_{\mathbf{k}}^* \end{aligned}$$

which is indeed identical to the first condition above. It also holds that both eigenvalues are orthogonal to each other. Thus, we know the unitary transformation that diagonalizes the above 2×2 matrix:

$$U_{\mathbf{k}}^{-1} \begin{pmatrix} \varepsilon_{\mathbf{k}} & -\Delta_{\mathbf{k}} \\ -\Delta_{\mathbf{k}}^* & -\varepsilon_{\mathbf{k}} \end{pmatrix} U_{\mathbf{k}} = \begin{pmatrix} E_{\mathbf{k}} & 0 \\ 0 & -E_{\mathbf{k}} \end{pmatrix}$$

where

$$U_{\mathbf{k}} = \begin{pmatrix} u_{\mathbf{k}} & -v_{\mathbf{k}}^* \\ v_{\mathbf{k}} & u_{\mathbf{k}}^* \end{pmatrix} \tag{174}$$

as well as

$$U_{\mathbf{k}}^{-1} = \begin{pmatrix} u_{\mathbf{k}}^* & v_{\mathbf{k}} \\ -v_{\mathbf{k}} & u_{\mathbf{k}} \end{pmatrix}$$

It is straightforward to determine $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ from the eigenvalue equations, keeping in mind that normalization (or unitarity) yields

$$|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$$

It follows

$$u_{\mathbf{k}} = -\frac{\Delta_{\mathbf{k}}}{E_{\mathbf{k}} - \varepsilon_{\mathbf{k}}} v_{\mathbf{k}}$$

It follows:

$$u_{\mathbf{k}}^2 = \frac{1}{2} \left(1 + \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right)$$

$$v_{\mathbf{k}}^2 = 1 - u_{\mathbf{k}}^2 = \frac{1}{2} \left(1 - \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right).$$

which also implies that

$$u_{\mathbf{k}} v_{\mathbf{k}}^* = \frac{\Delta_{\mathbf{k}}}{2E_{\mathbf{k}}}.$$

The above unitary transformation naturally transforms the Namu spinor according to

$$a_{\mathbf{k}} = U_{\mathbf{k}}^{-1} c_{\mathbf{k}}$$

with

$$a_{\mathbf{k}} = \begin{pmatrix} a_{\mathbf{k}\uparrow} \\ a_{-\mathbf{k}\downarrow}^\dagger \end{pmatrix},$$

and it follows

$$\begin{aligned} \sum_{\mathbf{k}} c_{\mathbf{k}}^\dagger \begin{pmatrix} \varepsilon_{\mathbf{k}} & -\Delta_{\mathbf{k}} \\ -\Delta_{\mathbf{k}}^* & -\varepsilon_{\mathbf{k}} \end{pmatrix} c_{\mathbf{k}} &= \sum_{\mathbf{k}} c_{\mathbf{k}}^\dagger U_{\mathbf{k}} \begin{pmatrix} E_{\mathbf{k}} & 0 \\ 0 & -E_{\mathbf{k}} \end{pmatrix} U_{\mathbf{k}}^{-1} c_{\mathbf{k}} \\ &= \sum_{\mathbf{k}} a_{\mathbf{k}}^\dagger \begin{pmatrix} E_{\mathbf{k}} & 0 \\ 0 & -E_{\mathbf{k}} \end{pmatrix} a_{\mathbf{k}} \\ &= \sum_{\mathbf{k}} E_{\mathbf{k}} \left(a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}\uparrow} - a_{-\mathbf{k}\downarrow}^\dagger a_{-\mathbf{k}\downarrow}^\dagger \right) \\ &= \sum_{\mathbf{k}} E_{\mathbf{k}} \left(a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}\uparrow} + a_{-\mathbf{k}\downarrow}^\dagger a_{-\mathbf{k}\downarrow}^\dagger - 1 \right) \\ &= \sum_{\mathbf{k}, \sigma} E_{\mathbf{k}} a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} - \sum_{\mathbf{k}} E_{\mathbf{k}} \end{aligned} \quad (175)$$

