

Theory of condensed matter

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Contents

6 Magnetism	68
6.1 Overview	68
6.2 The mean-field theory of Weiss	69
7 Superconductivity	72
7.1 Supercurrent and wave function	72
7.2 London equation and Meissner effect	74
7.3 Cooper instability	74
7.4 BCS theory	76

6 Magnetism

6.1 Overview

As we – as a consequence of lack of time – cannot deeply go into the theory of magnetism we shall present in the next section only the mean-field theory of Weiss.

Phenomenologically magnetism is described by Maxwell's equations, in which we encounter the magnetic induction \mathbf{B} , the magnetic field \mathbf{H} and the magnetization vector \mathbf{M} ¹ with

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \quad (6.1)$$

The absolute value of \mathbf{M} , $|\mathbf{M}| = M = n\mu$ ($n = N/V$)

gives the density of *magnetic moments* μ per volume, and its direction points into the direction of the moments. The moments are considered to be fixed in the material like little compass needles. In quantum theory we learn that we have two different microscopic magnetic moments, namely the *spin* and the *orbital moment*. The former is an intrinsic property of matter, whereas the latter stems from the angular momentum of electronic orbitals. The spins which form the (*localized*) moments of magnetic materials are composed of both. However the magnetic properties of metals are much more complicated as they involve mobile (*itinerant*) electrons, so that one has to deal with the *spin-resolved band structure* of metals like Fe or Ni. In our little theoretical section we shall deal only with localized spins. Their interaction can be derived from Hartree-Fock theory and is identified as *exchange interaction*. For localized spin operators \mathbf{S}_i we can write down the famous *Heisenberg Hamiltonian*

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0(\mathbf{B}) + \mathcal{H}_{\text{int}} \\ \mathcal{H}_0(\mathbf{B}) &= \sum_i \boldsymbol{\mu}_i \cdot \mathbf{B} = - \sum_i \frac{g\mu_B}{\hbar} \mathbf{S}_i \cdot \mathbf{B} \\ \mathcal{H}_{\text{int}} &= -\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \end{aligned} \quad (6.2)$$

Here $\mu_B = e\hbar/2m$ is the *Bohr magneton* and g is the *g factor* (which is equal to 2 for free electrons).

¹We use SI units as before, where we have to deal with the vacuum permeability $\mu_0 = 4\pi \cdot 10^{-7} \text{N/A}^2$

6.2 The mean-field theory of Weiss

We now sub-divide formally the spin operators into their mean values and their fluctuations

$$\mathbf{S}_i = \langle \mathbf{S}_i \rangle + \delta \mathbf{S}_i \quad (6.3)$$

and insert this into the interaction part of (6.2)

$$\begin{aligned} \mathcal{H}_{\text{int}} &= -\frac{1}{2} \sum_{i,j} J_{ij} \left(\langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_j \rangle + \delta \mathbf{S}_i \cdot \langle \mathbf{S}_j \rangle + \langle \mathbf{S}_i \rangle \cdot \delta \mathbf{S}_j + \delta \mathbf{S}_i \cdot \delta \mathbf{S}_j \right) \\ &= \underbrace{-\frac{1}{2} \sum_{i,j} J_{ij} \langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_j \rangle}_{\text{const.}} - \sum_{i,j} J_{ij} \left(\delta \mathbf{S}_i + \langle \mathbf{S}_i \rangle - \langle \mathbf{S}_i \rangle \right) \cdot \langle \mathbf{S}_j \rangle \\ &= \underbrace{\frac{1}{2} \sum_{i,j} J_{ij} \langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_j \rangle}_{\text{const.}} - \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \langle \mathbf{S}_j \rangle \\ &= \text{const.} - \sum_i \mathbf{S}_i \cdot \frac{g\mu_B}{\hbar} \underbrace{\sum_{j \neq i} \frac{\hbar}{g\mu_B} J_{ij} \langle \mathbf{S}_j \rangle}_{\mathbf{B}_W} \\ &= \text{const.} + \sum_i \mu_i \cdot \mathbf{B}_W \end{aligned} \quad (6.4)$$

So that we obtain for the total Hamiltonian (disregarding the constant)

$$\mathcal{H}(\mathbf{B}) = \sum_i \mu_i \cdot (\mathbf{B} + \mathbf{B}_W) \quad (6.5)$$

\mathbf{B}_W is the *Weiss field*.

$$\mathbf{B}_W = \sum_{j \neq i} \frac{\hbar}{g\mu_B} J_{ij} \langle \mathbf{S}_j \rangle = \frac{1}{ng^2\mu_B^2} M_z \sum_{j \neq i} J_{ij} \equiv \lambda M_z \quad (6.6)$$

where we have used $M_z = ng\mu_B \frac{1}{\hbar} \langle S_i \rangle$. The interaction is hidden in this field, which represents on the average the effect the other spins have on a given spin. The previous mean-field approximations encountered in the present lecture, namely the random-phase approximation (RPA), the Hartree and Hartree-Fock approximations, the coherent-potential and self-consistent Born approximations (CPA, SCBA) have a similar philosophy. In all cases one has to calculate an average of a quantity which is going to be calculated from the mean field. This constitutes a nonlinear self-consistency problem. In our case one has to calculate the average spin operator $\langle S_i \rangle$ with a guessed value of B_W , then one inserts this into (6.6), calculates $\langle S_i \rangle$ again, and so on, until the procedure has converged.

We shall now show that this nonlinear problem can be solved for a simple example more easily. We assume that $\langle S_i \rangle$ can be calculated as if we would deal with *non-interacting spins*, because the interactions have already accounted for. Denoting the eigenvalues of $S_i^z \hbar s$ we have and $B_{\text{eff}} = B^z + B_W^z$

$$\langle S_i \rangle = \langle S^z \rangle = \hbar \frac{\sum_s s e^{-sg\mu_B B_{\text{eff}}}}{\sum_s e^{-sg\mu_B B_{\text{eff}}}} \quad (6.7)$$

For simplicity we now assume $g = 2$ and $S = \frac{1}{2}$ so that we have $gs = \pm 1$.

