

# STRUTTURA DELLA MATERIA 1

## Problems on the statistics of the Fermi gas

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The general context is the (usually low-temperature) gas of identical fermions assumed to be noninteracting.

This model usually describes the electron gas representing the conduction electrons of metals, but we will apply it to different systems too.

The internal degrees of freedom are assumed to be degenerate, with degeneracy  $g_s$ : for most problems (with noteworthy exceptions) we focus on the translational degrees of freedom.

### 1 The $T = 0$ limit

Determine the Fermi energy, i.e. the energy-boundary between full and empty states, as a function of the fermion density, mass, and spin degeneracy.

#### 1.1 Solution

Recall the spectrum of a freely translating particle contained in a macroscopically large cubic box of volume  $V = L \times L \times L$ . Impose periodic boundary conditions, i.e. the eigenfunction is the same at opposite faces of the box. The allowed values of the  $u = x, y, z$  wave-vector components

$$k_u = \frac{2\pi}{L} n_u, \quad n_u = 0, \pm 1, \pm 2, \pm 3, \dots \quad (1)$$

are associated to plane-wave eigenfunctions

$$\psi_{\vec{k}}(\vec{r}) = L^{-3/2} \exp(i \vec{k} \cdot \vec{r}),$$

with translational kinetic energy

$$\mathcal{E}_{\vec{n}} = \frac{|\vec{p}|^2}{2M} = \frac{\hbar^2 |\vec{k}|^2}{2M} = \frac{(2\pi\hbar)^2}{2ML^2} (n_x^2 + n_y^2 + n_z^2) = \frac{(2\pi\hbar)^2}{2ML^2} |\vec{n}|^2 \quad (2)$$

( $M$  is the mass of these fermions).

At this point one can follow various equivalent strategies.

1. *Focus on  $\vec{n}$ .*

Obvious observation:  $\mathcal{E}$  is a monotonically increasing function of  $|\vec{n}|$ .

Therefore the filled states form a sphere in  $\vec{n}$  space.

The count of the  $\vec{n}$ -points inside the sphere equals the volume of the sphere, because the density of integer points are distributed with unit density. The radius  $n_F$  of this sphere is fixed by the number of the electrons.

Taking into account the spin degeneracy  $g_s$  (each orbital state can host  $g_s$  fermions with different  $m_s$  values, while still respecting Pauli's principle):

$$g_s \times \frac{4\pi}{3} n_F^3 = N.$$

Whence

$$n_F^3 = \frac{3}{4\pi} \frac{N}{g_s},$$

$$n_F = \left( \frac{3N}{4\pi g_s} \right)^{1/3}.$$

To get the Fermi wave vector, momentum and energy, we just substitute:

$$k_F = \frac{2\pi}{L} n_F = \frac{2\pi}{V^{1/3}} \left( \frac{3N}{4\pi g_s} \right)^{1/3} = \left( \frac{6\pi^2}{g_s} \frac{N}{V} \right)^{1/3},$$

$$p_F = \hbar k_F = \hbar \left( \frac{6\pi^2}{g_s} \frac{N}{V} \right)^{1/3},$$

$$\epsilon_F \equiv \mu(T=0) = \frac{\hbar^2}{2M} k_F^2 = \frac{\hbar^2}{2M} \left( \frac{6\pi^2}{g_s} \frac{N}{V} \right)^{2/3}. \quad (3)$$

## 2. Focus on $\vec{k}$ .

One can equivalently consider the  $\vec{k}$ -space.

There, each point is associated with a translational plane wave  $\psi_{\vec{k}}(\vec{r})$ .

$\vec{k}$  points compatible with the periodic boundary condition are spaced by  $2\pi/L$  in each direction.

Each  $\vec{k}$  point occupies a "volume" in reciprocal space given by  $(2\pi/L)^3$ .

Accordingly the density of  $\vec{k}$  points amounts to

$$g_{\text{tr}}(\vec{k}) = \left( \frac{L}{2\pi} \right)^3 = \frac{V}{8\pi^3}.$$

In  $\vec{k}$  space, the simple parabolic energy dispersion (2) is spherically symmetric because it only depends on  $k = |\vec{k}|$ . Therefore one can conveniently adopt spherical coordinates  $(k, \theta, \varphi)$  in reciprocal space. The angular integrations yield a trivial factor  $4\pi$ .

One can therefore define a "radial"  $k$ -density of states:

$$g_{\text{tr}}(k) dk = \frac{V}{8\pi^3} \times 4\pi k^2 dk = \frac{V}{2\pi^2} k^2 dk.$$

To include spin and obtain the total  $k$ -density of states we just multiply by  $g_s$ :

$$g(k) dk = g_s \frac{V}{2\pi^2} k^2 dk.$$

With the same argument used for  $|\vec{n}|$  above, the energy

$$\mathcal{E}(k) = \frac{\hbar^2 k^2}{2M}$$

increases monotonically in  $k$ .

Therefore, in  $\vec{k}$  space the boundary between empty and filled states is a sphere. Let  $k_F$  be its radius.

The number of free-particle states within the  $k_F$  sphere (including spin) is

$$\int_0^{k_F} g(k) dk.$$

Equating this number of states to the number of fermions  $N$  we determine  $k_F$ :

$$N = \int_0^{k_F} g(k) dk = \int_0^{k_F} g_s \frac{V}{2\pi^2} k^2 dk = g_s \frac{V}{2\pi^2} \int_0^{k_F} k^2 dk = g_s \frac{V}{2\pi^2} \frac{k_F^3}{3}.$$

Whence

$$k_F^3 = 3N \frac{2\pi^2}{g_s V},$$

i.e.

$$k_F = \left( \frac{6\pi^2 N}{g_s V} \right)^{1/3},$$

of course in agreement with what we found with the  $\vec{n}$  method.

Then the expression (3) for  $\epsilon_F$  is straightforward.

### 3. Focus on energy $\mathcal{E}$ .

Recall the energy-density of translational states

$$g_{\text{tr}}(\mathcal{E}) = \frac{M^{3/2} V}{\sqrt{2} \pi^2 \hbar^3} \mathcal{E}^{1/2},$$

obtained in a problem a couple of exercise-lectures back.

The total energy-density of states is

$$g(\mathcal{E}) = g_s g_{\text{tr}}(\mathcal{E}).$$

In terms of an energy integration, the number of fermions is

$$N = \int_0^{\epsilon_F} g(\mathcal{E}) [n_{\mathcal{E}}]_F d\mathcal{E}.$$

In the special  $T \rightarrow 0$  limit:

$$N = \int_0^{\epsilon_F} g(\mathcal{E}) d\mathcal{E} = g_s \frac{M^{3/2} V}{\sqrt{2} \pi^2 \hbar^3} \int_0^{\epsilon_F} \mathcal{E}^{1/2} d\mathcal{E} = \frac{g_s M^{3/2} V}{\sqrt{2} \pi^2 \hbar^3} \frac{2}{3} \epsilon_F^{3/2}, \quad (4)$$