In total holds

$$H_{\text{BCS}}^{\text{MF}} = \sum_{\mathbf{k}, \sigma} E_{\mathbf{k}} a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} + \sum_{\mathbf{k}} \left(\frac{\Delta_{\mathbf{k}}^2}{V_0} + \varepsilon_{\mathbf{k}} - \sqrt{\varepsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2} \right).$$

Thus, we managed to bring the Hamiltonian into the desired form of a free Fermi gas. In particular it holds

$$\langle a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} \rangle = f(E_{\mathbf{k}})$$

where

$$f(\varepsilon) = \frac{1}{\exp(\beta\varepsilon) + 1}$$

is the usual Fermi function.

Since $E_{\mathbf{k}} > 0$, it holds that at $T = 0$ that the ground state energy is

$$E_0 = \sum_{\mathbf{k}} \left(\frac{\Delta_{\mathbf{k}}^2}{V_0} + \varepsilon_{\mathbf{k}} - \sqrt{\varepsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2} \right).$$

All excitations are governed by the fermions $a_{\mathbf{k}\sigma}$. The spectrum of those excitations is $\sqrt{\varepsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2}$ which implies that it is gapped with gap $|\Delta_{\mathbf{k}}|$. The density of states of these excitations is

$$\begin{aligned} \rho(\omega) &= \frac{1}{N} \sum_{\mathbf{k}} \delta(\omega - E_{\mathbf{k}}) = \frac{1}{N} \sum_{\mathbf{k}} \delta\left(\omega - \sqrt{\varepsilon_{\mathbf{k}}^2 + |\Delta|^2}\right) \\ &= \int d\varepsilon \rho_0(\varepsilon) \delta\left(\omega - \sqrt{\varepsilon^2 + |\Delta|^2}\right) \end{aligned}$$

where $\rho_0(\varepsilon)$ is the density of states of the normal conductor. We substitute $z = \sqrt{\varepsilon^2 + |\Delta|^2}$ with $\frac{d\varepsilon}{dz} = \frac{z}{\sqrt{z^2 - \Delta^2}}$ and we obtain

$$\rho(\omega) = \theta(\omega^2 - \Delta^2) \frac{|\omega|}{\sqrt{\omega^2 - \Delta^2}} \rho_0\left(\frac{\omega}{\sqrt{\omega^2 - \Delta^2}}\right).$$

There are no states below Δ , while the density of states diverges above the gap edge.

Next we solve the gap equation. From the above unitary transformation follows:

$$\begin{aligned} c_{\mathbf{k}\uparrow} &= u_{\mathbf{k}}^* a_{\mathbf{k}\uparrow} + v_{\mathbf{k}} a_{-\mathbf{k}\downarrow}^\dagger \\ c_{-\mathbf{k}\downarrow}^\dagger &= -v_{\mathbf{k}} a_{\mathbf{k}\uparrow} + u_{\mathbf{k}} a_{-\mathbf{k}\downarrow}^\dagger \end{aligned}$$

which yields

$$c_{-\mathbf{k}\downarrow} = -v_{\mathbf{k}}^* a_{\mathbf{k}\uparrow}^\dagger + u_{\mathbf{k}}^* a_{-\mathbf{k}\downarrow}$$

This can be used to express the operator product $c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow}$ that is needed to determine $\Delta_{\mathbf{k}}$.