For the magnetization we obtain

$$M_z = n\mu_B \tanh \left(\frac{\mu_B}{k_B T} B_{\text{eff}} \right) \quad (6.8)$$

This is the *mean-field equation of states of Weiss*. It is a self-consistent equation for M_z , because B_{eff} has to be calculated from M_z via (6.6).

We want to calculate the magnetic susceptibility. Let us first set $J_{ij} = 0$, i.e. $\mathbf{B}_W = 0$. We have

$$\chi = \left. \frac{dM_z}{dB} \right|_{B=0} = n \frac{\mu_B^2}{k_B T} \quad (6.9)$$

We introduce the mean square magnetic moment $\langle \mu^2 \rangle = (2\mu_B^2)^2 S(S+1) = 3\mu_B^2$ and obtain the *Curie law*

$$\chi = n \frac{\langle \mu^2 \rangle}{3k_B T} \quad (6.10)$$

We now go back to the interacting case and define

$$k_B T_c = \frac{1}{3} n \langle \mu^2 \rangle \lambda \quad (6.11)$$

We then obtain from the Weiss equation of state (6.8) the *Curie-Weiss law*

$$\chi = \frac{n}{3k_B} \frac{\langle \mu^2 \rangle}{(T - T_c)} \quad (6.12)$$

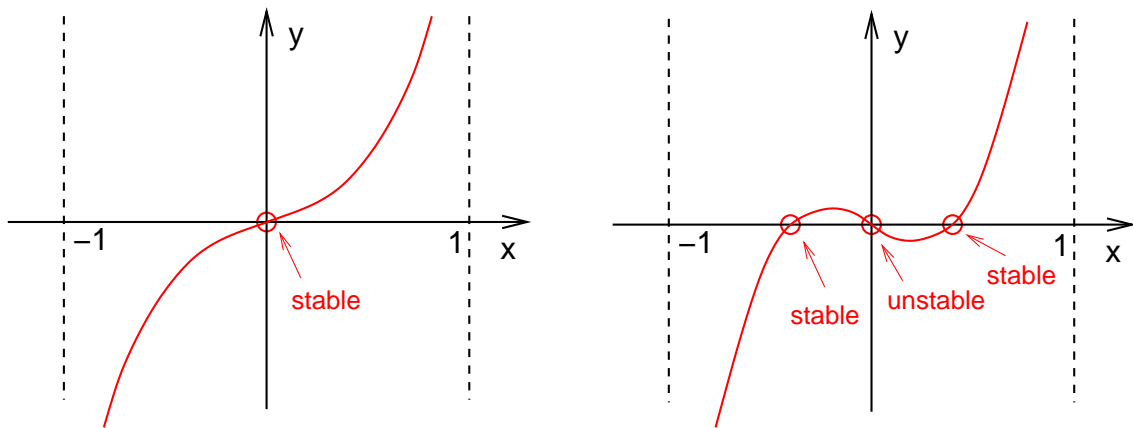
This equation shows that the magnetic susceptibility diverges at a certain *critical temperature* T_c in the same way as the compressibility in the case of the van-der-Waals mean-field theory of the liquid-vapor phase separation. Although the equations of state are rather different from each other, the behavior in the vicinity of the critical point is similar. In both cases a thermodynamic susceptibility diverges, and in both cases one can identify a so-called *order parameter*, which is finite below the transition and zero above the transition. In the case of a ferromagnet this is the *spontaneous magnetization* in the case of the liquid-vapor phase separation it is the difference of the densities of the liquid and the vapor.

We now want to discuss the equation of state of Weiss (6.8) around and in particular below T_c . In order to do so we define dimensionless parameters $x = \lambda \mu_B M_z / k_B T_c = M_z / n \mu_B$ and $y = B \mu_B / k_B T_c$. The equation of state (6.8) now becomes

$$x = \tanh \left[(x + y) \frac{T_c}{T} \right] \quad (6.13)$$

We can invert this equation to solve for y :

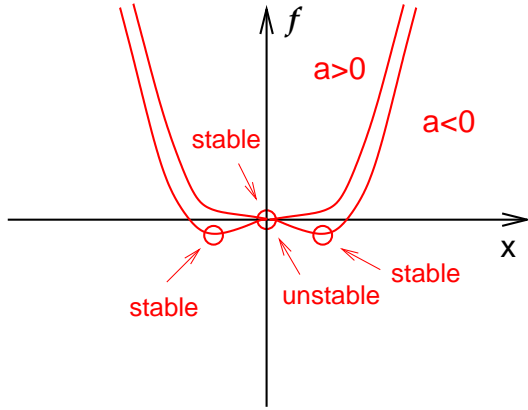
$$\begin{aligned} y &= \frac{T}{T_c} \operatorname{artanh}(x) - x \\ &= \frac{T}{T_c} \left(x + \frac{1}{3} x^3 + \dots \right) - x \\ &= \underbrace{\frac{T - T_c}{T_c}}_a x + \underbrace{\frac{T}{3T_c}}_b x^3 \end{aligned} \quad (6.14)$$



Dimensionless field $y = B\mu_0/k_B T_c$ vs. dimensionless magnetization $x = M/M_0$ for $a > 0$ (left) and $a < 0$ (right).

We see that for $a > 0$ (i.e. $T > T_c$) there is only one solution for $y = 0$, whereas for $a < 0$ there are three. The solution $x = 0$ is unstable, because for an infinitesimal field the magnetization starts to increase. The other two solutions are stable in this sense, and we have a situation with a finite (“spontaneous”) magnetization at zero field.