We invert this relation:

$$\begin{aligned} \frac{\sqrt{2} \pi^2 \hbar^3 N}{g_s M^{3/2} V} &= \frac{2}{3} \epsilon_F^{3/2}, \\ \epsilon_F^{3/2} &= \frac{3/2 \sqrt{2} \pi^2 \hbar^3 N}{g_s M^{3/2} V} = \frac{6\pi^2 \hbar^3 N}{g_s (2M)^{3/2} V}, \\ \epsilon_F &= \left( \frac{6\pi^2 \hbar^3 N}{g_s (2M)^{3/2} V} \right)^{2/3} = \frac{\hbar^2}{2M} \left( \frac{6\pi^2 N}{g_s V} \right)^{2/3}, \end{aligned}$$

which coincides with the expression (3). We invert the dispersion law (2), obtaining  $k = \sqrt{2M\mathcal{E}}/\hbar$ . We then substitute  $\epsilon_F$  and simplify:

$$k_F = \frac{\sqrt{2M\epsilon_F}}{\hbar} = \frac{\sqrt{2M \frac{\hbar^2}{2M} \left( \frac{6\pi^2 N}{g_s V} \right)^{2/3}}}{\hbar} = \frac{\sqrt{\hbar^2 \left( \frac{6\pi^2 N}{g_s V} \right)^{2/3}}}{\hbar} = \sqrt{\left( \frac{6\pi^2 N}{g_s V} \right)^{2/3}} = \left( \frac{6\pi^2 N}{g_s V} \right)^{1/3}.$$

## 2 Written test 17/06/2011, problem 4 – Pressure of the Fermi gas

Si consideri un campione di Rb metallico (densità di massa = 1532 Kg m<sup>-3</sup>). Si disegni un grafico dell'andamento della pressione  $P$  del gas di elettroni in funzione della temperatura, e si determini  $P$  alle temperature  $T = 0$  K e  $T = 200$  K.

[Si ricorda l'espressione  $C_V = N_A k_B \frac{\pi^2}{2} \frac{T}{T_F}$  per il calore specifico molare nel gas di Fermi non interagente a bassa temperatura.]

### 2.1 Solution

If one recalls the equality

$$P = \frac{2U}{3V},$$

the problem is quite straightforward. To determine  $P$ , one just needs to determine the value of  $U$ .

However, one may not recall that special identity, and stay on the safe side and just apply the definition of pressure:

$$P = -\frac{\partial F}{\partial V}.$$

At  $T = 0$ ,

$$P = -\frac{\partial U}{\partial V}.$$

The value of  $U$  can be determined by

$$U = \int_0^{\epsilon_F} \mathcal{E} g(\mathcal{E}) [n_{\mathcal{E}}]_F d\mathcal{E}.$$

In the special  $T \rightarrow 0$  limit:

$$\begin{aligned} U &= \int_0^{\epsilon_F} \mathcal{E} g(\mathcal{E}) d\mathcal{E} = g_s \frac{M^{3/2} V}{\sqrt{2} \pi^2 \hbar^3} \int_0^{\epsilon_F} \mathcal{E} \mathcal{E}^{1/2} d\mathcal{E} = g_s \frac{M^{3/2} V}{\sqrt{2} \pi^2 \hbar^3} \int_0^{\epsilon_F} \mathcal{E}^{3/2} d\mathcal{E} \\ &= \frac{g_s M^{3/2} V}{\sqrt{2} \pi^2 \hbar^3} \times \frac{2}{5} \epsilon_F^{5/2}, \end{aligned}$$

Recalling the similar result of Eq. (4):

$$N = \frac{g_s M^{3/2} V}{\sqrt{2} \pi^2 \hbar^3} \frac{2}{3} \epsilon_F^{3/2},$$

we can reorganize the expression for  $U$  as follows:

$$U = \frac{g_s M^{3/2} V}{\sqrt{2} \pi^2 \hbar^3} \epsilon_F^{3/2} \frac{2}{3} \times \frac{3}{2} \times \frac{2}{5} \epsilon_F = N \times \frac{3}{2} \times \frac{2}{5} \epsilon_F = N \times \frac{3}{5} \epsilon_F, \quad (5)$$

indicating an energy per electron  $\frac{3}{5} \epsilon_F$ .

If this approach seems too complicated, because of the hard-to-remember constant in the density of states, a simpler approach is as follows:

Just recall that  $g(\mathcal{E}) = A \mathcal{E}^{1/2}$

Then

$$\frac{U}{N} = \frac{\int_0^{\epsilon_F} \mathcal{E} g(\mathcal{E}) d\mathcal{E}}{\int_0^{\epsilon_F} g(\mathcal{E}) d\mathcal{E}} = \frac{A \int_0^{\epsilon_F} \mathcal{E} \mathcal{E}^{1/2} d\mathcal{E}}{A \int_0^{\epsilon_F} \mathcal{E}^{1/2} d\mathcal{E}} = \frac{\int_0^{\epsilon_F} \mathcal{E}^{3/2} d\mathcal{E}}{\int_0^{\epsilon_F} \mathcal{E}^{1/2} d\mathcal{E}} = \frac{\frac{2}{5} \epsilon_F^{5/2}}{\frac{2}{3} \epsilon_F^{3/2}} = \frac{3}{5} \epsilon_F$$

which is precisely the result obtained above.

Anyway, to obtain the pressure at  $T = 0$  (recalling that  $U = F$ ):

$$\begin{aligned}
P &= -\frac{\partial F}{\partial V} = -\frac{\partial U}{\partial V} = -\frac{\partial}{\partial V} \frac{3}{5} N \epsilon_F = -\frac{3}{5} N \frac{\partial}{\partial V} \epsilon_F = -\frac{3}{5} N \frac{\partial}{\partial V} \left[ \frac{\hbar^2}{2M} \left( \frac{6\pi^2 N}{g_s V} \right)^{2/3} \right] \\
&= -\frac{3}{5} N \frac{\hbar^2}{2M} \left( \frac{6\pi^2}{g_s} N \right)^{2/3} \frac{\partial}{\partial V} V^{-2/3} = -\frac{3}{5} N \frac{\hbar^2}{2M} \left( \frac{6\pi^2}{g_s} N \right)^{2/3} \left( -\frac{2}{3} \right) V^{-5/3} \\
&= \frac{2}{3} V^{-1} \frac{3}{5} N \frac{\hbar^2}{2M} \left( \frac{6\pi^2}{g_s} N \right)^{2/3} V^{-2/3} = \frac{2}{3} V^{-1} \frac{3}{5} N \frac{\hbar^2}{2M} \left( \frac{6\pi^2}{g_s} \frac{N}{V} \right)^{2/3} \\
&= \frac{2}{3} V^{-1} \frac{3}{5} N \epsilon_F = \frac{2}{3} V^{-1} U = \frac{2}{3} \frac{U}{V}.
\end{aligned}$$

which can also be expressed as

$$P = \frac{2}{5} \frac{N}{V} \epsilon_F.$$

To solve the problem at hand we need to evaluate the density of the conduction electrons of Rb. Each (monovalent, alkali) Rb atom contributes one electron to the conduction band.

