Bardeen-Cooper-Schrieffer theory of superconductivity

Patryk Kubiczek

Jagiellonian University in Kraków

Kraków, 8/12/2014

What is a superconductor?

The material which experiences a second order phase transition (discontinuity in the derivative of the heat capacity) at T_c after which

- It is perfectly conducting
- It (almost) completely repels the magnetic field (Meissner-Ochsenfeld effect)
- Some magnetic flux may be quantized in units $h/2e$
- There is an energy gap in the excitations spectrum

Hint for theorists: the critical temperature T_c depends on the lattice ion mass M ($T_c \sim 1/\sqrt{M}$)
Could it have anything to do with the ion lattice?

Occurence of superconductors

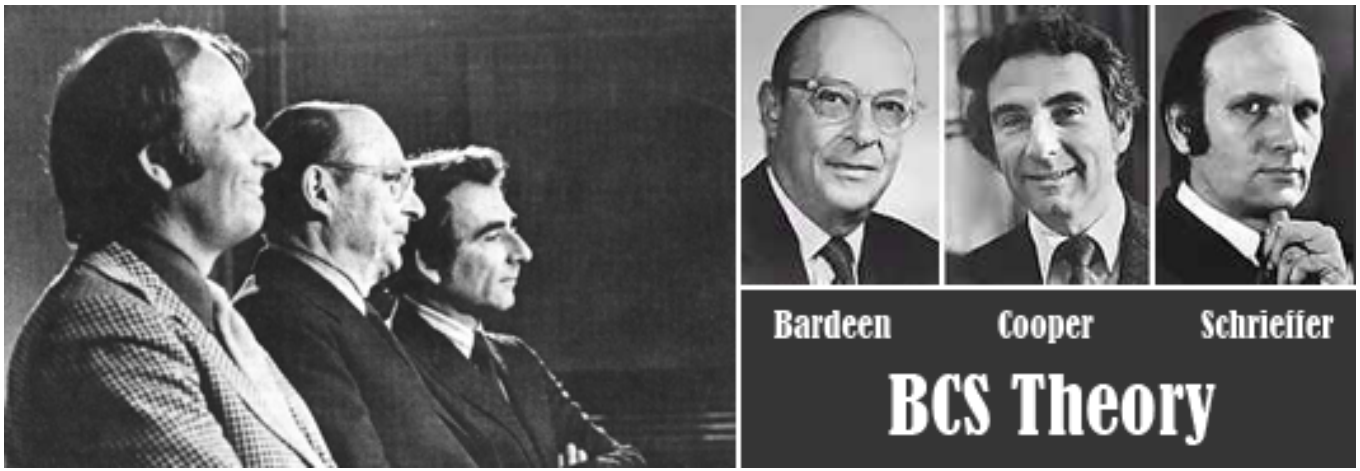
Li	**Be***										**B**	**C***	**N**	**O**	**Ne**
Na	**Mg**										**Al** T_c = 1.18 B_c = 105	**Si***	**P**	**S**	**Ar**
K	**Ca**	**Sc**	**Ti** 0.39 100	**V** 5.38 1420	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn** 0.87 53	**Ga** 1.09 51	**Ge***	**As**	**Se***	**Kr**
Rb	**Sr**	**Y***	**Zr** 0.54 47	**Nb** 9.20 1980	**Mo** 0.92 95	**Tc** 7.77 1410	**Ru** 0.51 70	**Rh**	**Pd**	**Ag**	**Cd** 3.40	**In** 3.40 293	**Sn** 3.72 309	**Sb***	**Te***	**Xe**
Cs*	**Ba***	**La** 6.00 1100	**Hf**	**Ta** 4.48 830	**W** 0.01 1.07	**Re** 1.69 198	**Os** 0.65 65	**Ir** 0.14 19	**Pt***	**Au**	**Hg** 4.15 412	**Tl** 2.39 171	**Pb** 7.19 803	**Bi***	**Po**	**Rn**
Fr	**Ra**	**Ac**														

Ce*	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Th 1.36 1.62	**Pa** 1.4	**U** 0.68	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lw**

BCS Theory

Theory of Superconductivity
J. Bardeen, L. N. Cooper, and J. R. Schrieffer
(University of Illinois in Urbana)
Phys. Rev. 108, 1175 (1957)

More than 10 000 citations
Consistent microscopic explanation of the superconducting state
Nobel Prize in 1972



(source: physics.illionois.edu)

Atomic lattice vibrations

We assume the interatomic potential is quadratic in displacements from the state of equilibrium.