This is a very important observation. We started with a Hamiltonian, which is symmetric with respect to the directions in space, i.e. rotationally symmetric (or, in our simplified case, symmetric with respect to the sign of μ_z). In the presence of the interactions the equilibrium state *breaks* this symmetry resulting in a thermodynamic state with a lower symmetry than that of the Hamiltonian. Such a *spontaneous symmetry breaking* at low enough temperatures is encountered frequently in nature. In fact, such a transition must have taken place at the early stage of our universe, because nowadays we have much more matter than anti-matter.



Free energy for $a > 0$ and $a < 0$

In order to explore the stability aspect, we can consider the *free energy* F , using the thermodynamic identity

$$B = \frac{1}{\mu_0} \frac{\partial F}{\partial M} \quad (6.15)$$

So we introduce the dimensionless free energy

$$y = \frac{df}{dx} \quad \Leftrightarrow \quad f(x) = \int_0^x d\tilde{x} y(\tilde{x}) \quad (6.16)$$

from which follows

$$f(x) = \frac{1}{2}ax^2 + \frac{1}{4}bx^4 \quad (6.17)$$

We see immediately which minima of the free energy in the two situations are stable. The free energy (6.17) has the canonical form introduced by Landau in his phenomenological discussion of phase transitions. x is called the *order parameter*, which has the property that it vanishes in the disordered high-temperature phase and is $\neq 0$ in the ordered, low-temperature phase.

In fact, we already encountered a free energy of such a form, namely that of an interacting liquid mixture (2.72). The order parameter in this case is the difference between the concentrations $x = c_1 - c_2$ in the demixed states, which is, because the free energy is symmetric w.r. to c and $1 - c$ equal to $2c - 1$

$$\begin{aligned} f(x) = \frac{1}{N} \Delta G &= \frac{\omega}{4}(1 - x^2) + k_B T \left(\frac{1+x}{2} \ln \frac{1+x}{2} + \frac{1-x}{2} \ln \frac{1-x}{2} \right) \\ &= \text{const.} + \frac{k_B}{2}(T - T_c)x^2 + \frac{k_B T}{12}x^4 \end{aligned} \quad (6.18)$$

with $T_c = \omega/2k_B$.

It is obvious that one can - by rescaling x - bring this into the form (6.17).

Let us now calculate the temperature dependence of the order parameter x near the transition with the help of (6.17). For $a < 0$ the order parameter is given by

$$0 = -|a| + bx^2 \quad \Rightarrow \quad x(T) \propto |T - T_c|^\beta \quad \beta = \frac{1}{2} \quad (6.19)$$

A phase transition at which the order parameter vanishes *continuously* is called *second-order phase transition*. The exponent according to which a physical quantity vanishes (or diverges) near a second-order phase transition is called *critical exponent*. There is another quantity, which becomes critical at T_c , which is the magnetic susceptibility in the disordered state, i.e. $a > 0$. In dimensionless units it is given by

$$\chi(T) = \frac{dx}{dy} = \frac{1}{dy/dx} = T_c [T - T_c]^{-\gamma} \quad \gamma = 1 \quad (6.20)$$

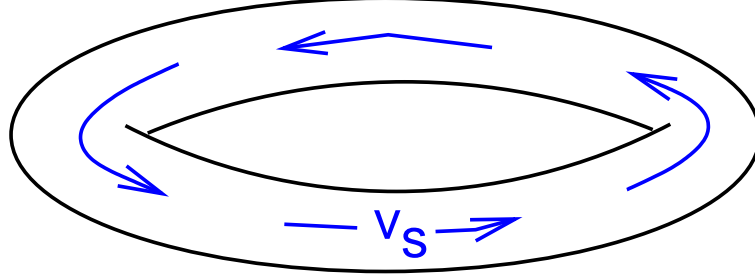
which is the Curie-Weiss law in dimensionless units.

There is, however, a serious drawback concerning the mean-field theories of Weiss and Landau: The critical exponents β and γ predicted by the theory (1/2 for the magnetization and 1 for the susceptibility) do not

agree with those measured experimentally. One can also perform Monte-Carlo computer simulations for a Heisenberg model and find exponents different from the mean-field ones. A third method to determine these exponents is the renormalization-group methods. The theoretical values for the Heisenberg model (which agree with the experimental ones for materials described by the Heisenberg model) are $\beta = 0.3646$ and $\gamma = 1.3866$.

7 Superconductivity

7.1 Supercurrent and wave function



We start by considering a ring containing a *superfluid* like ^4He . In such a ring a current with velocity v_s can flow forever, i.e. the viscosity is zero. We take for granted that this must be a *quantum* phenomenon. Let $\psi(\mathbf{r}, t)$ be the wave function of the superfluid and $n(\mathbf{r}, t) = \psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t)$ its density. Then we can calculate the *current density* $\mathbf{j}(\mathbf{r}, t)$ from the continuity equation

$$\frac{\partial}{\partial t}n(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0 \quad (7.1)$$