It holds:

$$c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow} = \left(u_{\mathbf{k}}^* a_{\mathbf{k}\uparrow} + v_{\mathbf{k}} a_{-\mathbf{k}\downarrow}^\dagger \right) \left(u_{\mathbf{k}}^* a_{-\mathbf{k}\downarrow} - v_{\mathbf{k}}^* a_{\mathbf{k}\uparrow}^\dagger \right)$$

which yields

$$\langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle = v_{\mathbf{k}} u_{\mathbf{k}} \left(2 \langle a_{-\mathbf{k}\downarrow}^\dagger a_{-\mathbf{k}\downarrow} \rangle - 1 \right)$$

and we obtain for the gap equation:

$$\Delta = -\frac{V_0}{N} \sum_{\mathbf{k}} \frac{\Delta}{2E_{\mathbf{k}}} (2f(E_{\mathbf{k}}) - 1)$$

In the vicinity of the transition temperature the gap Δ is small and we can linearize the equation. The linearized gap equation is

$$\Delta = V \sum_{\mathbf{k}} \frac{\Delta}{2\xi_{\mathbf{k}}} \tanh\left(\frac{\beta\xi_{\mathbf{k}}}{2}\right) \quad (176)$$

which we write with density of states ρ as

$$\Delta = V\rho\Delta \int_{-\omega_D}^{\omega_D} \frac{\tanh\left(\frac{\beta_c\varepsilon}{2}\right)}{2\varepsilon} d\varepsilon. \quad (177)$$

We perform the integral

$$\begin{aligned} \int_{-\omega_0}^{\omega_0} \frac{\tanh\left(\frac{\beta\varepsilon}{2}\right)}{2\varepsilon} d\varepsilon &= \int_0^{\beta\omega_D/2} \frac{\tanh(x)}{x} dx \\ &= -\int_0^{\beta\omega_D/2} \sec^2(x) \log(x) dx + \tanh(x) \log x \Big|_0^{\beta\omega_D/2} \\ &= \gamma_E - \log\frac{\pi}{4} + \log\left(\frac{\omega_D}{2T}\right) = \log\left(\frac{2\omega_D e^{\gamma_E}}{\pi T}\right), \end{aligned} \quad (178)$$

and obtain

$$\Delta = V\rho\Delta \log\left(\frac{2\omega_D e^{\gamma_E}}{\pi T_c}\right). \quad (179)$$

which yields for the transition temperature:

$$T_c = \frac{2\omega_D e^{\gamma_E}}{\pi} \exp\left(-\frac{1}{\lambda}\right) \simeq 1.134\omega_D \exp\left(-\frac{1}{\lambda}\right) \quad (180)$$

where $\lambda = V\rho$ is the dimensionless coupling constant.

Next we analyze the gap equation at $T = 0$. Since $E_{\mathbf{k}} > 0$ follows that $f(E_{\mathbf{k}}) = 0$ in the limit of $T = 0$ and the gap equation simplifies to

$$\begin{aligned} \Delta &= V_0\rho \int_{-\omega_D}^{\omega_D} d\varepsilon \frac{\Delta}{2\sqrt{\varepsilon^2 + \Delta^2}} \\ &= \lambda\Delta \log\left(\frac{\omega_D}{\Delta} + \sqrt{1 + \left(\frac{\omega_D}{\Delta}\right)^2}\right) \\ &\simeq \lambda\Delta \log\left(\frac{2\omega_D}{\Delta}\right). \end{aligned}$$

This yields the result:

$$\Delta(T = 0) = 2\omega_D \exp(-1/\lambda).$$

If we compare the value of the transition temperature with the zero temperature gap it follows

$$\begin{aligned}\frac{2\Delta(T=0)}{k_B T_c} &= \frac{4\omega_D \exp(-\frac{1}{\lambda})}{\frac{2e^{\gamma_E}}{\pi} \omega_D \exp(-\frac{1}{\lambda})} \\ &= 2\pi e^{-\gamma_E} \simeq 3.5273\end{aligned}$$

which is in agreement with numerous observations for elementary superconductors.