$$\mathbf{R}_i = \mathbf{R}_i^0 + \mathbf{u}_i$$

$$V_{\text{ions}} = \frac{1}{2}\sum_{i,j} V(\mathbf{R}_i - \mathbf{R}_j)$$

$$\simeq \frac{1}{2}\sum_{i,j} V(\mathbf{R}_i^0 - \mathbf{R}_j^0) + \frac{1}{4}\sum_{i,j}(\mathbf{u}_i - \mathbf{u}_j)_\mu (\mathbf{u}_i - \mathbf{u}_j)_\nu \frac{\partial^2 V(\mathbf{R}_i^0 - \mathbf{R}_j^0)}{\partial R_\mu \partial R_\nu}$$

$$\mu, \nu = x, y, z$$

Phonons

Phonon = normal mode of ion lattice vibration. Its amplitude given by the Fourier transform of the single ions vibration.

$$\mathbf{u_q} = \frac{1}{\sqrt{N}} \sum_i e^{-i\mathbf{q}\mathbf{R}_i^0} \mathbf{u}_i$$

The Hamiltonian can be diagonalized and three polarization are obtained

$$V_{\text{ions}} = V_0 + \sum_{\mathbf{q},s} \frac{M\omega_{\mathbf{q}s}^2}{2} (\mathbf{u_q})_s^* (\mathbf{u_q})_s \,, \quad s = 1,2,3$$

$$H_{\text{phonons}} = \sum_{\mathbf{q},s} \hbar\omega_{\mathbf{q}s} \left(a_{\mathbf{q}s}^\dagger a_{\mathbf{q}s} + \frac{1}{2} \right)$$

$$\mathbf{u_q} = \sum_s \sqrt{\frac{\hbar}{2M\omega_{\mathbf{q}s}}} \left(a_{-\mathbf{q}s}^\dagger + a_{\mathbf{q}s} \right) \mathbf{n}_{\mathbf{q}s}$$

Normal modes of vibrations in a solid - example

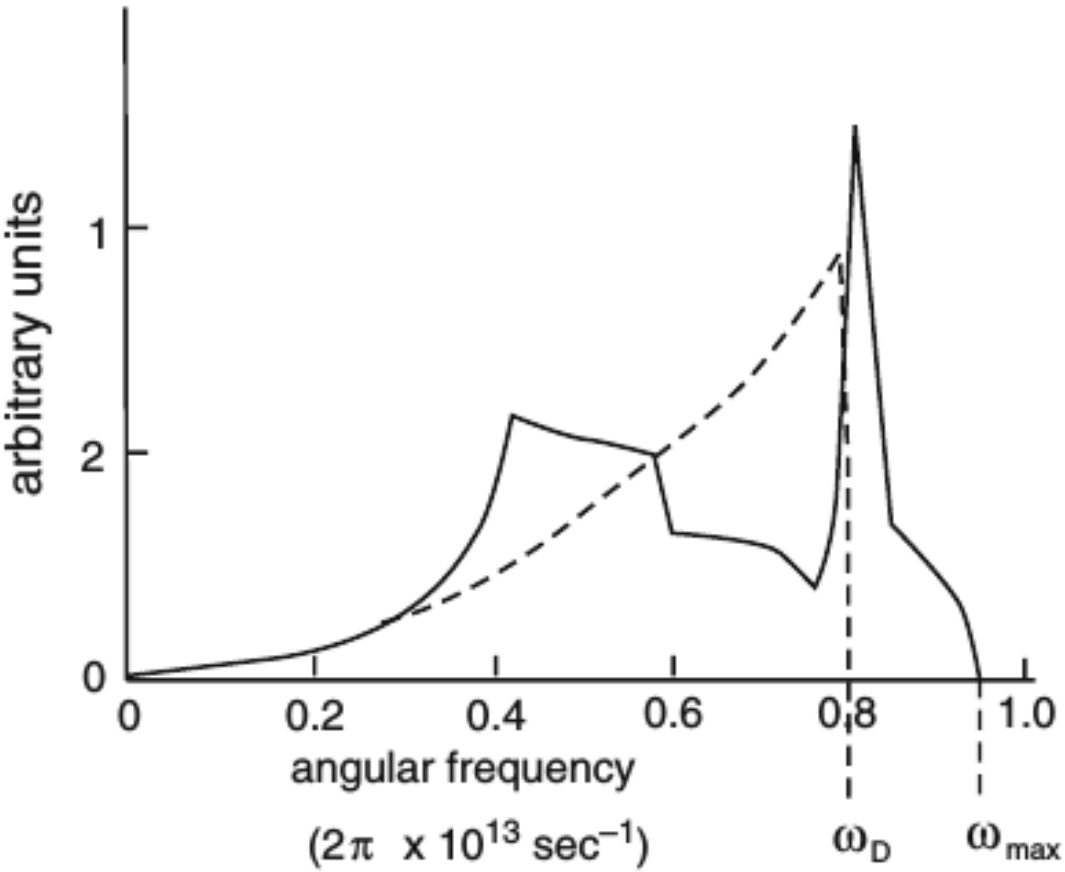


Figure : Density of normal modes for Al (source: Fujita *et al.*)