We have

$$\begin{aligned} \frac{\partial}{\partial t}n(\mathbf{r}, t) &= \frac{\partial}{\partial t}\psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t) = \psi^*(\mathbf{r}, t)\frac{\partial}{\partial t}\psi(\mathbf{r}, t) + \psi(\mathbf{r}, t)\frac{\partial}{\partial t}\psi^*(\mathbf{r}, t) \\ &= \frac{i}{\hbar}[\psi^*(\mathbf{r}, t)\mathcal{H}\psi(\mathbf{r}, t) - \psi(\mathbf{r}, t)\mathcal{H}\psi^*(\mathbf{r}, t)] \\ &= -\frac{i\hbar}{2m}[\psi^*(\mathbf{r}, t)\nabla^2\psi(\mathbf{r}, t) - \psi(\mathbf{r}, t)\nabla^2\psi^*(\mathbf{r}, t)] + \underbrace{\frac{i}{\hbar}\psi^*\psi(\mathcal{V} - \mathcal{V})}_0 \\ &\quad - \frac{i\hbar}{2m}\underbrace{[\nabla\psi^*(\mathbf{r}, t)\nabla\psi(\mathbf{r}, t) - \nabla\psi(\mathbf{r}, t)\nabla\psi^*(\mathbf{r}, t)]}_0 \\ &= -\frac{i\hbar}{2m}\nabla[\psi^*(\mathbf{r}, t)\nabla\psi(\mathbf{r}, t) - \psi(\mathbf{r}, t)\nabla\psi^*(\mathbf{r}, t)] \\ \Rightarrow \mathbf{j}(\mathbf{r}, t) &= \frac{i\hbar}{2m}[\psi^*(\mathbf{r}, t)\nabla\psi(\mathbf{r}, t) - \psi(\mathbf{r}, t)\nabla\psi^*(\mathbf{r}, t)] \end{aligned} \quad (7.2)$$

In a fluid near $T = 0$ we cannot imagine a strong spatial variation of the *density*, so we make the Ansatz

$$\psi(\mathbf{r}, t) = \sqrt{n_0}e^{i\phi(\mathbf{r}, t)} \quad (7.3)$$

where $n_0 = N/V$ is the density of the fluid at $T = 0$. Now

$$\nabla\psi(\mathbf{r}, t) = i\psi(\mathbf{r}, t)\nabla\phi(\mathbf{r}, t) \quad \nabla\psi^*(\mathbf{r}, t) = -i\psi(\mathbf{r}, t)^*\nabla\phi(\mathbf{r}, t) \quad (7.4)$$

so that

$$\mathbf{j}(\mathbf{r}, t) = \frac{\hbar}{m}n_0\nabla\phi(\mathbf{r}, t) \equiv n_0v_s(\mathbf{r}, t) \quad (7.5)$$

We end with the result

$$v_s = \frac{\hbar}{m}\nabla\phi(\mathbf{r}, t) \quad (7.6)$$

So, if there is a stationary current with constant velocity, there must be also a *stationary space dependent phase*, which must increase linearly along the ring. For this to be possible the stationary phase and hence the velocity must be stepwise quantized.

The wave function (7.3) is, in fact the *macroscopic ground state wave function* of the superfluid. As the ${}^4\text{He}$ particles are *bosons* the superfluid phenomenon is a *Bose-Einstein condensation* of the particles into a single macroscopic state.

As in the case of the binary liquid phase separation and the ferromagnetic transition the superfluid (and, as well the superconducting) transition is a transition to a state with a lower symmetry than that of the original Hamiltonian. In the normal state governed by the Hamiltonian of interacting ${}^4\text{He}$ particles or electrons in a solid the phases of the wave functions can be re-gauged arbitrarily. This is no more the case in the supra-state, as the phase now is connected with the supra-current.

Let us now consider the case of a *superconductor* in a metallic ring, in which the circular electric current lasts forever (zero resistance). So there must also be a macroscopic wave function with a stationary phase given by

$$\nabla\phi = \frac{m^*}{\hbar}v_s \quad (7.7)$$

where m^* is the mass of the superconducting particle. However, as electrons are fermions, there can be no Bose-Einstein condensation of single electrons because of the Pauli principle. Only if the electrons are combined to form *composite bosons* with integer spin, they can eventually behave as bosons. The simplest composite boson is a *pair*, and we shall see that one can explain superconductivity by ‘‘Cooper pair’’ formation. So we have $m^* = 2m$ and consequently

$$v_s = \frac{\hbar}{2m}\nabla\phi \quad (7.8)$$

where ϕ belongs to a *two-electron wave function*

$$\Psi(\mathbf{r}) = \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \psi_{2\text{el}}(\mathbf{r}, \mathbf{r}') \propto e^{i\phi(\mathbf{r})} \quad (7.9)$$

We now consider the case of a finite magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$, where \mathbf{A} is the vector potential. We have to be careful as the gauge of the wave function is related to the gauge of the vector potential. We remember: If we perform a gauge transformation for the vector potential

$$\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}'(\mathbf{r}) + \nabla\lambda(\mathbf{r}) \quad (7.10)$$

we have also to re-gauge the wave function as

$$\psi(\mathbf{r}) \rightarrow \psi'(\mathbf{r}) = e^{\frac{ie}{\hbar}\lambda(\mathbf{r})}\psi(\mathbf{r}) \quad (7.11)$$

Now, if the wave function is supposed to be composed of two electrons we expect

$$\begin{aligned} \psi(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}' \rightarrow \mathbf{r}} &\rightarrow e^{\frac{2ie}{\hbar}\lambda(\mathbf{r})}\psi(\mathbf{r}) \\ \text{or} & \\ \phi(\mathbf{r}) &\rightarrow \frac{2e}{\hbar}\lambda(\mathbf{r}) + \phi(\mathbf{r}) \end{aligned} \quad (7.12)$$

So, in order to have a gauge invariant expression for the supra velocity we must write

$$v_s = \frac{\hbar}{2m} \left(\nabla\phi - \frac{2e}{\hbar}\mathbf{A} \right) \quad (7.13)$$

We obtain for the supercurrent

$$\mathbf{j} = \frac{e\hbar}{2m} \left(\nabla\phi - \frac{2e}{\hbar}\mathbf{A} \right) \quad (7.14)$$

7.2 London equation and Meissner effect

We now consider the second striking effect of superconductivity (in addition to zero resistance), namely the *Meissner effect*: A magnetic field \mathbf{B} is *expelled* from a superconductor.