The number density is obtained by dividing the mass density  $\rho$  by the density of a single Rb atom:

$$\frac{N}{V} = \frac{\rho}{85.47 \text{ a.m.u.}} = 1.0795 \times 10^{28} \text{ m}^{-3}$$

Substituting in Eq. (3), we obtain the Fermi energy:

$$\begin{aligned}
\epsilon_F &= \frac{(1.055 \times 10^{-34} \text{ J s})^2}{2 \times 9.109 \times 10^{-31} \text{ kg}} \left( \frac{6\pi^2}{2} 1.0795 \times 10^{28} \text{ m}^{-3} \right)^{2/3} \\
&= 6.104 \times 10^{-39} \text{ kg m}^4 \text{ s}^{-2} \times (6.837 \times 10^8 \text{ m}^{-1})^2 \\
&= 2.8535 \times 10^{-19} \text{ J} = 1.781 \text{ eV}
\end{aligned}$$

The  $T = 0$  pressure is therefore:

$$P = \frac{2}{5} \frac{N}{V} \epsilon_F = \frac{2}{5} \times 1.0795 \times 10^{28} \text{ m}^{-3} \times 2.8535 \times 10^{-19} \text{ J} = 1.23207 \text{ GPa}.$$

For the pressure at finite temperature, one could either use the volume dependence of the internal energy  $F$ , or directly the grand canonical potential  $J$ , or more simply the proportionality of pressure and temperature valid at all  $T$ :

$$P = \frac{2}{3} \frac{U}{V}.$$

One can then use the suggestion to obtain the  $T$ -dependence of  $U$  valid for  $T \ll T_F$ :

$$\begin{aligned}
U(T) &= U(T=0) + \int_0^T C_V(T') dT' = \frac{3}{5} N \epsilon_F + \int_0^T N k_B \frac{\pi^2}{2} \frac{T'}{T_F} dT' \\
&= \frac{3}{5} N \epsilon_F + N k_B \frac{\pi^2}{2} \frac{1}{T_F} \frac{T^2}{2} = \frac{3}{5} N \epsilon_F + N \frac{\pi^2}{4} k_B \frac{T^2}{T_F} = \frac{3}{5} N \epsilon_F + N \frac{\pi^2}{4} \epsilon_F \left( \frac{T}{T_F} \right)^2 \\
&= \frac{3}{5} N \epsilon_F \left[ 1 + \frac{5\pi^2}{12} \left( \frac{T}{T_F} \right)^2 \right].
\end{aligned}$$

In this problem  $T_F = 20668$  K, therefore at  $T = 200$  K,  $T/T_F = 0.009677$ .

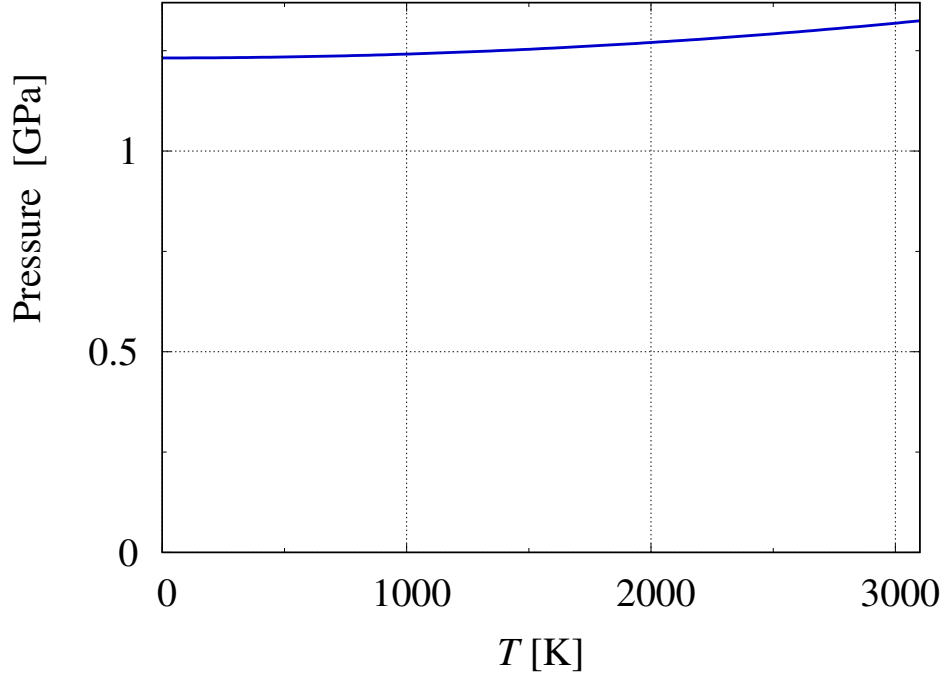
As a result

$$U(T) = \frac{3}{5} N \epsilon_F [1 + 0.00038508] = 1.00038508 \times U(T = 0).$$

As a consequence, also  $P$  scales by the same factor:

$$P = 1.00038508 \times 1.23207 \text{ GPa} = 1.23254 \text{ GPa}.$$

The pressure increment due to thermal excitations is as small as 474453 Pa.



### 3 The $T = 0$ Fermi gas: average momentum

Evaluate  $[\vec{p}]$  in the  $T = 0$  Fermi gas.

#### 3.1 Solution

$$\vec{p} = \hbar \vec{k},$$

thus

$$|\vec{p}| = \hbar |\vec{k}| = \hbar k,$$

the radial polar coordinate in  $\vec{k}$  space.

Therefore:

$$\begin{aligned} [\vec{p}] &= \hbar [k] = \hbar \int_0^{k_F} k g(k) dk = \hbar \int_0^{k_F} k g_s \frac{V}{2\pi^2} k^2 dk \\ &= \hbar g_s \frac{V}{2\pi^2} \int_0^{k_F} k^3 dk = \frac{\hbar g_s V}{2\pi^2} \frac{k_F^4}{4} = k_F \times \frac{\hbar g_s V}{8\pi^2} k_F^3 \\ &= k_F \times \frac{\hbar g_s V}{8\pi^2} \left( \frac{6\pi^2 N}{g_s V} \right) = k_F \times \frac{\hbar V}{8\pi^2} 6\pi^2 \frac{N}{V} = k_F \times \frac{\hbar}{8} 6 N \\ &= \frac{3}{4} \hbar k_F \times N. \end{aligned}$$

This indicates an average momentum per electron amounting to  $\frac{3}{4} \hbar k_F = \frac{3}{4} p_F$ .

## 4 The main ingredient of Fermi-gas problems: the electron density

Evaluate the number density  $N_{\text{el}}/V$  of conduction electrons, with different kinds of input data.

### 4.1 Solution

$$\frac{N_{\text{el}}}{V} = n_v \times \frac{N_{\text{at}}}{V}$$

1. First of all, identify how many electrons per atom take place in the conduction band. Let's call these "valence" electrons  $n_v$ . This is given by the position in the periodic table:

alkalis (Na)  $\rightarrow n_v = 1$

alkali earths (Mg)  $\rightarrow n_v = 2$

group-3 and group-13 metals (Al)  $\rightarrow n_v = 3$

group-11 (noble) metals (Cu)  $\rightarrow n_v = 1$

2. Then, determine the atomic number density  $N_{\text{at}}/V$ .

Depending on the kind of problem data there are two main routes:

- a) With density data: E.g. pb. 1 of the 20/01/2016 written test.

Cs metal, density  $\rho = 1879 \text{ kg m}^{-3}$ .

$$\frac{N_{\text{at}}}{V} = \frac{\rho}{M_{1 \text{ atom}}} = \frac{1879 \text{ kg m}^{-3}}{132.9 \text{ a.m.u.}} = 1.0795 \times 10^{28} \text{ m}^{-3},$$

using that  $1 \text{ a.m.u.} = 1.6606 \times 10^{-27} \text{ kg}$ .

[Then, with this density  $\epsilon_{\text{F}} = 2.436 \times 10^{-19} \text{ J} = 1.520 \text{ eV}$ .]

