

## Assignments to Condensed Matter Theory I

### Sheet 9

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sheet online: <http://www-MCG.uni-R.de/teaching/>

#### Problem set: Specific heat of metals and semiconductors

When we introduced the second quantization for Fermions we also calculated (Sheet 4) the partition function for a set of non interacting electrons with generic dispersion relation  $\epsilon_\lambda$ . Now we want to specialize our calculation to two given simple models: namely of free electron in a metal and electron-holes of an intrinsic semiconductor. In particular the calculation of the temperature dependence of the chemical potential and internal energy of the metal reveals how the thermodynamical properties of a metal are determined by electrons at the Fermi surface. On the other hand the presence of a gap between the valence and the conduction band of an intrinsic semiconductor implies that only the *classical* high energy tail of the Fermi distribution for the electron (holes) gas in the conduction (valence) band must be taken into account.<sup>1</sup>

#### 9.1. Thermodynamics of a metal

Calculate the temperature dependence of the chemical potential and of the internal energy of a system of  $N$  free non relativistic fermions in the limit of small temperatures ( $k_B T \ll E_F$ ). In steps:

- Refresh the definition and calculation of the grand canonical partition function for a fermionic system.
- Evaluate the grand canonical partition function for a set of free non relativistic fermions with dispersion relation of the form:  $\epsilon_k = \frac{\hbar^2 k^2}{2m}$  (in 3D).
- Calculate the density of states for the fermionic system just introduced.  
*Hint: Remember that we are in 3D and use spherical coordinates for a spherically symmetrical dispersion relation.*
- The total number of particles in the system is the average of the particle number operator in the grand canonical ensemble. How can I write this number in terms of the Fermi distribution and the density of states?
- The chemical potential at zero temperature is the Fermi energy: can you prove this statement?

*Hint: What is the form of the Fermi distribution at zero temperature? And what is the Fermi energy?*

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<sup>1</sup>As a guide in the solution of the present sheet we suggest to study paragraphs 4.8 and 4.9 of Czycholl, *Theoretische Festkörperphysik*, Springer, 2nd Edition (2004).

- (f) The relation defined in point (d) defines implicitly the temperature dependence of the chemical potential. Explain why. Finally, calculate the low temperature dependence of the chemical potential making use of the Sommerfeld expansion. *Note: See the already cited Czycholl's book for detailed explanations about the Sommerfeld expansion.*
- (g) The internal energy,  $U(T)$ , is the average energy of the system. Recall how this can be calculated starting from the grandcanonical partition function. Express the internal energy as a function of the density of states and the Fermi distribution function and, making again use of the Sommerfeld expansion, calculate its low temperature dependence.
- (h) How does the specific heat,  $c_V = \frac{\partial U}{\partial T}$ , of a metal depend on the temperature at very low temperatures?
- (i) **[Kür]** The detailed calculation that you performed shows the linear dependence of the specific heat of a Fermi gas on the temperature at low temperatures. Could you guess this proportionality simply using the Pauli exclusion principle and the equipartition theorem (i.e. each electron considered as a classical particle should receive the same amount of average thermal energy  $3/2k_B T$ )?

## 9.2. **[Kür]** Thermodynamics of a semiconductor

- (a) Study the derivation of the specific heat for a semiconductor given at the pages 113-116 of the cited Czycholl's book and give the detail of the calculations leading from equation (4.200) to (4.202) of the text.
- (b) Consider the following model of semiconductor with constant density of states for the valence and conduction band:

$$\text{DOS}(E) = \begin{cases} \frac{1}{E_0} & \text{for } 0 < E < E_0 \text{ and } E_0 + \Delta < E < 2E_0 + \Delta \\ 0 & \text{elsewhere} \end{cases}$$

Assume that the chemical potential lies well inside the gap and calculate for this model the temperature dependence of the specific heat in the limit of small temperatures.