We apply the curl operator to (7.14) to obtain

$$\nabla \times \mathbf{j} = -\frac{e^2 n_s}{m} \mathbf{B} \quad (7.15)$$

This is the famous *London equation* (F. London and H. London, Proc. Roy. Soc. A **149**, 71 (1935), which was introduced by the authors to describe the superconducting state in a phenomenological way.

We also consider now the Maxwell equations

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j} \quad \nabla \cdot \mathbf{B} = 0 \quad (7.16)$$

and perform another curl on $\nabla \times \mathbf{B}$ to obtain

$$\begin{aligned} \nabla \times (\nabla \times \mathbf{B}) &= \nabla(\nabla \times \mathbf{B}) - \nabla^2 \mathbf{B} \\ &= -\nabla^2 \mathbf{B} = \mu_0 \nabla \times \mathbf{j} = \frac{\mu_0 e^2 n_s}{m} \mathbf{B} \end{aligned} \quad (7.17)$$

or

$$B = \delta^2 \nabla^2 \mathbf{B} \quad (7.18)$$

where

$$\delta = \sqrt{\frac{m}{\mu_0 e^2 n_s}} \quad (7.19)$$

is the *London penetration depth*.

	Sn	Al	Pb	Nb
λ / nm	34	16	37	39
T_c / K	3.7	1.2	7.2	9.3

To understand the meaning of this and to relate the London equation to the Meissner effect we consider the entire half space $x > 0$ to be filled with a superconductor, in which (7.15) holds.

At the boundary $x = 0$ we assume to have a constant magnetic field \mathbf{B}_0 . The second boundary condition for solving the second-order differential equation (7.18) is $\mathbf{B}(x = \infty) = 0$. The solution of (7.18) with these two boundary conditions is

$$\mathbf{B}(x) = \mathbf{B}_0 e^{-\delta x} \quad (7.20)$$

The field penetrates only the distance δ into the superconductor.

7.3 Cooper instability

Consider the ground state of a free electron gas in the presence of an *attractive* electron-electron interaction potential $\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2)$. Let $\psi(\mathbf{r}_1, \mathbf{r}_2)$ be the wave function of a *pair* of electrons. Consider only states in which $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) = 0$ (center of gravity = 0) so that we have

$$\psi = \psi(\mathbf{r}_1 - \mathbf{r}_2) = \sum_{\mathbf{k}} g(\mathbf{k}) e^{i\mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2)} \quad (7.21)$$

$g(\mathbf{k})$ is the probability amplitude for finding one electron in the state $|\mathbf{k}\rangle$ and the other in state $|\mathbf{-k}\rangle$. Since the rest of the electrons ($N \sim 10^{23}$) occupy the states with $k = |\mathbf{k}| < k_F$ we have $g(\mathbf{k}) = 0$ for $k > k_F$. The Schrödinger equation for the two electrons is

$$\left[-\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + \mathcal{V}(\mathbf{r}_1 - \mathbf{r}_2) \right] \psi(\mathbf{r}_1 - \mathbf{r}_2) = E \psi(\mathbf{r}_1 - \mathbf{r}_2) \quad (7.22)$$

Since for each individual electron of the pair we must have $E_i > E_F$ ($i = 1, 2$), the total energy of the pair must be of the order of $2E_F$. If the pair energy becomes smaller than $2E_F$ the normal state is *unstable*.

Inserting (7.21) into (7.22) we have

$$\frac{\hbar^2}{m}k^2g(\mathbf{k}) + \sum_{\mathbf{k}'} g(\mathbf{k}')\mathcal{V}_{\mathbf{k}\mathbf{k}'} = Eg(\mathbf{k}) \equiv (2E_F + \epsilon)g(\mathbf{k}) \quad (7.23)$$

with

$$\mathcal{V}_{\mathbf{k}\mathbf{k}'} = \langle \mathbf{k} | \mathcal{V} | \mathbf{k}' \rangle = \frac{1}{V} \int d^3\mathbf{r}_{12} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}_{12}} \mathcal{V}(\mathbf{r}_{12}) \quad (7.24)$$

with $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. $\mathcal{V}_{\mathbf{k}\mathbf{k}'}$ can be interpreted as the *scattering amplitude* of the electron pair from the state $|k, -\mathbf{k}\rangle$ into the state $|-\mathbf{k}, \mathbf{k}\rangle$. We now consider a *simplified attractive interaction* mediated by the interaction with phonons of frequencies $0 \leq \omega_q \leq \omega_D$, where ω_D is the Debye frequency.

$$\mathcal{V}_{\mathbf{k}\mathbf{k}'} = \begin{cases} -\kappa/V & \text{for } E_F < \frac{\hbar^2 k_i^2}{2m} < E_F + \hbar\omega_D \\ 0 & \text{otherwise} \end{cases} \quad (7.25)$$

with $k_i = |\mathbf{k}|, |\mathbf{k}'|$.

From this follows

$$\sum_{\mathbf{k}'} g(\mathbf{k}')\mathcal{V}_{\mathbf{k}\mathbf{k}'} = -\frac{\kappa}{V} \sum_{\mathbf{k}'} g(\mathbf{k}') = \text{const.} \equiv C \quad (7.26)$$

and we have

$$\begin{aligned} & \left(-\frac{\hbar^2 k^2}{m} + 2E_F + \epsilon \right) g(\mathbf{k}) = C \\ \Rightarrow & C = -\frac{\kappa}{V} \sum_{\mathbf{k}} g(\mathbf{k}) = -\frac{\kappa}{V} \sum_{\mathbf{k}} \frac{C}{-2\epsilon_k + \epsilon + 2E_F} \\ & = -C\kappa \int_{E_F}^{E_F + \hbar\omega_D} d\epsilon_k \frac{N(\epsilon_k)}{-2\epsilon_k + \epsilon + 2E_F} \end{aligned} \quad (7.27)$$