Full Hamiltonian

$$H = H_{\text{electrons}} + H_{\text{ions}} + H_{\text{electrons}-\text{ions}} + H_{\text{electrons}-\text{electrons}}$$

In the second quantization:

$$\begin{aligned} H_{\text{e}-\text{i}} &= \int d^3r\, \Psi^\dagger(\mathbf{r}) \sum_i V(\mathbf{r} - \mathbf{R}_i^0 - \mathbf{u}_i)\Psi(\mathbf{r}) \\ &\simeq \int d^3r\, \Psi^\dagger(\mathbf{r}) \sum_i \left[V(\mathbf{r} - \mathbf{R}_i^0) - \mathbf{u}_i \nabla V(\mathbf{r} - \mathbf{R}_i^0)\right] \Psi(\mathbf{r}) \\ &\equiv H^0_{\text{e}-\text{i}} + H_{\text{electrons}-\text{phonons}} \end{aligned}$$

where the electron field operator $\Psi(\mathbf{r})$ is a superposition of all momentum anihilation operators

$$\Psi(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} c_{\mathbf{k}}$$

Electron-phonon interaction Hamiltonian

If we express the electron-phonon interaction Hamiltonian H_{e-p} in terms of momenta we obtain

$$H_{\mathrm{e-p}} = -i\sqrt{N}\sum_{\mathbf{k},\mathbf{q}} V_{\mathbf{q}}\mathbf{q}\mathbf{u}_{\mathbf{q}}c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}$$

where

$$V_{\mathbf{q}} = \frac{1}{\Omega}\int d^3r\, e^{-i\mathbf{q}\mathbf{r}}V(\mathbf{r})$$

Now $\mathbf{u}_{\mathbf{q}}$ becomes an operator and is expressed via bosonic creation and anihilation operators

$$\mathbf{u}_{\mathbf{q}} = \sum_s \sqrt{\frac{\hbar}{2M\omega_{\mathbf{q}s}}}\left(a^{\dagger}_{-\mathbf{q}s} + a_{\mathbf{q}s}\right)\mathbf{n}_{\mathbf{q}s}$$

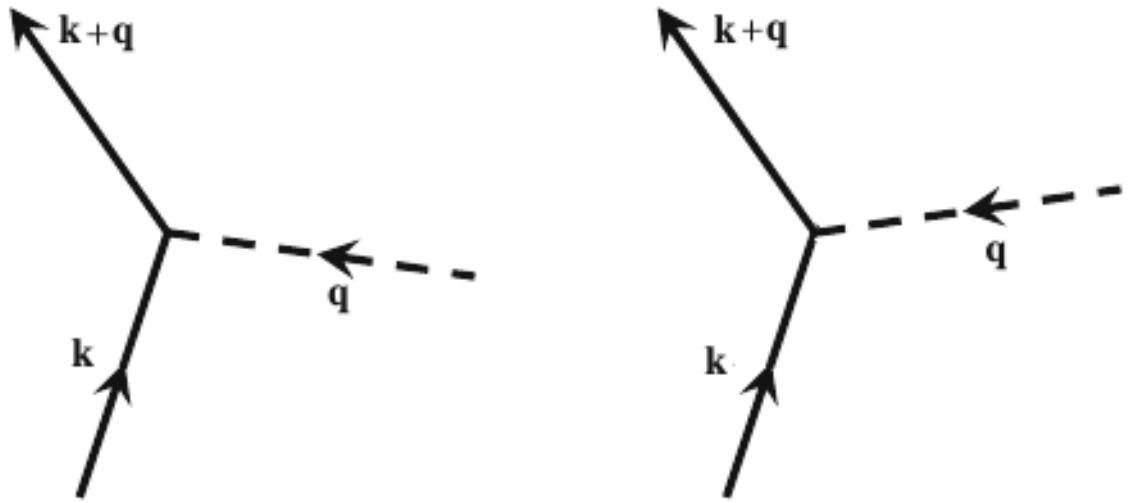
Only the longitudinal mode gives non-zero contribution (further we drop the subscript s)

Electron-phonon interaction Hamiltonian

Eventually

$$H_{\mathrm{e-p}} = \sum_{\mathbf{k},\mathbf{q}} M_{\mathbf{q}} \left(a^{\dagger}_{-\mathbf{q}} + a_{\mathbf{q}} \right) c^{\dagger}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}}$$

$$M_{\mathbf{q}} = -i \sqrt{\frac{\hbar N}{2M\omega_{\mathbf{q}s}}}\, qV_{\mathbf{q}}$$