SOLUTION OF THE EXERCISES FOR THE SHEET 9 OF QTKM1

9.1) a) The grandcanonical partition function  $Z_{GC}$  is defined as:

$$Z_{GC} = \text{Tr} e^{-\beta(H - \mu N)}$$

where the trace is taken over the Fock space of the system. More in detail, if  $\{\lambda\}$  is a set of quantum numbers defining the single particle basis.

$$Z_{GC} = \sum_{\{n_\lambda\}} \langle \{n_\lambda\} | e^{-\beta(H - \mu N)} | \{n_\lambda\} \rangle$$

For a set of non interacting particles we can assume that  $\lambda$  is labelling the eigenstates of  $H$  and that  $H = \sum_{\lambda} c_{\lambda}^{\dagger} c_{\lambda} \epsilon_{\lambda}$

$$\begin{aligned} Z_{GC} &= \sum_{\{n_\lambda\}} \langle \{n_\lambda\} | \prod_{\lambda} e^{-\beta(\epsilon_{\lambda} - \mu) c_{\lambda}^{\dagger} c_{\lambda}} | \{n_\lambda\} \rangle = \\ &= \prod_{\lambda} \sum_{n_{\lambda}=0}^1 e^{-\beta(\epsilon_{\lambda} - \mu) n_{\lambda}} = \prod_{\lambda} [1 + e^{-\beta(\epsilon_{\lambda} - \mu)}] \end{aligned}$$

b) The arguments presented at point a) hold. The quantum number for the single particle basis is the momentum  $\vec{k}$ . Thus:

$$Z_{GC} = \prod_{\vec{k}} [1 + e^{-\beta(\epsilon_k - \mu)}]$$

N.B. since  $\epsilon_{\vec{k}} = \epsilon_k = \frac{\hbar^2 k^2}{2m}$  the dimensionality is here hidden in the  $\prod_{\vec{k}}$ . All the factors with  $|\vec{k}| = c$  give the same contribution  $e^{-\beta(\epsilon_c - \mu)}$ .

c) For the reason just given in the end of point b) it is useful to calculate the density of states.

$$g_{\text{spin}} \left( \frac{2}{2\pi} \right) V \int \frac{d^3 k}{(2\pi)^3} \longrightarrow V \int \frac{4\pi k^2}{(2\pi)^3} dk \quad \epsilon_k = \frac{\hbar^2 k^2}{2m}$$

$$d\epsilon = \frac{\hbar^2}{m} k dk$$

$$2V \int \frac{k^2}{2\pi^2} dk =$$

$$\frac{m}{\hbar^2} d\epsilon = k dk \quad k = \sqrt{\frac{2m\epsilon}{\hbar^2}}$$

$$= 2V \int \frac{4\pi m \sqrt{2m\epsilon}}{h^3} d\epsilon$$

$$\frac{m}{\hbar^3} \sqrt{2m\epsilon} d\epsilon = k^2 dk$$

$$\rho(\epsilon) = \frac{8\pi V m \sqrt{2m\epsilon}}{h^3} \quad \text{in other terms } \rho(\epsilon) \propto \sqrt{\epsilon}$$

$$d) N_e = \langle \hat{N} \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_{GC}$$

$$= -\frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \prod_{\vec{k}} \left( 1 + e^{-\beta(\epsilon_{\vec{k}} - \mu)} \right)$$

$$= \sum_{\vec{k}} \frac{1}{e^{\beta(\epsilon_{\vec{k}} - \mu)} + 1} = \int_0^{\infty} dE \rho(E) n_F(E)$$

where  $n_F(E) = \frac{1}{e^{\beta(E - \mu)} + 1}$ .

e) In the limit  $T \rightarrow 0$   $n_F(E) \rightarrow \Theta(\mu - E)$  where  $\Theta$  is the Heaviside function. This means that

$$N_e = \int_0^{\mu} dE \rho(E)$$

The last electronic level occupied has thus energy  $\mu$  which means  $E_F = \mu$ .

f) 
$$N_e = \int_0^{\infty} dE \rho(E) n_F(E, \mu, T)$$

since  $\rho(E)$  is fixed, the only way to change the temperature and maintain the integral fixed is to assume  $\mu = \mu(T)$ .