- b) With structural data.

1D crystal – atoms regularly spaced at distance  $a$ . The number density is

$$\frac{N_{\text{at}}}{L} = \frac{1}{a}$$

[NB! not  $2/a...$ ]

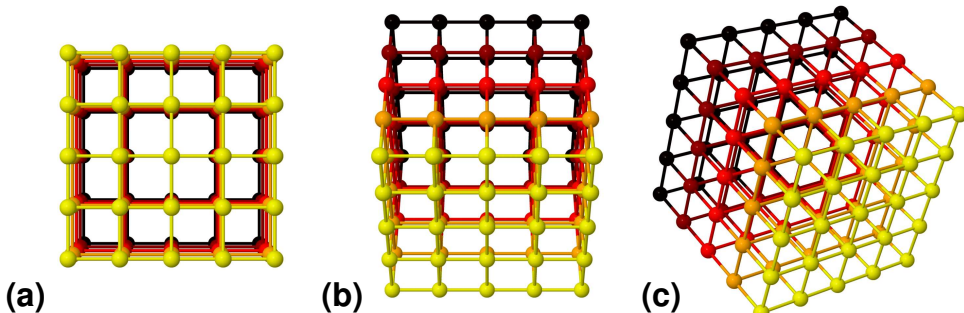
2D square-lattice crystal – atoms arranged in a square lattice with side  $a$ .

The number density is

$$\frac{N_{\text{at}}}{A} = \frac{1}{a^2}$$

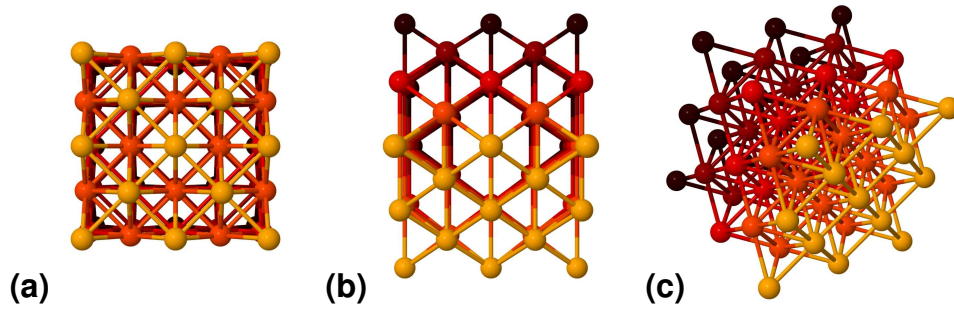
[NB! not  $4/a...$ ]

3D simple-cubic lattice (spacing  $a$ )



$$\frac{N_{\text{at}}}{V} = \frac{1}{a^3}$$

3D fcc lattice (side of conventional cubic cell =  $a$ )



$$\frac{N_{\text{at}}}{V} = \frac{4}{a^3}$$

E.g. pb. 1 of the 06/12/2001 test.

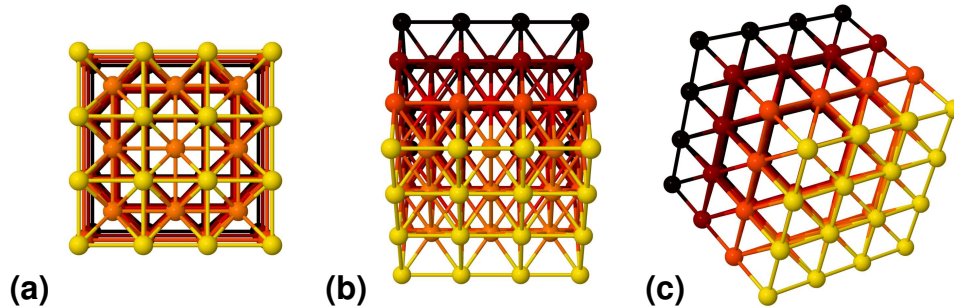
Ca,  $a = 558$  pm, fcc

$$\frac{N_{\text{at}}}{V} = \frac{4}{a^3} = 2.302 \times 10^{28} \text{ m}^{-3},$$

whence

$$\frac{N_{\text{el}}}{V} = 2 \times \frac{N_{\text{at}}}{V} = 4.605 \times 10^{28} \text{ m}^{-3}.$$

3D bcc lattice (side of conventional cubic cell =  $a$ )



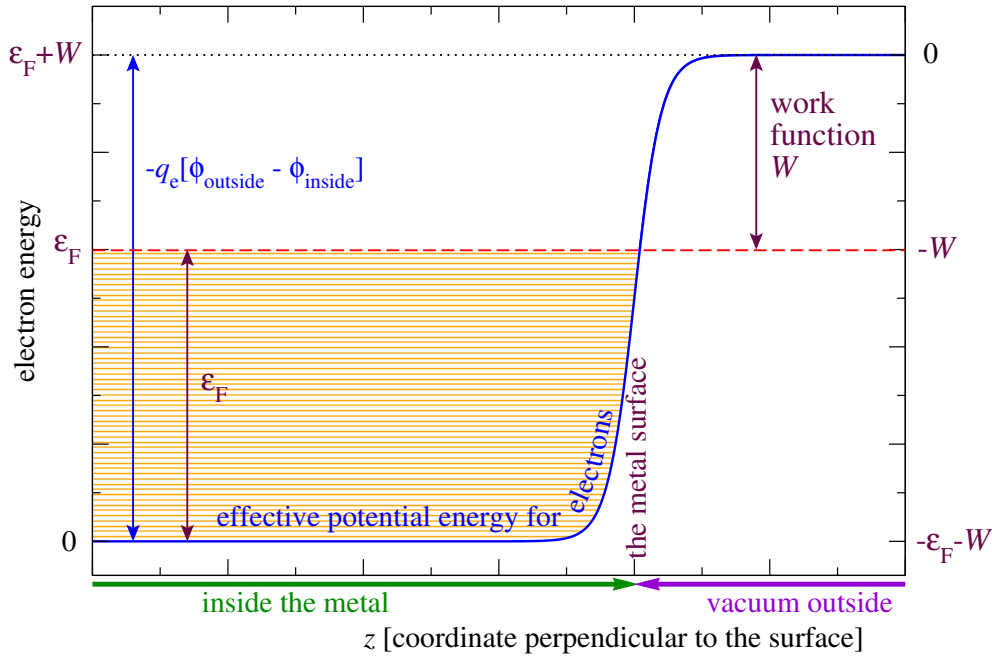
$$\frac{N_{\text{at}}}{V} = \frac{2}{a^3}$$

E.g. pb. 4 of the 19/06/2017 written test.

Na,  $a = 429$  pm, bcc

$$\frac{N_{\text{at}}}{V} = \frac{2}{a^3} = 2.533 \times 10^{28} \text{ m}^{-3} \equiv \frac{N_{\text{el}}}{V}$$

## 5 Fermi-gas and photoemission-related problems



The “work function”  $W$  is the minimum energy needed to extract an electron from the  $T = 0$  metal into the vacuum.

The only actual electric potential-energy difference is  $\phi_{\text{outside}} - \phi_{\text{inside}} < 0$ . The energy  $-q_e (\phi_{\text{outside}} - \phi_{\text{inside}}) > 0$  represents the work needed to overcome the electric forces and extract a stationary (i.e. sitting at the band bottom) electron from inside the metal and bring it to a stationary point far outside the metal.