Fröhlich Hamiltonian

$$H_{\mathrm{F}} = H_{\mathrm{electrons}} + H_{\mathrm{phonons}} + H_{\mathrm{electrons-phonons}} - \mathrm{const}$$
$$= \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} c^{\dagger}_{\mathbf{k}} c_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} a^{\dagger}_{\mathbf{q}} a_{\mathbf{q}} + \lambda \sum_{\mathbf{k},\mathbf{q}} M_{\mathbf{q}} \left(a^{\dagger}_{-\mathbf{q}} + a_{\mathbf{q}} \right) c^{\dagger}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}}$$

We want to treat the electrons and phonons as independent degrees of freedom. In order to accomplish this we perform a canonical transformation

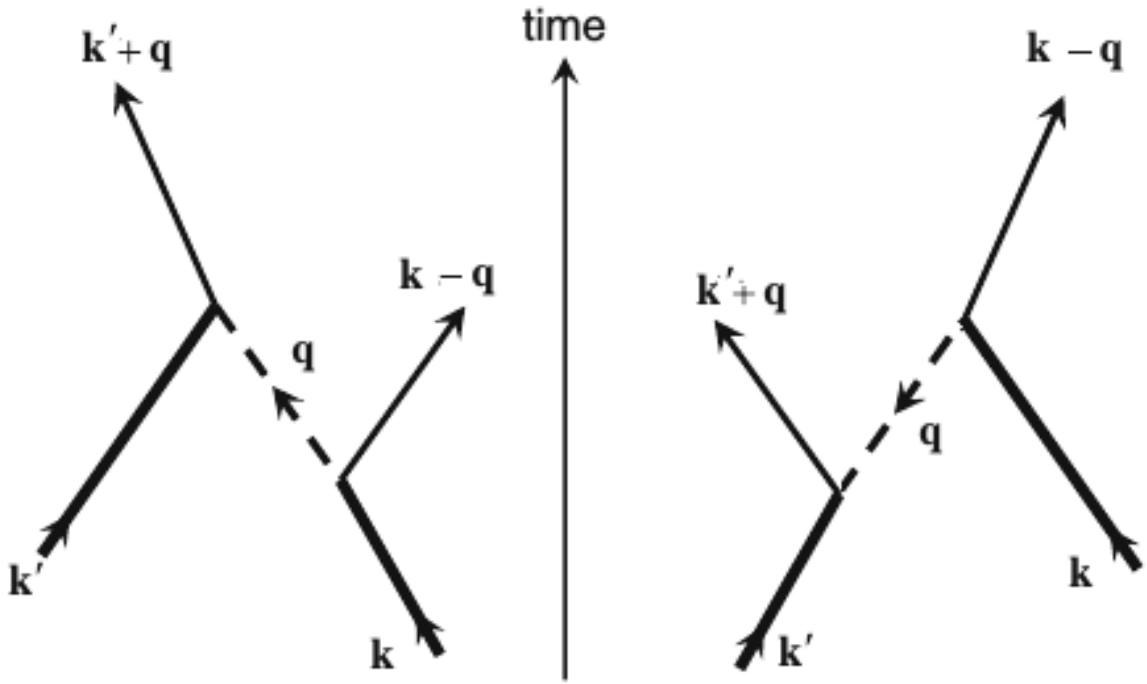
$$\tilde{H}_{\mathrm{F}} = e^{-i\lambda S} H_{\mathrm{F}} e^{i\lambda S} \quad , S = S^{\dagger}$$

so that the interaction term vanishes in the first order of λ. The effective second order interaction between the pair of electrons caused by the exchange of virtual phonon turns out to be:

$$H_{\mathrm{e-p-e}} = \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} |M_{\mathbf{q}}|^2 \frac{2\hbar\omega_{\mathbf{q}}}{(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}})^2 - (\hbar\omega_{\mathbf{q}})^2} c^{\dagger}_{\mathbf{k}'+\mathbf{q}} c^{\dagger}_{\mathbf{k}-\mathbf{q}} c_{\mathbf{k}} c_{\mathbf{k}'}$$

Second order electron-electron interaction

$$H_{\mathrm{e-p-e}} = \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} |M_{\mathbf{q}}|^2 \frac{2\hbar\omega_{\mathbf{q}}}{(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}})^2 - (\hbar\omega_{\mathbf{q}})^2} c^{\dagger}_{\mathbf{k}'+\mathbf{q}} c^{\dagger}_{\mathbf{k}-\mathbf{q}} c_{\mathbf{k}} c_{\mathbf{k}'}$$