The Sommerfeld expansion states:

$$\int_{-\infty}^{+\infty} dE H(E) n_F(E) = \int_{-\infty}^{+\infty} dE k(E) \left( -\frac{\partial n_F}{\partial E} \right) + \underbrace{k(E) n_F(E)}_0 \Big|_{-\infty}^{+\infty}$$

but  $k(E) = \int_{-\infty}^E dE' H(E')$  and make assumption of regularity of  $H(E)$  in  $-\infty$ .

$$\lim_{E \rightarrow -\infty} k(E) = 0$$

Similarly we can demonstrate (under regularity assumption of  $k(E)$ ) that

$$\lim_{E \rightarrow +\infty} k(E) n_F(E) = 0$$

$-\frac{\partial n_F}{\partial E}$  is a function with support close to  $\mu$ . We thus expand  $k(E)$  around  $\mu$  and obtain

$$\int_{-\infty}^{+\infty} dE H(E) f(E) = \int_{-\infty}^{\mu} dE H(E) + \sum_{n=1}^{\infty} a_n (k_B T)^{2n} \frac{\partial^{2n-1} H(E)}{\partial E^{2n-1}} \Big|_{E=\mu}$$

with 
$$a_n = \int_{-\infty}^{+\infty} dx \frac{x^{2n}}{(2n)!} \frac{1}{(e^x+1)(e^{-x}+1)} \quad a_1 = \frac{\pi^2}{6}$$

$$N_e = \int_{-\infty}^{\mu} dE g(E) + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + \mathcal{O}(T^4)$$

$$\int_{-\infty}^{\bar{E}_F} dE \rho(E) + (\mu - \bar{E}_F) \rho(\bar{E}_F) = N_e + (\mu - \bar{E}_F) \rho(\bar{E}_F)$$

$\Rightarrow$

$$N_e \approx N_e + (\mu - \bar{E}_F) \rho(\bar{E}_F) + \frac{\pi^2}{6} (k_B T)^2 \rho'(\bar{E}_F)$$

$$\mu = \bar{E}_F - \frac{\pi^2}{6} (k_B T)^2 \frac{\rho'(\bar{E}_F)}{\rho(\bar{E}_F)} = \bar{E}_F - \frac{\pi^2}{6} (k_B T)^2 \frac{1}{2E_F}$$

g) The internal energy expressed as a function of the grand canonical partition function reads:

$$U = - \frac{\partial}{\partial \beta} \ln \mathcal{Z} + \frac{\mu}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z}$$

$$= \sum_{\lambda} \frac{\epsilon_{\lambda}}{\lambda} \frac{1}{1 + e^{\beta(\epsilon_{\lambda} - \mu)}} = \int_0^{\infty} dE \rho(E) E n_F(E)$$

One again we can use the Sommerfeld expansion:

$$U \approx \int_{-\infty}^{\bar{E}_F} \rho(E) E dE + (\mu - \bar{E}_F) \bar{E}_F \rho(\bar{E}_F) + \frac{\pi^2}{6} (k_B T)^2 [\rho(\bar{E}_F) + \rho'(\bar{E}_F) \bar{E}_F]$$

$$= \underbrace{\int_{-\infty}^{\bar{E}_F} dE E \rho(E)}_{:= V_0} - \frac{\pi^2}{6} \bar{E}_F \rho'(\bar{E}_F) (k_B T)^2 + \frac{\pi^2}{6} (k_B T)^2 \bar{E}_F \rho'(\bar{E}_F) + \frac{\pi^2}{6} (k_B T)^2 \rho(\bar{E}_F)$$

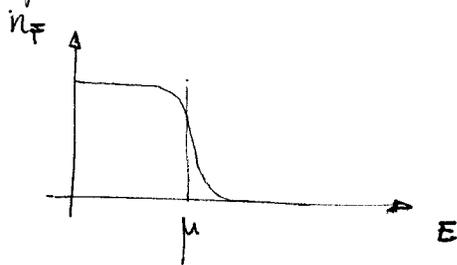
$$U \approx U_0 + \frac{3\pi V_m}{h^3} \sqrt{2mE_F} \frac{\pi^2}{6} (k_B T)^2$$

$$= U_0 + \frac{V_m}{6h^3} \sqrt{2mE_F} (k_B T)^2$$

h)  $C_V = \frac{\partial U}{\partial T} = \frac{V_m}{3h^3} \sqrt{2mE_F} k_B^2 \cdot T$  We obtain a linear

dependence given by a free electron gas. In a metal we would expect also a cubic dependence due to the crystal phonons. Nevertheless below the Debye temperature the linear contribution prevails.