The fundamental relation among the involved energies is

$$W + \epsilon_F = q_e (\phi_{\text{inside}} - \phi_{\text{outside}}).$$

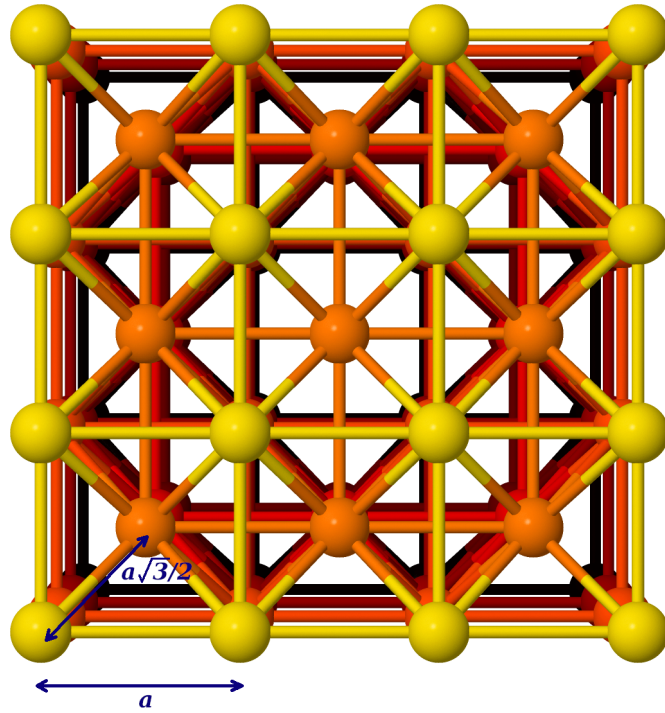
As the nature of  $\epsilon_F$  is kinetic,  $W$  has a mixed (partly electric potential, partly kinetic) nature.

$W$  is sometimes reported as  $W = q_e \phi$ . This “extraction potential”  $\phi \equiv W/q_e$  is just a pretext to express the work function in Volt units. Notably  $\phi$  does *not* represent any actual electric-potential difference.

## 6 Written test 15/01/2004, problem 4

Trattando gli elettroni di conduzione del cesio come liberi e non interagenti, ed essendo noto il potenziale di estrazione (2.14 V) di tale metallo, si valuti l’energia del fondo della banda di conduzione, misurata rispetto all’energia di vuoto all’esterno del solido. È nota da esperimenti di diffrazione la distanza d’equilibrio (5.35 Å) tra atomi primi vicini della struttura cubica a corpo centrato (bcc) del cesio.

## 6.1 Solution



The bcc lattice

With

$$d = \frac{\sqrt{3}}{2} a$$

we obtain

$$a = \frac{2}{\sqrt{3}} d = \frac{2}{\sqrt{3}} 5.35 \text{ \AA} = 6.178 \text{ \AA}.$$

Accordingly, the conventional-cell volume

$$a^3 = 235.8 \text{ \AA}^3 = 235.8 \times 10^{-30} \text{ m}^3.$$

Therefore

$$\frac{N_{\text{at}}}{V} = \frac{2}{a^3} = 8.483 \times 10^{27} \text{ m}^{-3} \equiv \frac{N_{\text{el}}}{V}.$$

And this electron density implies

$$\epsilon_{\text{F}} = 2.43 \times 10^{-19} \text{ J} = 1.517 \text{ eV}.$$

Whence, by summing, we get the potential energy at the bottom of the flat well inside the crystal:

$$V_b = -q_e \phi - \epsilon_{\text{F}} = -2.14 \text{ eV} - 1.517 \text{ eV} = -3.66 \text{ eV},$$

measured relative to the vacuum outside the crystal.

## 7 Written test 12/06/2003, problem 5

La densità del sodio solido è  $968 \text{ Kg m}^{-3}$  ed il potenziale di estrazione è  $2.75 \text{ V}$ . Assumendo una banda di conduzione parabolica (elettroni liberi) occupata da un elettrone per atomo, valutare il fondo di tale banda misurato rispetto al potenziale del “vuoto”, all’esterno del solido. Se pretendessimo di applicare la stessa approssimazione a *tutti* gli elettroni del sodio (11 per atomo), a che energia (rispetto al vuoto) si troverebbe il fondo della banda? Se identificassimo quest’ultima energia con l’energia della shell atomica K, a quale carica nucleare  $Z^{\text{eff}}$  di un modello di atomo a elettroni indipendenti essa corrisponderebbe?

### 7.1 Solution

1.

$$\frac{N_{\text{at}}}{V} = \frac{\rho}{M_{1 \text{ atom}}} = \frac{968 \text{ kg m}^{-3}}{23 \text{ a.m.u.}} = 2.53 \times 10^{28} \text{ m}^{-3} = \frac{N_{\text{el}}}{V},$$

whence

$$\epsilon_{\text{F}} = 5.04 \times 10^{-19} \text{ J} = 3.146 \text{ eV}.$$

Average potential energy inside the crystal:

$$V_b = -q_e \phi - \epsilon_{\text{F}} = -2.75 \text{ eV} - 3.146 \text{ eV} = -5.896 \text{ eV},$$

measured relative to the vacuum outside the crystal.

2. With  $Z = 11$  electrons per atom:

$$\frac{N_{\text{el}}^*}{V} = 11 \frac{N_{\text{at}}}{V} = 2.788 \times 10^{29} \text{ m}^{-3},$$

$$\epsilon_{\text{F}}^* = 2.493 \times 10^{-18} \text{ J} = 15.562 \text{ eV}.$$

Average potential energy inside the crystal:

$$V_b = -q_e \phi - \epsilon_{\text{F}}^* = -2.75 \text{ eV} - 15.562 \text{ eV} = -18.312 \text{ eV},$$

measured relative to the vacuum outside the crystal.

As required, we equate this energy to a 1-electron atom expression:

$$V_b = -\frac{E_{\text{Ha}}}{2} \frac{Z_{\text{eff}}^2}{n^2}$$

with  $n = 1$ .

$$-\frac{2V_b}{E_{\text{Ha}}} = Z_{\text{eff}}^2,$$

$$Z_{\text{eff}} = \sqrt{-\frac{2V_b}{E_{\text{Ha}}}} = \sqrt{-\frac{2 \times (-18.312 \text{ eV})}{27.2114 \text{ eV}}} = 1.160.$$

## 8 Test 06/12/2001, problem 1

Un laser da 2.4 W di potenza e 320 nm di lunghezza d'onda invia uno spot di luce monocromatica su un campione di calcio (potenziale di estrazione = 2.87 eV). Si calcoli:

- l'energia cinetica massima e minima (in eV) degli elettroni fotoemessi;
- il numero di fotoni incidente sul campione per unità di tempo;
- la corrente elettronica (in A) circolante in un anodo di raccolta opportunamente piazzato che intercetti il 30% degli elettroni fotoemessi (collegato al campione tramite un circuito esterno), assumendo un'efficienza di fotoestrazione pari al 2.3%.
- Dato il parametro reticolare  $a = 5.58 \text{ \AA}$  del Ca, stabilire se, oltre alla fotoemissione, si ha diffrazione alla Bragg dei fotoni sui piani reticolari separati da una distanza  $d = a$ , ed in caso affermativo si determini l'angolo  $\theta$  per il primo ordine.