The result for the zero temperature gap can alternatively be obtained from the ground state energy. Earlier we found

$$E_0 = \sum_{\mathbf{k}} \left(\frac{\Delta_{\mathbf{k}}^2}{V_0} + \varepsilon_{\mathbf{k}} - \sqrt{\varepsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2} \right).$$

Performing the momentum integration and subtracting the value of the energy in the normal state for $\Delta = 0$ follows

$$\begin{aligned}E_0 &= E_0(\Delta = 0) + N \left(\frac{\Delta^2}{V_0} + \rho \int d\varepsilon \left(\varepsilon - \sqrt{\varepsilon^2 + \Delta^2} \right) - 2\rho \int d\varepsilon \theta(-\varepsilon) \varepsilon \right) \\ &= E_0(\Delta = 0) + N \left(\frac{\Delta^2}{V_0} + 2\rho \int_0^{\omega_D} d\varepsilon \left(\varepsilon - \sqrt{\varepsilon^2 + \Delta^2} \right) \right) \\ &= E_0(\Delta = 0) + N \left(\frac{\Delta^2}{V_0} + \rho \Delta^2 \log \left(\frac{\Delta}{2\omega_D} \right) - \frac{\rho}{2} \Delta^2 \right)\end{aligned}$$

Minimizing the ground state energy with respect to Δ yields

$$\frac{1}{N} \frac{\partial E_0}{\partial \Delta} = 2 \frac{\Delta}{V_0} + 2\rho \Delta \log \left(\frac{\Delta}{2\omega_D} \right) = 0$$

which has the nontrivial solution

$$\Delta(T=0) = 2\omega_D \exp(-1/\lambda).$$

in full agreement with our earlier result.

C. Heat capacity

To analyze thermodynamic properties we analyze the internal energy

$$\begin{aligned}U(T) &= E_0 + \sum_{\mathbf{k}, \sigma} E_{\mathbf{k}} \langle a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} \rangle \\ &= E_0 + 2 \sum_{\mathbf{k}} E_{\mathbf{k}} f(E_{\mathbf{k}})\end{aligned}$$

It implies for the heat capacity

$$C(T) = \frac{1}{V} \frac{\partial U(T)}{\partial T} = \frac{2k_B}{V} \sum_{\mathbf{k}} \left(\frac{E_{\mathbf{k}}^2}{k_B^2 T^2} - \frac{E_{\mathbf{k}}}{k_B^2 T} \frac{\partial E_{\mathbf{k}}}{\partial T} \right) \frac{e^{\beta E_{\mathbf{k}}}}{(e^{\beta E_{\mathbf{k}}} + 1)^2}$$

where

$$\frac{\partial E_{\mathbf{k}}}{\partial T} = \frac{1}{E_{\mathbf{k}}} \frac{\partial \Delta_{\mathbf{k}}}{\partial T}.$$

Thus we obtain:

$$C_V = 2 \sum_{\mathbf{k}} E_{\mathbf{k}} \left(-\frac{E_{\mathbf{k}}}{T} + \frac{\Delta}{E_{\mathbf{k}}} \frac{\partial \Delta}{\partial T} \right) \frac{\partial f(E_{\mathbf{k}})}{\partial E_{\mathbf{k}}} \quad (181)$$

First, we analyze this result at $T \rightarrow T_c$. There $E_k \approx \xi_k$.

With

$$\frac{\partial f}{\partial E} \approx -\delta(E) - \frac{\pi^2}{6} (k_B T)^2 \delta''(E), \quad (182)$$

and

$$\Delta(T) \approx 3.06 k_B T_c \sqrt{1 - \frac{T}{T_c}} \quad (183)$$

as determined earlier it follows for $T = T_c - 0^+$

$$\begin{aligned} C_V(T_c - 0) &= 2\nu_0 \int d\xi \left(-\frac{\xi^2}{T} \right) \frac{\partial f}{\partial \xi} + \nu_0 \int d\xi \frac{\partial \Delta^2}{\partial T} \frac{\partial f}{\partial \xi} \\ &= \frac{2\pi^2 \nu_0 k_B^2}{3} T_c + (3.06)^2 \nu_0 k_B^2 T_c = C_V(T_c + 0) + \Delta C_V \end{aligned} \quad (184)$$

Thus one obtains

$$\frac{\Delta C_V}{C_V(T_c + 0)} \approx 1.43 \quad (185)$$

Jump in $\frac{\partial \Delta}{\partial T}$ leads to jump in C_V (see Fig. ??).