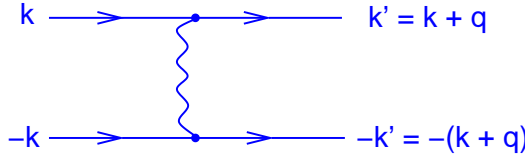
Because $N(E)$ is nearly constant near the Fermi level we can put $N(E) \approx N(E_F)$ out of the integral and we have with the substitution $\xi = \epsilon_k - E_F$

$$\begin{aligned} \Rightarrow & 1 = -\kappa N(E_F) \int_0^{\hbar\omega_D} d\xi \frac{1}{2\xi - \epsilon} = \frac{1}{2}\kappa N(E_F) \ln \left(\frac{\epsilon - 2\hbar\omega_D}{\epsilon} \right) \\ & \frac{2}{\kappa N(E_F)} = \ln \left(1 - \frac{2\hbar\omega_D}{\epsilon} \right) \\ & e^{\frac{2}{\kappa N(E_F)}} = 1 - \frac{2\hbar\omega_D}{\epsilon} \\ \epsilon & = -2\hbar\omega_D \frac{1}{e^{\frac{2}{\kappa N(E_F)}} - 1} \approx -2\hbar\omega_D e^{-\frac{2}{\kappa N(E_F)}} \end{aligned} \quad (7.28)$$

We conclude that in the presence of the attractive interaction in the vicinity of the Fermi level there exists a “bound state” with $\epsilon < 0$, i.e. $E < 2E_F$, which means that the normal state with a filled Fermi sphere is unstable with respect to the formation of a Cooper pair.

Remarks:

- The presence of the other 10^{23} electrons is very important, as they provide the “normal” density of states $N(\epsilon_k) \propto \epsilon_k^{1/2}$.
- The result $\epsilon \propto e^{-2/\kappa N(E_F)}$ cannot be obtained by perturbation theory because this function has an *essential singularity* for $\kappa \rightarrow 0$ and, therefore, cannot be expanded in a power series around $\kappa = 0$. This was an *obstacle* for the formulation of a theory of superconductivity.



We now want to consider more carefully the origin of the attraction of the electrons via the Debye phonons.

The scattering amplitude $\mathcal{V}_{\mathbf{k}\mathbf{k}'}$ is given in 2nd order (Born) approximation as

$$\mathcal{V}_{\mathbf{k}\mathbf{k}'} = \frac{1}{2} \sum_i \langle \mathbf{k} | \mathcal{H}_{\text{ep}} | i \rangle \langle i | \mathcal{H}_{\text{ep}} | \mathbf{k}' \rangle \left(\frac{1}{2\epsilon_k - E_i} + \frac{1}{2\epsilon_{k'} - E_i} \right) \quad (7.29)$$

$|i\rangle$ are the *intermediate states* and E_i the corresponding energies. There are two intermediate states allowed by momentum conservation:

<p style="text-align: center;">$i = 1:$</p> <ul style="list-style-type: none"> • electron 1 in state $\mathbf{k}'\rangle = \mathbf{k} + \mathbf{q}\rangle$ • electron 2 in state $\mathbf{-k}\rangle$ • one phonon with momentum $-\mathbf{q}$ • intermediate energy $E_1 = \epsilon_k + \epsilon_{k'} + \hbar\omega$ 	<p style="text-align: center;">$i = 2:$</p> <ul style="list-style-type: none"> • electron 1 in state $\mathbf{k}\rangle$ • electron 2 in state $\mathbf{-k}'\rangle = \mathbf{-(k + q)}\rangle$ • one phonon with momentum \mathbf{q} • intermediate energy $E_2 = \epsilon_k + \epsilon_{k'} + \hbar\omega = E_1$
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If we assume that the matrix elements depend only on $|\mathbf{k}| \approx k_F$ and $|\mathbf{q}| = q$, i.e.

$$\langle \mathbf{k} | \mathcal{H}_{\text{ep}} | i \rangle \equiv M(k_F, q) \quad \langle i | \mathcal{H}_{\text{ep}} | \mathbf{k}' \rangle \equiv M^*(k_F, q) \quad (7.30)$$

we have

$$\begin{aligned} \mathcal{V}_{\mathbf{k}\mathbf{k}'} &= |M(k_F, q)|^2 \left(\frac{1}{\underbrace{\epsilon_k - \epsilon_{k'}}_{\hbar\omega} - \hbar\omega_q} + \frac{1}{\epsilon_{k'} - \epsilon_k - \hbar\omega_q} \right) \\ &= \frac{1}{\hbar} |M(k_F, q)|^2 \left(\frac{1}{\omega - \omega_1} - \frac{1}{\omega + \omega_1} \right) \\ &= \frac{1}{\hbar} |M(k_F, q)|^2 \frac{\omega_q}{\omega^2 - \omega_q^2} \end{aligned} \quad (7.31)$$

If $\hbar|\epsilon_k - \epsilon_{k'}| < \omega_q < \omega_D$ we have an *attractive interaction!*

An important experimental check, whether we are really dealing with phonons is to examine, whether the superconducting transition temperature T_c depends on the mass of the material, i.e. studying superconducting materials with different isotopes (*isotope effect*).

7.4 BCS theory

We have convinced ourselves that the ground state of an electron gas with an attractive interaction near the Fermi level is unstable with respect to the formation of Cooper pairs. We found that the indirect interaction provided by the phonons give such an interaction. This was the achievement of L. N. Cooper (Phys. Rev. **104**, 1189 (1956)). J. Bardeen, L. N. Cooper and J. R. Schrieffer (BCS) constructed a trial wave function from Cooper pairs and were able to formulate a mean-field theory of superconductivity (Phys. Rev. **106**, 162 (1957)) by means of a variation calculation. This was finally a microscopic theory of superconductivity, which appeared 46 years after its discovery by Heike Kamerlingh Onnes in 1911.