Effective electron-electron interaction

$$H_{\mathrm{e-e}} = \frac{1}{2}\int\int d^3r_1 d^3r_2\, \Psi^\dagger(\mathbf{r}_1)\Psi^\dagger(\mathbf{r}_2)\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_2-\mathbf{r}_1|}\Psi(\mathbf{r}_2)\Psi(\mathbf{r}_1)$$
$$= \frac{1}{2}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} \frac{e^2}{\varepsilon_0\Omega}\frac{1}{q^2} c^\dagger_{\mathbf{k}'+\mathbf{q}} c^\dagger_{\mathbf{k}-\mathbf{q}} c_{\mathbf{k}} c_{\mathbf{k}'}$$

$$H_{\mathrm{e-p-e}} = \frac{1}{2}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} |M_{\mathbf{q}}|^2 \frac{2\hbar\omega_{\mathbf{q}}}{(\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}})^2-(\hbar\omega_{\mathbf{q}})^2} c^\dagger_{\mathbf{k}'+\mathbf{q}} c^\dagger_{\mathbf{k}-\mathbf{q}} c_{\mathbf{k}} c_{\mathbf{k}'}$$

$$V^{\mathrm{eff}}_{\mathbf{k},\mathbf{k}'} = \frac{e^2}{\varepsilon_0\Omega}\frac{1}{q^2} + |M_{\mathbf{q}}|^2 \frac{2\hbar\omega_{\mathbf{q}}}{(\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}})^2-(\hbar\omega_{\mathbf{q}})^2}$$

If $|\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}}| < \hbar\omega_{\mathbf{q}}$ the potential can be **attractive** in the momentum space!

Interacting pair of electrons

Consider two electrons at the Fermi surface. Their energy is $2\epsilon_{\mathrm{F}}$ if we don't take into account the attractive interaction. Now, let's include it. We approximate the pair potential in the following way

$$V^{\mathrm{eff}}_{\mathbf{k},\mathbf{k}'} = \begin{cases} -V_0 & \text{if } \epsilon_{\mathrm{F}} < \epsilon_{\mathbf{k}}, \epsilon_{\mathbf{k}'} < \epsilon_{\mathrm{F}} + \hbar\omega_{\mathrm{D}} \\ 0 & \text{otherwise} \end{cases}$$

Let us separate the motion of the center of mass:

$$\mathbf{K} = \mathbf{k}_1 + \mathbf{k}_2, \quad \mathbf{p} = \frac{1}{2}(\mathbf{k}_2 - \mathbf{k}_1)$$

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_2 - \mathbf{r}_1), \quad \mathbf{r} = \mathbf{r}_1 + \mathbf{r}_2$$

Interacting pair of electrons

The solution is of the form:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\Omega} e^{i\mathbf{KR}} \sum_{\mathbf{p}} a_{\mathbf{p}} e^{i\mathbf{pr}}$$

The Schrödinger equation for coefficients $a_{\mathbf{p}}$

$$\left(\epsilon_{\mathbf{p}+\frac{1}{2}\mathbf{K}} + \epsilon_{-\mathbf{p}+\frac{1}{2}\mathbf{K}} - E\right) a_{\mathbf{p}} = \sum_{\substack{\mathbf{p}' \\ \epsilon_{\mathrm{F}} < \epsilon_{\mathbf{k}'_1, \mathbf{k}'_2} \\ < \epsilon_{\mathrm{F}} + \hbar\omega_{\mathrm{D}}}} V_0 \, a_{\mathbf{p}'}$$

can be solved self-consistently

$$\frac{1}{V_0} = \sum_{\substack{\mathbf{k} \\ \epsilon_{\mathrm{F}} < \epsilon_{\mathbf{k}_1, \mathbf{k}_2} \\ < \epsilon_{\mathrm{F}} + \hbar\omega_{\mathrm{D}}}} \frac{1}{\epsilon_{\mathbf{p}+\frac{1}{2}\mathbf{K}} + \epsilon_{-\mathbf{p}+\frac{1}{2}\mathbf{K}} - E}$$

Cooper pair

We seek bound state solutions ($E < 2\epsilon_{\mathrm{F}}$). For $\mathbf{K} = 0$

$$\frac{1}{V_0} \approx \mathcal{N}(\epsilon_{\mathrm{F}}) \int_{\epsilon_{\mathrm{F}}}^{\epsilon_{\mathrm{F}}+\hbar\omega_{\mathrm{D}}} \frac{d\epsilon}{2\epsilon - E} = \frac{1}{2}\mathcal{N}(\epsilon_{\mathrm{F}}) \ln\left(\frac{2\hbar\omega_{\mathrm{D}} + 2\epsilon_{\mathrm{F}} - E}{2\epsilon_{\mathrm{F}} - E}\right)$$

$$E = 2\epsilon_{\mathrm{F}} - \frac{2\hbar\omega_{\mathrm{D}}}{e^{\frac{2}{V_0\mathcal{N}(\epsilon_{\mathrm{F}})}} - 1}$$

For any $\mathbf{K}$

$$E \approx 2\epsilon_{\mathrm{F}} - \frac{2\hbar\omega_{\mathrm{D}}}{e^{\frac{2}{V_0\mathcal{N}(\epsilon_{\mathrm{F}})}} - 1} + \frac{v_{\mathrm{F}}}{2}K$$

This bound state is called a Cooper pair (size $\sim 10^{-4}$ cm). The energy is non-analytical as a function of V_0. The existence of such a solution leads to the instability of the Fermi surface - the Fermi liquid model breaks down.