For $k_B T \ll k_B T_c \sim \Delta(0)$ one obtains $C_V \propto e^{-\frac{\Delta}{k_B T}}$.

D. BCS-wave function

We want to determine the ground state that corresponds to the start from a mean field Hamiltonian

$$H_0 = \sum_{\mathbf{k}, \sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}} \left(\Delta_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger + h.c. \right) \quad (186)$$

As outlined above, the Hamiltonian can be written as

$$H_0 = \sum_{\mathbf{k}} \begin{pmatrix} c_{\mathbf{k}\uparrow} \\ c_{-\mathbf{k}\downarrow}^\dagger \end{pmatrix}^\dagger \begin{pmatrix} \varepsilon_{\mathbf{k}} & \Delta_{\mathbf{k}} \\ \Delta_{\mathbf{k}}^* & -\varepsilon_{\mathbf{k}} \end{pmatrix} \begin{pmatrix} c_{\mathbf{k}\uparrow} \\ c_{-\mathbf{k}\downarrow}^\dagger \end{pmatrix}. \quad (187)$$

H_0 is diagonalized by a 2×2 unitary matrix leading to the creation and destruction operator of the Bogoliubov quasiparticles of the problem

$$\begin{pmatrix} a_{\mathbf{k}\uparrow} \\ a_{-\mathbf{k}\downarrow}^\dagger \end{pmatrix} = \begin{pmatrix} u_{\mathbf{k}} & -v_{\mathbf{k}} \\ v_{\mathbf{k}}^* & u_{\mathbf{k}}^* \end{pmatrix} \begin{pmatrix} c_{\mathbf{k}\uparrow} \\ c_{-\mathbf{k}\downarrow}^\dagger \end{pmatrix}. \quad (188)$$

It then holds

$$H_0 = E_0 + \sum_{\mathbf{k}, \sigma} E_{\mathbf{k}} a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma}. \quad (189)$$

The last result follows from the fact that the eigenvalues of H_0 always come in pairs with opposite sign. In Eq.189 we included the ground state energy as additional constant. To obtain the actual BCS wave function we use the fact that Eq.189 implies that the ground state wave function is the vacuum state of the Bogoliubov quasiparticles. Thus, it holds

$$a_{\mathbf{k}\sigma} |\Phi_{\text{BCS}}\rangle = 0 \text{ for all } \mathbf{k}, \sigma. \quad (190)$$

We assume

$$|\Phi_{\text{BCS}}\rangle = C e^{\sum_{\mathbf{k}} \phi_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger} |0\rangle \quad (191)$$

where Here $|0\rangle$ is the vacuum state of the original operators, i.e. $c_{i\sigma} |0\rangle = 0$.

- We next determine the pair wave function ϕ_{ij} from the condition Eq.190. Eq.190 corresponds to $a_{\mathbf{k}\sigma} |\Phi_{\mathbf{k}}\rangle = 0$, where

$$|\Phi_{\text{BCS}}\rangle = C \prod_{\mathbf{k}} e^{\phi_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger} |0\rangle = \prod_{\mathbf{k}} |\Phi_{\mathbf{k}}\rangle$$