### 8.1 Solution

1.

$$E_{\text{phot}} = \frac{hc}{\lambda} = 6.20765 \times 10^{-19} \text{ J} = 3.87451 \text{ eV} > 2.87 \text{ eV},$$

thus photoemission is possible.

$$E_{\text{kin}}^{\text{max}} = 1.00451 \text{ eV},$$

$$E_{\text{kin}}^{\text{min}} = 0,$$

because the Fermi energy certainly exceeds 1 eV.

2.

$$\frac{dN_{\text{phot}}}{dt} = \frac{\text{Power}}{E_{\text{phot}}} = \frac{2.4 \text{ W}}{6.20765 \times 10^{-19} \text{ J}} = 3.8662 \times 10^{18} \text{ photons/s}$$

$$\frac{dN_{\text{el}}}{dt} = 2.3\% \times \frac{dN_{\text{phot}}}{dt} = 8.89226 \times 10^{16} \text{ electrons/s}$$

$$\frac{dN_{\text{el}}^{\text{captured}}}{dt} = 30\% \times \frac{dN_{\text{el}}}{dt} = 2.6678 \times 10^{16} \text{ electrons/s}$$

3.

$$I = q_e \times \frac{dN_{\text{el}}^{\text{captured}}}{dt} = 0.00427409 \frac{\text{C}}{\text{s}} = 4.27409 \text{ mA}.$$

4. Diffraction Bragg relation

$$n\lambda = 2d \sin \theta$$

Indicating

$$\sin \theta = \frac{n\lambda}{2d}.$$

Even for  $n = 1$

$$\frac{\lambda}{2d} \gg 1,$$

therefore no diffraction.

## 9 Written test 19/09/2002, problem 2

Supponendo che gli elettroni di conduzione siano assimilabili a un gas di fermioni non interagenti, calcolare la pressione del gas alla temperatura  $T = 0$  nel caso del rame. L'energia del fondo della banda di conduzione rispetto al livello di vuoto è  $-11.14$  eV, la soglia fotoelettrica corrisponde a una lunghezza d'onda  $\lambda = 3024.39$  Å.

### 9.1 Solution

Photoelectric wavelength threshold indicates that the work function

$$W = \frac{hc}{\lambda} = 6.5685 \times 10^{-19} \text{ J} = 4.0995 \text{ eV}.$$

Given the average potential energy of the electrons inside the metal  $V_b = -11.14$  eV, one can obtain

$$\epsilon_F = -V_b - W = 1.12802 \times 10^{-18} \text{ J} = 7.04 \text{ eV}.$$

From this information one can obtain the electron density by inverting the expression

$$\epsilon_F = \frac{\hbar^2}{2M} \left( \frac{6\pi^2 N}{g_s V} \right)^{2/3},$$

using  $M = m_e$ .

$$\epsilon_F^{3/2} = \left( \frac{\hbar^2}{2m_e} \right)^{3/2} \frac{6\pi^2 N}{g_s V},$$

$$\left( \frac{2m_e}{\hbar^2} \right)^{3/2} \epsilon_F^{3/2} = \frac{6\pi^2 N}{g_s V},$$

$$\frac{N}{V} = \frac{g_s}{6\pi^2} \frac{(2m_e \epsilon_F)^{3/2}}{\hbar^3} = \frac{1}{3\pi^2} \frac{(2m_e \epsilon_F)^{3/2}}{\hbar^3} = 8.48 \times 10^{28} \text{ m}^{-3},$$

where we have used  $g_s = 2$ .

Recall the expression for pressure obtained in Problem 2:

$$P = \frac{2}{5} \frac{N}{V} \epsilon_F.$$

Substituting the obtained quantities:

$$P = \frac{2}{5} \times 8.48 \times 10^{28} \text{ m}^{-3} \times 1.12802 \times 10^{-18} \text{ J} = 3.828 \times 10^{10} \text{ Pa}.$$

## 10 Written test 17/06/2005, problem 1 – Ultrarelativistic Fermi gas

Le stelle denominate nane bianche possono avere al loro interno una densità dell'ordine di  $10^{11} \text{ kg m}^{-3}$ . Assumiamo per semplicità che

- queste stelle siano costituite da protoni ed elettroni non interagenti in pari numero e di densità uniforme;
- che gli elettroni presenti al loro interno siano relativistici con energia  $E = pc = \hbar ck$ ;
- che la temperatura sia nulla.

In queste ipotesi si valuti la pressione esercitata da questo gas di elettroni.

### 10.1 Solution

The (ultra)relativistic dispersion relation does not affect the spatial dependence of the eigenfunctions:

$$\psi_{\vec{k}}(\vec{r}) = L^{-3/2} \exp(i \vec{k} \cdot \vec{r}),$$

with

$$k_u = \frac{2\pi}{L} n_u, \quad n_u = 0, \pm 1, \pm 2, \pm 3, \dots$$

in a cubic box of side  $L$ .

To proceed solving this problem, our main observation is that the relativistic dispersion

$$E = \hbar c |\vec{k}|$$

yields a *monotonically increasing* energy dependence on  $|\vec{k}|$  (or  $|\vec{n}|$ ), like the usual nonrelativistic one.

This means that the filled states form a Fermi sphere in  $\vec{k}$  space, and that its radius is identically the same as for the nonrelativistic case:

$$k_F = \left( \frac{6\pi^2}{g_s} \frac{N}{V} \right)^{1/3}.$$

To determine the electrons number density, we proceed as follows:

$$\frac{N_{\text{el}}}{V} = \frac{N_{\text{proton}}}{V} = \frac{\rho}{m_e + m_p} = 5.975 \times 10^{37} \text{ m}^{-3}.$$

Note the huge value, 8 orders of magnitude larger than in ordinary metals!

From the density, one can evaluate

$$k_F = 1.21 \times 10^{13} \text{ m}^{-1}.$$

Then the Fermi energy is obtained by substituting  $k_F$  in the dispersion relation:

$$\begin{aligned} \epsilon_F &= \hbar c k_F = 1.0545718 \cdot 10^{-34} \text{ J s} \times 299792458 \text{ m/s} \times 1.21 \times 10^{13} \text{ m}^{-1} \\ &= 3.824 \times 10^{-13} \text{ J} = 2.39 \text{ MeV}. \end{aligned}$$

(Note that the ordinary  $\epsilon_F \propto k_F^2$  relation would yield a completely wrong result!)

With these informations, now we need to compute the pressure.

It would be risky to rely on the usual result  $P = \frac{2}{3}U/V$  obtained for the nonrelativistic Fermi gas. Therefore, we proceed following the same steps as in Problem 2:

$$P = -\frac{\partial F}{\partial V}.$$

At  $T = 0$ ,

$$P = -\frac{\partial U}{\partial V}.$$

The value of  $U$  can be determined as a  $k$  integration:

$$U = \int_0^\infty E(k) g(k) [n_{E(k)}]_F dk.$$

The  $k$ -density of states is the same as for the nonrelativistic problems, because the  $\vec{k}$  points are the same:

$$g(k) dk = g_s \frac{V}{2\pi^2} k^2 dk = \frac{V}{\pi^2} k^2 dk.$$

In the  $T \rightarrow 0$  limit suggested by this problem:

$$\begin{aligned} U &= \int_0^{k_F} E(k) g(k) dk = \frac{V}{\pi^2} \int_0^{k_F} \hbar c k \times k^2 dk = \frac{\hbar c V}{\pi^2} \int_0^{k_F} k^3 dk \\ &= \frac{\hbar c V}{\pi^2} \frac{k_F^4}{4} = \frac{\hbar c k_F V}{4\pi^2} k_F^3 \\ &= \frac{\epsilon_F V}{4\pi^2} \left( 3\pi^2 \frac{N}{V} \right)^{3/3} = \epsilon_F \frac{V}{4\pi^2} 3\pi^2 \frac{N}{V} = \epsilon_F \frac{1}{4} \times 3N \\ &= N \frac{3}{4} \epsilon_F. \end{aligned}$$

Note that this result differs from the analogous formula (5) obtained for the nonrelativistic gas in Problem 2!