BCS ground state

Bardeen, Cooper, Schrieffer postulated the superconducting ground state is a superposition of Fock states in which one particle states are occupied in pairs $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$

$$|\Psi_0\rangle = \prod_{\mathbf{k}} \left(u_{\mathbf{k}} + v_{\mathbf{k}} e^{i\phi_{\mathbf{k}}} c^{\dagger}_{\mathbf{k}\uparrow} c^{\dagger}_{-\mathbf{k}\downarrow} \right) |0\rangle$$

The real coeffcients $u_{\mathbf{k}}, v_{\mathbf{k}}, \phi_{\mathbf{k}}$ will be obtained by the variational method. In case of a Fermi liquid

$$u_{\mathbf{k}} = \begin{cases} 0 & \text{if } |\mathbf{k}| < k_{\mathrm{F}} \\ 1 & \text{if } |\mathbf{k}| > k_{\mathrm{F}} \end{cases}$$

$$v_{\mathbf{k}} = \begin{cases} 1 & \text{if } |\mathbf{k}| < k_{\mathrm{F}} \\ 0 & \text{if } |\mathbf{k}| > k_{\mathrm{F}} \end{cases}$$

and $\phi_{\mathbf{k}}$ has no physical meaning

Reduced Hamiltonian

$$H_0 = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \left(c^\dagger_{\mathbf{k}\uparrow} c_{\mathbf{k}\uparrow} + c^\dagger_{\mathbf{k}\downarrow} c_{\mathbf{k}\downarrow} \right) - \sum_{\substack{\mathbf{k},\mathbf{k}' \\ |\epsilon_{\mathbf{k},\mathbf{k}'} - \epsilon_{\mathrm{F}}| \\ < \hbar\omega_{\mathrm{D}}}} V_0 c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow} c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow}$$

$$W_0 = \langle \Psi_0 | \, H_0 \, | \Psi_0 \rangle = \sum_{\mathbf{k}} 2\epsilon_{\mathbf{k}} v^2_{\mathbf{k}} - \sum_{\substack{\mathbf{k},\mathbf{k}' \\ |\epsilon_{\mathbf{k},\mathbf{k}'} - \epsilon_{\mathrm{F}}| \\ < \hbar\omega_{\mathrm{D}}}} V_0 \, u_{\mathbf{k}} v_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} \cos(\phi_{\mathbf{k}} - \phi_{\mathbf{k}'})$$

The phase has to be the same for all the pairs

$$\phi_{\mathbf{k}} = \phi_{\mathbf{k}'} \equiv \phi$$

and the energy does not depend on ϕ. The ground state breaks the symmetry $U(1)$ of the Hamiltonian.

Variational approach

Let

$$v_{\mathbf{k}}^2 = \frac{1}{2}\left(1 - \frac{\epsilon_{\mathbf{k}} - \epsilon_{\mathrm{F}}}{\sqrt{(\epsilon_{\mathbf{k}} - \epsilon_{\mathrm{F}})^2 + \Delta_{\mathbf{k}}^2}}\right), \; u_{\mathbf{k}}^2 = \frac{1}{2}\left(1 + \frac{\epsilon_{\mathbf{k}} - \epsilon_{\mathrm{F}}}{\sqrt{(\epsilon_{\mathbf{k}} - \epsilon_{\mathrm{F}})^2 + \Delta_{\mathbf{k}}^2}}\right)$$