We write explicitly:

$$\begin{aligned} a_{\mathbf{k}\uparrow} &= u_{\mathbf{k}} c_{\mathbf{k}\uparrow} - v_{\mathbf{k}} c_{-\mathbf{k}\downarrow}^\dagger \\ a_{\mathbf{k}\downarrow} &= v_{\mathbf{k}} c_{-\mathbf{k}\uparrow}^\dagger + u_{\mathbf{k}} c_{\mathbf{k}\downarrow}. \end{aligned} \quad (192)$$

and obtain from $a_{\mathbf{k}\sigma} |\Phi_{\mathbf{k}}\rangle = 0$ that:

$$u_{\mathbf{k}} c_{\mathbf{k}\uparrow} |\Phi_{\text{BCS}}\rangle = v_{\mathbf{k}} c_{\mathbf{k}\downarrow}^\dagger |\Phi_{\text{BCS}}\rangle. \quad (193)$$

We first analyze $c_{\mathbf{k}\uparrow} |\Phi_{\mathbf{k}}\rangle$. It is useful to introduce the operator

$$\theta = \sum_{\mathbf{k}} \phi_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger \quad (194)$$

and it holds for the wave function

$$|\Phi_{\text{BCS}}\rangle \propto \sum_{n=0}^{\infty} \frac{\theta^n}{n!} |0\rangle \quad (195)$$

It is easy to show that

$$[c_{\mathbf{k}\uparrow}, \theta] = b_{-\mathbf{k}\downarrow}^\dagger \quad (196)$$

with operator

$$b_{-\mathbf{k}\downarrow}^\dagger = \phi_{\mathbf{k}} c_{-\mathbf{k}\downarrow}^\dagger \quad (197)$$

follows that $[b_{-\mathbf{k}\downarrow}^\dagger, \theta] = 0$. It is now easy to apply $c_{\mathbf{k}\uparrow}$ to each term in the sum of Eq.195 separately. It holds:

$$\begin{aligned} c_{\mathbf{k}\uparrow} \theta |0\rangle &= b_{-\mathbf{k}\downarrow}^\dagger |0\rangle \\ c_{\mathbf{k}\uparrow} \theta^2 |0\rangle &= b_{-\mathbf{k}\downarrow}^\dagger \theta |0\rangle + \theta c_{\mathbf{k}\uparrow} \theta |0\rangle = 2\theta b_{-\mathbf{k}\downarrow}^\dagger |0\rangle \\ &\vdots \\ c_{\mathbf{k}\uparrow} \theta^n |0\rangle &= n\theta^{n-1} b_{-\mathbf{k}\downarrow}^\dagger |0\rangle. \end{aligned} \quad (198)$$

This result allows to resum the series Eq.195 and we obtain

$$c_{\mathbf{k}\uparrow} |\Phi_{\text{BCS}}\rangle = b_{-\mathbf{k}\downarrow}^\dagger |\Phi_{\text{BCS}}\rangle \quad (199)$$

The condition $a_{\mathbf{k}\sigma} |\Phi_{\text{BCS}}\rangle = 0$ in form of Eq.193 can then we written as

$$u_{\mathbf{k}} \phi_{\mathbf{k}} c_{\mathbf{k}\downarrow}^\dagger |\Phi_{\text{BCS}}\rangle = v_{\mathbf{k}} c_{-\mathbf{k}\downarrow}^\dagger |\Phi_{\text{BCS}}\rangle. \quad (200)$$

This implies immediately $\phi_{\mathbf{k}} = v_{\mathbf{k}}/u_{\mathbf{k}}$. It is easy to show that the condition $a_{-\mathbf{k}\downarrow} |\Phi_{\text{BCS}}\rangle = 0$ leads to the same condition. It follows with normalization factor:

$$C = \prod_{\mathbf{k}} u_{\mathbf{k}}$$

for the wave function

$$\begin{aligned} |\Phi_{\text{BCS}}\rangle &= C e^{\sum_{\mathbf{k}} v_{\mathbf{k}}/u_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}\downarrow}^\dagger} |0\rangle \\ &= \prod_{\mathbf{k}} u_{\mathbf{k}} e^{v_{\mathbf{k}}/u_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}\downarrow}^\dagger} |0\rangle \\ &= \prod_{\mathbf{k}} \left(u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}\downarrow}^\dagger \right) |0\rangle \end{aligned}$$

where the last step is a consequence of the fact that due to Pauli Principle $(c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}\downarrow}^\dagger)^n = 0$ if $n > 1$. The above approach also allows to project the BCS-wave function into the space of fixed number of electrons $N = N_p/2$.