Finally we can compute the pressure:

$$\begin{aligned} P &= -\frac{\partial U}{\partial V} = -\frac{\partial}{\partial V} \left( N \frac{3}{4} \epsilon_F \right) = -\frac{3}{4} N \frac{\partial}{\partial V} \epsilon_F = -\frac{3}{4} N \hbar c \frac{\partial}{\partial V} k_F \\ &= -\frac{3}{4} N \hbar c \frac{\partial}{\partial V} \left( 3\pi^2 \frac{N}{V} \right)^{1/3} = -\frac{3}{4} N \hbar c (3\pi^2 N)^{1/3} \frac{\partial}{\partial V} V^{-1/3} \\ &= -\frac{3}{4} N \hbar c (3\pi^2 N)^{1/3} \times \left( -\frac{1}{3} V^{-4/3} \right) = \frac{1}{4} N \hbar c (3\pi^2 N)^{1/3} V^{-4/3} \\ &= \frac{1}{4} N \hbar c \left( 3\pi^2 \frac{N}{V} \right)^{1/3} V^{-1} = \frac{1}{4} N \hbar c k_F V^{-1} = \frac{1}{4} \frac{N}{V} \epsilon_F \\ &= \frac{1}{3} \frac{3}{4} N \epsilon_F \frac{1}{V} = \frac{1}{3} \frac{U}{V}. \end{aligned}$$

Note the difference (by a factor 1/2) with the nonrelativistic relation between  $P$  and  $U$ !

The numerical result:

$$P = \frac{1}{4} \frac{N}{V} \epsilon_F = \frac{1}{4} \times 5.975 \times 10^{37} \text{ m}^{-3} \times 3.824 \times 10^{-13} \text{ J} = 5.712 \times 10^{24} \text{ Pa}.$$

## 11 Written test 19/01/2011, problem 3

Nel litio metallico gli elettroni di conduzione formano approssimativamente un gas di Fermi mentre gli ioni positivi stanno essenzialmente fissi in posizioni di equilibrio cristalline. La densità di questo materiale è  $535 \text{ kg m}^{-3}$ . Valutare la pressione del gas di elettroni a temperatura 0 K. Se invece si riuscisse a realizzare un gas di atomi di  ${}^6\text{Li}$  debolmente interagenti di pari densità, si determini la pressione di tale gas di fermioni a temperatura 0 K.

### 11.1 Solution sketch

Follow the strategy of the first part of Problem 2.

For the second part, replace  $m_e$  with  $M_{\text{Li}} = 6 \text{ a.m.u.}$

## 12 Written test 23/02/2010, problem 3

Applicando il modello di elettroni liberi non interagenti alla temperatura di 0 K, si calcoli la velocità di Fermi degli elettroni di conduzione del calcio metallico (2 elettroni per atomo in banda di conduzione), sapendo che la sua densità è di  $1550 \text{ kg m}^{-3}$ . Sempre alla temperatura dello zero assoluto, si valuti inoltre il contributo degli elettroni di conduzione al modulo di bulk, definito come  $B = -V(\partial P/\partial V)$  ( $P$  è la pressione e  $V$  il volume).

### 12.1 Solution

$$\frac{N_{\text{at}}}{V} = \frac{\rho}{M_{\text{Ca}}} = \frac{1550 \text{ kg m}^{-3}}{40.078 \text{ a.m.u.}} = 2.329 \times 10^{28} \text{ m}^{-3},$$

$$\frac{N_{\text{el}}}{V} = 2 \frac{N_{\text{at}}}{V} = 4.658 \times 10^{28} \text{ m}^{-3},$$

$$\begin{aligned} \epsilon_{\text{F}} &= \frac{(1.055 \times 10^{-34} \text{ J s})^2}{2 \times 9.109 \times 10^{-31} \text{ kg}} (3\pi^2 \times 4.658 \times 10^{28} \text{ m}^{-3})^{2/3} \\ &= 6.104 \times 10^{-39} \text{ kg m}^4 \text{ s}^{-2} \times (1.113 \times 10^{10} \text{ m}^{-1})^2 \\ &= 7.5634 \times 10^{-19} \text{ J} = 4.721 \text{ eV}. \end{aligned}$$

The Fermi velocity is

$$\begin{aligned} v_{\text{F}} &= \frac{p_{\text{F}}}{m_e} = \frac{\hbar k_{\text{F}}}{m_e} \\ &= \frac{1.055 \times 10^{-34} \text{ J s} \times 1.113 \times 10^{10} \text{ m}^{-1}}{9.109 \times 10^{-31} \text{ kg}} = 1.289 \times 10^6 \frac{\text{m}}{\text{s}}. \end{aligned}$$

The bulk modulus

$$B = -V \frac{\partial P}{\partial V}$$

can be calculated using the convenient  $P$  expression derived and used in previous problems:

$$P = \frac{2}{5} \frac{N}{V} \epsilon_{\text{F}}.$$

$$\begin{aligned}
B &= -V \frac{\partial}{\partial V} \left( \frac{2}{5} \frac{N}{V} \epsilon_F \right) = -\frac{2}{5} N V \frac{\partial}{\partial V} (\epsilon_F V^{-1}) \\
&= -\frac{2}{5} N V \frac{\partial}{\partial V} \left[ \frac{\hbar^2}{2M} \left( 3\pi^2 \frac{N}{V} \right)^{2/3} \times V^{-1} \right] \\
&= -\frac{2}{5} N V \frac{\hbar^2}{2M} (3\pi^2 N)^{2/3} \times \frac{\partial}{\partial V} V^{-5/3} \\
&= -\frac{2}{5} N V \frac{\hbar^2}{2M} (3\pi^2 N)^{2/3} \times \left( -\frac{5}{3} V^{-8/3} \right) \\
&= \frac{2}{3} N V \frac{\hbar^2}{2M} (3\pi^2 N)^{2/3} \times V^{-8/3} \\
&= \frac{2}{3} N V \frac{\hbar^2}{2M} \left( 3\pi^2 \frac{N}{V} \right)^{2/3} \times V^{-2} \\
&= \frac{2}{3} \frac{N}{V} \epsilon_F = \frac{5}{3} \times \frac{2}{5} \frac{N}{V} \epsilon_F = \frac{5}{3} P.
\end{aligned}$$

Numerically:

$$B = \frac{5}{3} P = \frac{5}{3} \times 1.409 \times 10^{10} \text{ Pa} = 2.349 \times 10^{10} \text{ Pa}.$$

### 13 The $0 < T \ll T_F$ Fermi gas: heat capacity

Determine the heat capacity per electron, per mole and per unit volume of the ideal Fermi gas at  $T \ll T_F$ .