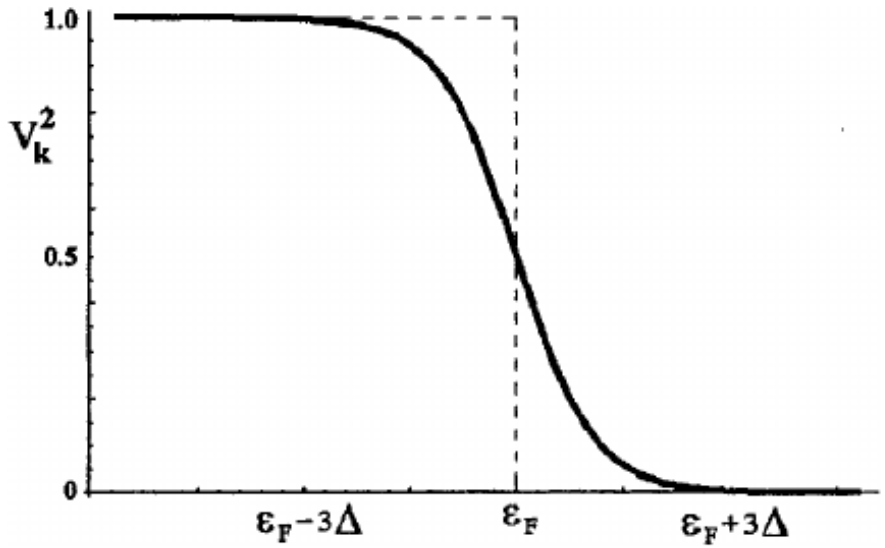
Then

$$\frac{\delta\left(W_0 - \epsilon_{\mathrm{F}}\langle N\rangle\right)}{\delta\Delta_{\mathbf{k}}} = 0 \quad \Leftrightarrow \quad \Delta_{\mathbf{k}} = \sum_{\substack{\mathbf{k}' \\ |\epsilon_{\mathbf{k}'} - \epsilon_{\mathrm{F}}| \\ < \hbar\omega_{\mathrm{D}}}} V_0 \frac{\Delta_{\mathbf{k}'}}{2\sqrt{(\epsilon_{\mathbf{k}'} - \epsilon_{\mathrm{F}})^2 + \Delta_{\mathbf{k}'}^2}} \equiv \Delta$$

By integration we obtain

$$\Delta = \frac{\hbar\omega_{\mathrm{D}}}{\sinh\left(\frac{1}{V_0 \mathcal{N}(\epsilon_{\mathrm{F}})}\right)}$$

Coherence factors



Ground state energy and excitation spectrum

Knowing $u_{\mathbf{k}}, v_{\mathbf{k}}$ we can finally calculate the ground state energy:

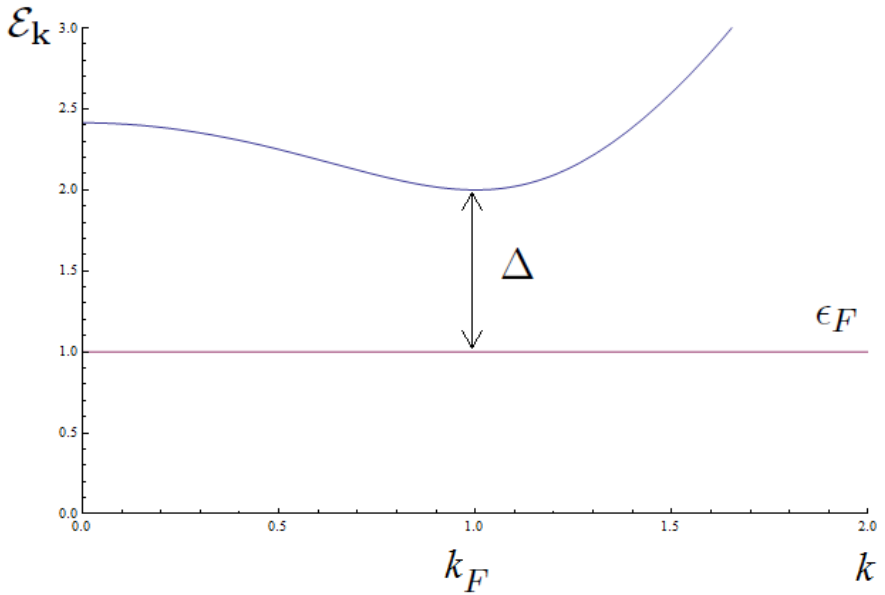
$$W_0 = \sum_{\substack{\mathbf{k} \\ \epsilon_{\mathbf{k}} < \epsilon_{\mathrm{F}}}} \epsilon_{\mathbf{k}} - \frac{2\mathcal{N}(\epsilon_{\mathrm{F}})(\hbar\omega_{\mathrm{D}})^2}{e^{\frac{2}{V_0\mathcal{N}(\epsilon_{\mathrm{F}})}} - 1} = W_{\text{Fermi liquid}} - \frac{2\mathcal{N}(\epsilon_{\mathrm{F}})(\hbar\omega_{\mathrm{D}})^2}{e^{\frac{2}{V_0\mathcal{N}(\epsilon_{\mathrm{F}})}} - 1}$$

Excitations spectrum

Excited states are those in which there are some unpaired 'electrons'. If we exclude one pair $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ from the sum determining W_0 and add one single electron energy we convince ourselves that it increases the energy of the system by