$$|\Psi_{\text{BCS}}, N\rangle = C \left(\sum_{\mathbf{k}} \phi_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}\downarrow}^\dagger \right)^{N_p} |0\rangle.$$

E. Microscopic derivation of London equation

Next we analyze the behavior of the BCS state in an external magnetic field. The magnetic field modifies the kinetic energy of the electrons as follows:

$$H_{kin} = \frac{(\mathbf{p} - \frac{e}{c}\mathbf{A})^2}{2m}, \quad (201)$$

with $\mathbf{p} = -i\hbar\nabla$. In second quantized form

$$\begin{aligned} H_{kin} &= \sum_{\sigma} \int d^3r \psi_{\sigma}^\dagger(r) \frac{(\mathbf{p} - \frac{e}{c}\mathbf{A})^2}{2m} \psi_{\sigma}(r) \\ &= H_{0,kin} + H_1 + O(A^2), \end{aligned}$$

where

$$H_1 = -\frac{e}{mc} \sum_{\sigma} \int d^3r \psi_{\sigma}^\dagger(r) \mathbf{A} \cdot \mathbf{p} \psi_{\sigma}(r). \quad (202)$$

The order of the two operators \mathbf{A} and \mathbf{p} is unimportant since $\nabla \cdot \mathbf{A} = 0$.

The first order correction to the BCS ground state $|0\rangle = |BCS\rangle$ is

$$|\Phi_1\rangle = \sum_{l \neq 0} |l\rangle \frac{\langle l | H_1 | 0 \rangle}{E_0 - E_l} \quad (203)$$

Current. Velocity

$$\mathbf{v} = \frac{\mathbf{p} - \frac{e}{c}\mathbf{A}}{m} \quad (204)$$

Current density

$$\begin{aligned} \mathbf{j} &= e \sum_{\sigma} \psi_{\sigma}^\dagger(r) \frac{\mathbf{p} - \frac{e}{c}\mathbf{A}}{m} \psi_{\sigma}(r) = e \sum_{\sigma} \psi_{\sigma}^\dagger(r) \frac{\mathbf{p}}{m} \psi_{\sigma}(r) - \frac{e^2}{cm} \mathbf{A} \sum_{\sigma} \psi_{\sigma}^\dagger(r) \psi_{\sigma}(r) \\ &= \mathbf{j}_p + \mathbf{j}_d \end{aligned} \quad (205)$$

The \mathbf{j}_d contribution immediately gives the London equation

$$\mathbf{j}_d = -\frac{e^2 n}{mc} \mathbf{A} \quad (206)$$

Another contribution linear in \mathbf{A} could come from \mathbf{j}_p :

$$\langle \mathbf{j}_p \rangle = \langle \Phi_1 | \mathbf{j}_p | 0 \rangle + \langle 0 | \mathbf{j}_p | \Phi_1 \rangle \quad (207)$$

To calculate $|\Phi_1\rangle$ we need $\langle l | H_1 | 0 \rangle$, where $|l\rangle$ is an excited state. We assume $\mathbf{A} = \mathbf{A}_q e^{i\mathbf{q}\cdot\mathbf{r}}$ and $\mathbf{q} \cdot \mathbf{A}_q = 0$. Using $\psi_\sigma = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{q}\cdot\mathbf{r}}$ we obtain

$$H_1 = -\frac{\hbar e}{mc} \sum_{\mathbf{k}, \mathbf{q}, \sigma} c_{\mathbf{k}+\mathbf{q}, \sigma}^\dagger c_{\mathbf{k}, \sigma} \mathbf{k} \cdot \mathbf{A}_q$$