In the superconducting ground state we have to expect that *all* the electrons are paired, so we write down a total wave function of the form

$$\Psi = \mathcal{N}\mathcal{A}\{\varphi(\mathbf{r}_1 - \mathbf{r}_2, s_1, s_2)\varphi(\mathbf{r}_3 - \mathbf{r}_4, s_3, s_4)\dots\} \quad (7.32)$$

where \mathcal{N} is the normalization and \mathcal{A} is the antisymmetrization operator. We can perform a Fourier transform as before

$$\varphi(\mathbf{r}_1 - \mathbf{r}_2, s_1, s_2) = \sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2)} g(\mathbf{k}, s_1, s_2) \quad (7.33)$$

and have for *singlet pairing*

$$g(\mathbf{k}, s_1, s_2) = g(\mathbf{k}) \frac{1}{\sqrt{2}} \left(\uparrow\downarrow - \downarrow\uparrow \right) \quad (7.34)$$

To keep the 1-2 pair wavefunction antisymmetric we must have $g(\mathbf{k}) = g(-\mathbf{k})$.

To work with the generalized Slater determinant generated by the \mathcal{A} operator is very cumbersome, and one has to use the *occupation number representation* instead. This representation of quantum-mechanical states is also called *second quantization* and we won't introduce this formalism in detail.

We just note that Ψ is now written in terms of the *state of occupation* of different *pairs* of single-particle states $|\mathbf{k} \uparrow, -\mathbf{k} \downarrow\rangle$:

$$|\Psi\rangle = \prod_{\text{all } \mathbf{k}} |\Phi_{\mathbf{k}}\rangle \quad (7.35)$$

$$|\Phi_{\mathbf{k}}\rangle = u_k |0, 0\rangle_k + v_k |1, 1\rangle_k = |\Phi_{-\mathbf{k}}\rangle$$

$|0, 0\rangle_k$ denotes that both $|\mathbf{k} \uparrow\rangle$ and $|\mathbf{k} \downarrow\rangle$ are empty;

$|1, 1\rangle_k$ denotes that both $|\mathbf{k} \uparrow\rangle$ and $|\mathbf{k} \downarrow\rangle$ are occupied.

In second-quantization notation we have

$$|\Psi\rangle = \prod_{\text{all } \mathbf{k}} (u_k + v_k a_{\mathbf{k}\uparrow}^\dagger a_{-\mathbf{k}\downarrow}^\dagger) |0\rangle \quad (7.36)$$

$u_k = u_{-k}$ and $v_k = v_{-k}$ are variational parameters which obey the normalization condition

$$u_k^2 + v_k^2 = 1 \quad (7.37)$$

With the trial wavefunction (7.35) or (7.36) we have to minimize the expectation value of the energy subject to the side condition that there are exactly N electrons. The corresponding Lagrangian multiplier is the chemical potential μ :

$$\tilde{E} = \langle \Psi | (\mathcal{H} - \mu N) | \Psi \rangle = \sum_{\mathbf{k}} 2\epsilon_{\mathbf{k}} v_{\mathbf{k}}^2 + \sum_{\mathbf{k}\mathbf{k}'} \mathcal{V}_{\mathbf{k}\mathbf{k}'} u_{\mathbf{k}} v_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} \quad (7.38)$$

We introduce again the schematic attractive interaction near the Fermi level

$$\mathcal{V}_{\mathbf{k}\mathbf{k}'} = -\frac{\kappa}{V} \lambda_{\mathbf{k}} \lambda_{\mathbf{k}'} \quad \lambda_{\mathbf{k}} = \begin{cases} 1 & \text{for } 0 < \epsilon_{\mathbf{k}} < \hbar\omega_D \\ 0 & \text{else} \end{cases} \quad (7.39)$$

So we have

$$\begin{aligned} \frac{\tilde{E}}{V} &= \frac{1}{V} \sum_{\mathbf{k}} 2\epsilon_{\mathbf{k}} v_{\mathbf{k}}^2 - \frac{\kappa}{V^2} \sum_{\mathbf{k}\mathbf{k}'} \lambda_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}} \lambda_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}'} \\ &= \frac{1}{V} \sum_{\mathbf{k}} 2\epsilon_{\mathbf{k}} v_{\mathbf{k}}^2 - \kappa \left[\frac{1}{V} \sum_{\mathbf{k}} \lambda_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}} \right]^2 \end{aligned} \quad (7.40)$$

We parametrize now

$$u_k = \cos \theta_k \quad v_k = \sin \theta_k \quad (7.41)$$

and obtain

$$\frac{\tilde{E}}{V} = f(\theta_{k_1} \dots \theta_{k_N}) = \frac{1}{V} \sum_{\mathbf{k}} 2\epsilon_k \cos^2 \theta_k - \kappa \left[\frac{1}{V} \sum_{\mathbf{k}} \lambda_k \underbrace{\cos \theta_k \sin \theta_k}_{\frac{1}{2} \sin 2\theta_k} \right]^2 \quad (7.42)$$

We take a particular k_0 and minimize with respect to θ_{k_0} :

$$0 = \frac{\partial F}{\partial \theta_{k_0}} = \frac{1}{V} 2\epsilon_{k_0} \underbrace{\left(-2 \sin \theta_{k_0} \cos \theta_{k_0} \right)}_{\frac{1}{2} \sin 2\theta_{k_0}} - \frac{2}{V} \kappa \lambda_{k_0} \cos 2\theta_{k_0} \frac{1}{2V} \sum_{\mathbf{k}} \lambda_k \sin 2\theta_k \quad (7.43)$$