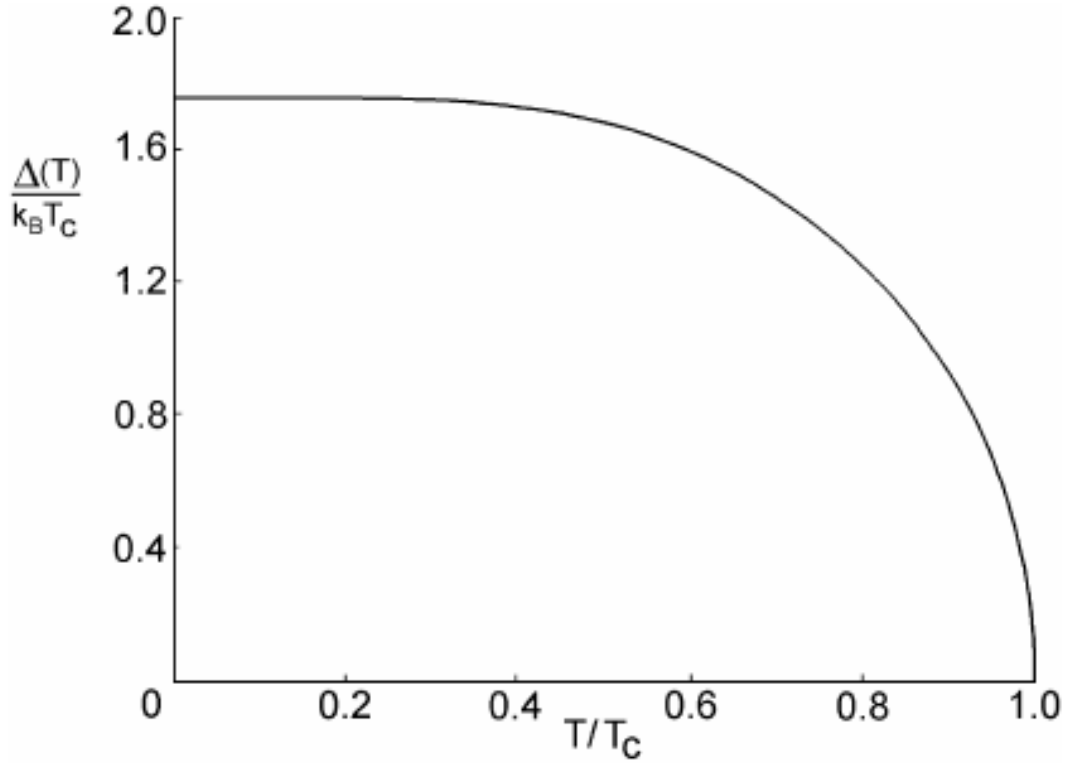
$$\mathcal{E}_{\mathbf{k}} = \sqrt{(\epsilon_{\mathbf{k}} - \epsilon_{\mathrm{F}})^2 + \Delta^2} + \epsilon_{\mathrm{E_F}}$$

which is a single excited particle energy.



Energy gap temperature dependence

By minimizing the free energy $F = W - TS - \epsilon_{\mathrm{F}} N$ we obtain the temperature dependence of the energy gap $\Delta = \Delta(T)$



$$k_{\mathrm{B}} T_c \approx 1.13\, \hbar\omega_{\mathrm{D}}\, e^{-\frac{1}{V_0 \mathcal{N}(\epsilon_{\mathrm{F}})}} \approx 1.13\, \Delta(0)$$

Repetition

- Due to the electron-phonon interaction electrons can be effectively attracted to each other
- The electrons bind forming singlet Cooper pairs $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$
- The ground state is a coherent state: does not conserve the number of particles and breaks the $U(1)$ symmetry
- The excited states spectrum is separated from the ground state by the energy gap $\Delta(T)$

Plausible hypotheses

- Due to the energy gap in the excitation spectrum charge carriers (cooper pairs) are not scattered - superconductivity
- The magnetic field destroys the superconducting state. The critical field:

$$W_{\text{Fermi liquid}} - W_0 = \frac{\Omega B_c^2}{2\mu_0}$$

Literature I

- H. Fröhlich: Interaction of Electrons with Lattice Vibrations *Proc. Roy. Soc.* (London) A 215, 291 (1952)
- Leon N. Cooper: Bound Electron Pairs in a Degenerate Fermi Gas *Phys. Rev.* 104, 1189 (1956)
- J. J. Bardeen, L. N. Cooper, and J. R. Schrieffer: Theory of Superconductivity *Phys. Rev.* 108, 1175 (1957)
- S. Fujita *et al.*: Quantum Theory of Conducting Matter, New York, NY : Springer Science+Business Media, LLC, (2009)