We use

$$c_{\mathbf{k}, \sigma} = u_{\mathbf{k}} \alpha_{\mathbf{k}, \sigma} + \sigma v_{\mathbf{k}} \alpha_{-\mathbf{k}, -\sigma}^\dagger, \quad c_{\mathbf{k}, \sigma}^\dagger = u_{\mathbf{k}} \alpha_{\mathbf{k}, \sigma}^\dagger + \sigma v_{\mathbf{k}} \alpha_{-\mathbf{k}, -\sigma} \quad (208)$$

and conclude that

$$\langle l | c_{\mathbf{k}+\mathbf{q}, \sigma}^\dagger c_{\mathbf{k}, \sigma} | 0 \rangle = \sigma u_{\mathbf{k}+\mathbf{q}} v_{\mathbf{k}} \langle l | \alpha_{\mathbf{k}+\mathbf{q}, \sigma}^\dagger \alpha_{-\mathbf{k}, -\sigma}^\dagger | 0 \rangle \quad (209)$$

but also

$$\begin{aligned} \langle l | c_{-\mathbf{k}, -\sigma}^\dagger c_{-\mathbf{k}-\mathbf{q}, -\sigma} | 0 \rangle &= -\sigma u_{\mathbf{k}} v_{\mathbf{k}+\mathbf{q}} \langle l | \alpha_{-\mathbf{k}, -\sigma}^\dagger \alpha_{\mathbf{k}+\mathbf{q}, \sigma}^\dagger | 0 \rangle \\ &= \sigma u_{\mathbf{k}} v_{\mathbf{k}+\mathbf{q}} \langle l | \alpha_{\mathbf{k}+\mathbf{q}, \sigma}^\dagger \alpha_{-\mathbf{k}, -\sigma}^\dagger | 0 \rangle \end{aligned} \quad (210)$$

Thus in both cases $|l\rangle$ the same, i.e., the same two quasiparticles created. For this particular $|l\rangle$ we obtain

$$\begin{aligned} \langle l | H_1 | 0 \rangle &= -\frac{\hbar e}{mc} ((\mathbf{k} \cdot \mathbf{A}_q) \sigma u_{\mathbf{k}+\mathbf{q}} v_{\mathbf{k}} + ((-\mathbf{k} - \mathbf{q}) \cdot \mathbf{A}_q) \sigma u_{\mathbf{k}} v_{\mathbf{k}+\mathbf{q}}) \\ &= -\frac{\hbar e}{mc} (\mathbf{k} \cdot \mathbf{A}_q) \sigma (u_{\mathbf{k}+\mathbf{q}} v_{\mathbf{k}} - u_{\mathbf{k}} v_{\mathbf{k}+\mathbf{q}}) \end{aligned} \quad (211)$$

For $\vec{q} \rightarrow 0$ we see that the matrix element vanishes. Together with the fact that $|E_0 - E_l| > 2\Delta$ this gives "rigidity" and

$$\langle \mathbf{j}_p \rangle = 0. \quad (212)$$

For the total current $\mathbf{j} = \mathbf{j}_d + \mathbf{j}_p$ follows the London equation

$$\mathbf{j} = -\frac{e^2 n}{mc} \mathbf{A}.$$

Of course only the total current is a gauge invariant quantity and therefore only this sum of $\mathbf{j}_d + \mathbf{j}_p$ determines the electrodynamic properties of the superconductor. Since we obtain the London equation, we obviously managed to explain the Meissner effect and thus the key experimental observation of superconductivity. Had we performed the same calculation

(again in Coulomb gauge) for the normal state, we would also have obtained $\mathbf{j}_d = -\frac{e^2 n}{mc} \mathbf{A}$. However the "paramagnetic" current in the normal state follows as $\mathbf{j}_p = \frac{e^2 n}{mc} \mathbf{A}$, such that in the normal state $\mathbf{j} = 0$. Thus, the key difference is the lack of rigidity of the normal state wave function.