i) The linear contribution of the specific heat at low temperatures can be "guessed" only using equipartition theorem and Pauli exclusion principle.



$$U - U_0 \approx \underbrace{N_{\text{excited el.}} \cdot \frac{3}{2} k_B T}_{\sim T}$$

Only electrons in a shell of size  $T$  from  $\mu$  can be excited thermally due to the Pauli exclusion principle.

9.2

a) (4.200)

$$C_V = e^{\beta(E_V - \mu)} \int_0^{E_V} dE E \left( \frac{E - \mu}{k_B T^2} + \frac{1}{k_B T} \frac{\partial \mu}{\partial T} \right) \rho_V(E) e^{\beta(E - E_V)} \\ + e^{-\beta(E_C - \mu)} \int_{E_C}^{\infty} dE E \left( \frac{E - \mu}{k_B T^2} + \frac{1}{k_B T} \frac{\partial \mu}{\partial T} \right) \rho_C(E) e^{-\beta(E - E_C)}$$

At low temperatures the  $\frac{1}{k_B T^2}$  is the leading term, thus:

$$C_V \approx e^{\beta(E_V - \mu)} \int_0^{E_V} dE \frac{E(E - \mu)}{k_B T^2} \rho_V(E) e^{\beta(E - E_V)} \\ + e^{-\beta(E_C - \mu)} \int_{E_C}^{\infty} dE \frac{E(E - \mu)}{k_B T^2} \rho_C(E) e^{-\beta(E - E_C)}$$

But:

$$\mu = \frac{1}{2} (E_C + E_V) + \frac{3}{4} k_B T \ln \left( \frac{m_h}{m_e} \right)$$

$$E_V - \mu = \frac{E_V - E_C}{2} - \frac{3}{4} k_B T \ln \left( \frac{m_h}{m_e} \right) = -\frac{\Delta}{2} - \frac{3}{4} k_B T \ln \left( \frac{m_h}{m_e} \right)$$

$$E_C - \mu = \frac{E_C - E_V}{2} - \frac{3}{4} k_B T \ln \left( \frac{m_h}{m_e} \right) = \frac{\Delta}{2} - \frac{3}{4} k_B T \ln \left( \frac{m_h}{m_e} \right)$$

$$C_V = \frac{e^{-\frac{\Delta}{2k_B T}}}{k_B T^2} \left( \int_0^{E_V} dE \frac{E(E - E_F)}{1} \rho_V(E) e^{-\beta(E_V - E)} \right. \\ \left. + \int_{E_C}^{\infty} dE E(E - E_F) \rho_C(E) e^{-\beta(E - E_C)} \right) \quad k_B T \ll \Delta$$

since  $\mu(T=0) = E_F = \frac{1}{2} (E_C + E_V)$

We are now finally left with the calculation of the integrals:

$$\left. \begin{aligned} f_v(E) &= C_v \sqrt{E_v - E} \\ f_c(E) &= C_c \sqrt{E - E_c} \end{aligned} \right\} C_{c,v} = \frac{V}{2\pi^2 \hbar^3 N} (2m_{e,h})^{3/2}$$

$$\left\{ \begin{aligned} x &= \sqrt{\frac{E_v - E}{k_B T}} \Rightarrow x^2 = \frac{E_v - E}{k_B T} & E &= E_v - k_B T \cdot x^2 \\ dE &= -2k_B T x dx \end{aligned} \right.$$