We now divide by $2 \cos 2\theta_{k_0}$

$$\epsilon_{k_0} \tan 2\theta_{k_0} = -\frac{\kappa}{2V} \left(\sum_{\mathbf{k}} \lambda_k \sin 2\theta_k \right) \lambda_{k_0} \quad (7.44)$$

and define

$$\begin{aligned} \cos 2\theta_k &= \frac{-\epsilon_k}{\sqrt{\epsilon_k^2 + \Delta_k^2}} & \sin 2\theta_k &= \frac{\Delta_k}{\sqrt{\epsilon_k^2 + \Delta_k^2}} \\ \Rightarrow & & \tan 2\theta_{k_0} &= -\frac{\Delta}{\epsilon_{k_0}} \end{aligned} \quad (7.45)$$

from which we obtain

$$\Delta_{k_0} = \frac{\kappa}{2V} \lambda_{k_0} \sum_{\mathbf{k}} \frac{\lambda_k \Delta_k}{\sqrt{\epsilon_k^2 + \Delta_k^2}} \quad (7.46)$$

This is the famous BCS gap equation. Δ is the energy gap which separates the energies of the Cooper pair condensate from the continuum of possible excitations.

We can solve (7.46) for the gap parameter Δ if we assume it to be k -independent:

$$\Delta = \Delta \frac{\kappa}{V} \sum_{\mathbf{k}} \frac{\lambda_k}{\sqrt{\epsilon_k^2 + \Delta^2}} \quad (7.47)$$

This equation has the trivial solution $\Delta = 0$, which corresponds to the normal state. For a nontrivial solution $\Delta \neq 0$ we have the equation

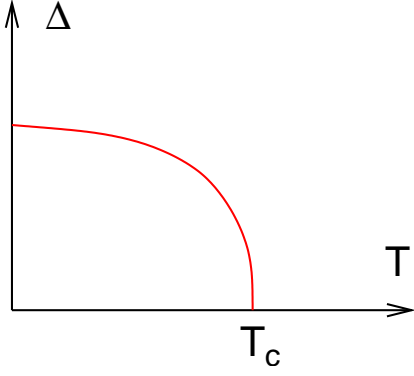
$$\begin{aligned} 1 &= \frac{\kappa}{2} \int_{-\omega_D}^{\omega_D} N(E_F + \epsilon) \frac{1}{\sqrt{\epsilon^2 + \Delta^2}} \approx \frac{N(E_F)\kappa}{2} \int_{-\omega_D}^{\omega_D} \frac{1}{\sqrt{\epsilon^2 + \Delta^2}} \\ &= \frac{N(E_F)\kappa}{2} \ln \left[\frac{\omega_D + \sqrt{\omega_D^2 + \Delta^2}}{-\omega_D + \sqrt{\omega_D^2 + \Delta^2}} \right] \end{aligned} \quad (7.48)$$

from which follows

$$\Delta = 2\omega_D \frac{e^{-\frac{1}{\kappa N(E_F)}}}{1 - e^{-\frac{2}{\kappa N(E_F)}}} \approx 2\omega_D e^{-\frac{1}{\kappa N(E_F)}} \quad (7.49)$$

We now consider the situation at finite temperatures T . In order to do this we convince ourselves that the occupation number of pairs in the superconducting ground state is just 1 minus the double of the (Fermi) probability to be in the normal state ($\beta = 1/k_B T$):

$$F(E_k) = 1 - 2f(E_k) = 1 - \frac{2}{e^{\beta E_k} + 1} = \tanh \beta E_k / 2 \quad (7.50)$$



Defining the pair excitation energy as $E_k = \sqrt{\epsilon_k^2 + \Delta_k^2}$ we arrive at the *finite temperature Gap equation*

$$\Delta_{\mathbf{k}} = -\frac{1}{2V} \sum_{\mathbf{k}'} \mathcal{V}_{\mathbf{k}\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{E_{\mathbf{k}'}} \quad (7.51)$$

Applying again the previous simplifications for Δ and \mathcal{V} and $N(\epsilon)$ we arrive at

$$1 = \kappa N(E_F) \int_0^{\hbar\omega_D} d\epsilon \frac{\tanh \beta E_k/2}{E(\epsilon)} = \kappa N(E_F) \int_0^{\epsilon(\hbar\omega_D)} \frac{\tanh \beta E_k/2}{\epsilon(E)} \quad (7.52)$$

with $\epsilon(E) = \sqrt{E^2 - \Delta^2}$.

From this simplified finite-temperature gap equation the function $\Delta(T)$ can be determined numerically, e.g. by a Newton routine.

We can determine the critical temperature T_c from this equation by setting $\Delta = 0$

$$1 = \kappa N(E_F) \int_0^{\hbar\omega_D} dE \frac{1}{E} \tanh \beta E/2 \quad (7.53)$$

Making the approximation $\tanh(x) = x$ for $x < 1$ and $\tanh(x) = 1$ for $x > 1$ we arrive at

$$1 = \kappa N(E_F) [1 + \ln(\hbar\omega_D/2k_B T_c)] = \kappa N(E_F) \ln(e\hbar\omega_D/2k_B T_c) \quad (7.54)$$

leading to

$$T_c = \underbrace{\frac{e}{2}}_{1.35} \underbrace{[\hbar\omega_D/k_B]}_{\Theta_D} e^{\frac{1}{\kappa N(E_F)}} \quad (7.55)$$

The numerical calculation gives

$$T_c = 1.14 \Theta_D e^{\frac{1}{\kappa N(E_F)}} \quad (7.56)$$

	Zn	Cd	Hg	Al	In	Tl	Sn	Pb
Θ_D / K	235	164	70	375	109	100	195	96
T_c / K	0.9	0.56	4.16	1.2	3.4	2.4	3.75	7.22
$\kappa N(E_F)$	0.18	0.18	0.35	0.18	0.29	0.27	0.25	0.39

where Θ_D is the Debye temperature.