And analogously for the conduction band:

$$y = \sqrt{\frac{E - E_c}{k_B T}} \Rightarrow y^2 = \frac{E - E_c}{k_B T} \quad E = E_c + k_B T y^2 \quad dE = 2y k_B T dy$$

$$C_V = \frac{e^{-\Delta/2k_B T}}{k_B T^2} \left[ C_v \int_{\sqrt{\frac{E_v}{k_B T}} \rightarrow \infty}^0 -2k_B T x dx (E_v - k_B T x^2) \left( -k_B T x - \frac{\Delta}{2} \right) \sqrt{k_B T} e^{-x^2} \right. \\ \left. + C_c \int_0^{\infty} 2k_B T y dy (E_c + k_B T y^2) \left( k_B T y^2 + \frac{\Delta}{2} \right) \sqrt{k_B T} y e^{-y^2} \right]$$

We keep the dominant component for  $T \rightarrow 0$ :

$$C_V \approx \frac{e^{-\frac{\Delta}{2k_B T}}}{\sqrt{k_B T}} \underbrace{k_B \Delta}_{\frac{\sqrt{\pi}}{4}} \int_0^{\infty} dx x^2 e^{-x^2} (C_c E_c - C_v E_v) \\ = 2 \frac{V}{N} \frac{i}{(2\pi \hbar^2)^{3/2}} \frac{\Delta}{2} (m_c^{3/2} E_c - m_h^{3/2} E_v) \frac{e^{-\Delta/2k_B T}}{\sqrt{k_B T}}$$

b) Since the density of states is symmetrical around the point  $\bar{\epsilon}_0 + \frac{\Delta}{2}$  we can assume the chemical potential to be independent from the temperature  $T$ :

$$\mu(T) = \bar{\epsilon}_0 + \frac{\Delta}{2}$$

For the specific heat it holds:

$$c_v = \int d\bar{\epsilon} \rho(\bar{\epsilon}) \bar{\epsilon} \frac{\partial n_{\bar{\epsilon}}}{\partial T} = \int d\bar{\epsilon} \bar{\epsilon} \rho(\bar{\epsilon}) \frac{\bar{\epsilon} - \mu}{k_B T^2} \frac{1}{(e^{\beta(\bar{\epsilon} - \mu)} + 1)(e^{-\beta(\bar{\epsilon} - \mu)} + 1)}$$

$$= \frac{1}{T} \int k_B T dx (\mu + k_B T x) \frac{x}{(e^x + 1)(e^{-x} + 1)} \rho(\mu + k_B T x)$$

$$= \frac{2}{T \bar{\epsilon}_0} (k_B T)^2 \left[ \int_{\frac{-(\bar{\epsilon}_0 + \frac{\Delta}{2})}{k_B T}}^{-\frac{\Delta/2}{k_B T}} dx \frac{x^2}{(e^x + 1)(e^{-x} + 1)} + \int_{\frac{\Delta/2}{k_B T}}^{\frac{\bar{\epsilon}_0 + \frac{\Delta}{2}}{k_B T}} dx \frac{x^2}{(e^x + 1)(e^{-x} + 1)} \right]$$

$x = \beta(\bar{\epsilon} - \mu)$

$$\approx \frac{2}{T \bar{\epsilon}_0} (k_B T)^2 \left[ \int_{\frac{\Delta/2}{k_B T}}^{\frac{\bar{\epsilon}_0 + \frac{\Delta}{2}}{k_B T}} dx \frac{x^2}{(e^x + 1)(e^{-x} + 1)} \right] \quad \begin{matrix} \Delta \gg k_B T \\ \bar{\epsilon}_0 \gg k_B T \end{matrix}$$

$$\approx \frac{2}{T \bar{\epsilon}_0} (k_B T)^2 \int_{\frac{\Delta/2}{k_B T}}^{\infty} x^2 e^{-x} dx \approx \frac{2 k_B^2 T}{\bar{\epsilon}_0} \frac{-x^2 - 2x - 2}{e^x} \Big|_{\frac{\Delta/2}{k_B T}}^{\infty}$$

$$\approx \frac{2 k_B^2 T}{\bar{\epsilon}_0} \left( \frac{\Delta}{2 k_B T} \right)^2 e^{-\frac{\Delta}{2 k_B T}} = \boxed{\frac{\Delta^2}{2 T \bar{\epsilon}_0} e^{-\frac{\Delta}{2 k_B T}}}$$