#### 13.1 Solution

We first evaluate the density of free-fermions states at the Fermi energy:

$$\begin{aligned}
g(\epsilon_F) &= g_s g_{\text{tr}}(\epsilon_F) = \frac{g_s M^{3/2} V}{\sqrt{2} \pi^2 \hbar^3} \epsilon_F^{1/2} \\
&= \frac{g_s M^{3/2} V}{\sqrt{2} \pi^2 \hbar^3} \left[ \frac{\hbar^2}{2M} \left( \frac{6\pi^2 N}{g_s V} \right)^{2/3} \right]^{1/2} \\
&= \frac{3}{3} \frac{N}{N} \frac{g_s (2M)^{3/2} V}{4\pi^2 \hbar^3} \left[ \frac{\hbar^2}{2M} \left( \frac{6\pi^2 N}{g_s V} \right)^{2/3} \right]^{1/2} \\
&= \frac{3}{2} N \frac{g_s (2M)^{3/2} V}{6\pi^2 \hbar^3 N} \left[ \frac{\hbar^2}{2M} \left( \frac{6\pi^2 N}{g_s V} \right)^{2/3} \right]^{1/2} \\
&= \frac{3}{2} N \left[ \frac{2M}{\hbar^2} \left( \frac{g_s V}{6\pi^2 N} \right)^{2/3} \right]^{3/2} \left[ \frac{\hbar^2}{2M} \left( \frac{6\pi^2 N}{g_s V} \right)^{2/3} \right]^{1/2} \\
&= \frac{3}{2} N \epsilon_F^{-3/2} \times \epsilon_F^{1/2} \\
&= \frac{3N}{2\epsilon_F}.
\end{aligned} \tag{6}$$

Now we use this result to express the  $T \ll T_F$  Sommerfeld expansion for the internal energy in terms of  $\epsilon_F$ :

$$\begin{aligned}
U &= U(T=0) + \frac{\pi^2}{6} g(\epsilon_F) (k_B T)^2 + \dots \\
&= U(T=0) + \frac{\pi^2}{6} \frac{3N}{2\epsilon_F} (k_B T)^2 + \dots \\
&= \frac{3}{5} N \epsilon_F + \frac{\pi^2}{4} N \epsilon_F \left( \frac{k_B T}{\epsilon_F} \right)^2 + \dots \\
&= \frac{3}{5} N \epsilon_F \left[ 1 + \frac{\frac{\pi^2}{4} N \epsilon_F}{\frac{3}{5} N \epsilon_F} \left( \frac{k_B T}{\epsilon_F} \right)^2 + \dots \right] \\
&= \frac{3}{5} N \epsilon_F \left[ 1 + \frac{5\pi^2}{12} \left( \frac{T}{T_F} \right)^2 + \dots \right].
\end{aligned} \tag{7}$$

By deriving  $U$  with respect to temperature, we obtain the heat capacity:

$$C_V = \frac{3}{5} N \epsilon_F \frac{5\pi^2}{12} T_F^{-2} \times 2T + \dots = \frac{\pi^2}{2} N \frac{\epsilon_F}{T_F} \frac{T}{T_F} + \dots = N k_B \frac{\pi^2}{2} \frac{T}{T_F} + \dots \quad [T \ll T_F]. \tag{8}$$

The heat capacity per fermion:

$$C_{V1} = k_B \frac{\pi^2}{2} \frac{T}{T_F} + \dots$$

Note that, compared to the high-temperature value  $3/2k_B$ , the  $T \ll T_F$  heat capacity of the ideal gas is suppressed by a factor  $\propto T/T_F$ . More precisely, the ratio

$$\frac{C_{V1}^{\text{cold Fermi gas}}}{C_{V1}^{\text{hi-}T \text{ gas}}} = \frac{k_B \frac{\pi^2}{2} \frac{T}{T_F}}{\frac{3}{2} k_B} = \frac{\pi^2}{3} \frac{T}{T_F} \ll 1.$$

The heat capacity per mole is of course:

$$C_{V \text{ mol}} = k_B N_A \frac{\pi^2}{2} \frac{T}{T_F} + \dots$$

The heat capacity per unit volume:

$$C_{V \text{ volume}} = k_B \frac{\pi^2}{2} \frac{N}{V} \frac{T}{T_F} + \dots$$

## 14 Written test 19/09/2005, problem 1

L'alluminio ha densità 2702 Kg/m<sup>3</sup>. Assumendo una banda di elettroni liberi occupata da 3 elettroni per atomo, si determini il contributo elettronico al calore specifico molare a 5 K.

### 14.1 Solution

$$\frac{N_{\text{at}}}{V} = \frac{\rho}{M_{\text{Al}}} = \frac{2702 \text{ kg m}^{-3}}{26.98154 \text{ a.m.u.}} = 6.0307 \times 10^{28} \text{ m}^{-3},$$

$$\frac{N_{\text{el}}}{V} = 3 \frac{N_{\text{at}}}{V} = 1.8092 \times 10^{29} \text{ m}^{-3},$$

$$\begin{aligned}
\epsilon_F &= \frac{(1.055 \times 10^{-34} \text{ J s})^2}{2 \times 9.109 \times 10^{-31} \text{ kg}} (3\pi^2 \times 1.8092 \times 10^{29} \text{ m}^{-3})^{2/3} \\
&= 6.104 \times 10^{-39} \text{ kg m}^4 \text{ s}^{-2} \times (1.7497 \times 10^{10} \text{ m}^{-1})^2 \\
&= 1.86885 \times 10^{-18} \text{ J} = 11.664 \text{ eV}.
\end{aligned}$$

The heat capacity per mole *of electrons* is:

$$C_{V \text{ 1 mol of electrons}} = N_A k_B \frac{\pi^2}{2} \frac{k_B T}{\epsilon_F}.$$

However this is not what the problem asks for: the *molar* heat capacity of Al refers to 1 mol of aluminum, which contains  $3 \times N_A$  electrons:

$$\begin{aligned}
C_{V \text{ mol}} &= 3 \times N_A k_B \frac{\pi^2}{2} \frac{k_B T}{\epsilon_F} = 3 \times 8.31446 \frac{\text{J}}{\text{mol K}} \times \frac{\pi^2}{2} \frac{k_B \times 5 \text{ K}}{1.86885 \times 10^{-18} \text{ J}} \\
&= 123.091 \frac{\text{J}}{\text{mol K}} \times 3.69384 \times 10^{-5} = 0.00455 \frac{\text{J}}{\text{mol K}}.
\end{aligned}$$

## 15 (Spin) magnetic susceptibility of the Fermi gas

Evaluate the magnetic response of a homogeneous Fermi gas of electrons under the effect of a weak magnetic field coupled to the spin degree of freedom only.

Evaluate the magnetic susceptibilities for sodium ( $\rho = 968 \text{ kg m}^{-3}$ ) at  $T = 300 \text{ K}$ .

[See e.g. Ashcroft-Mermin p. 661-664, and Manini p. 135-136.]

### 15.1 Solution

In the absence of external fields, the Fermi gas is nonmagnetic, because both spin states are degenerate and therefore equally occupied. The application of a weak external magnetic field strength  $\vec{H} = H_z \hat{z}$  generates a total magnetic induction field  $\vec{B} = B_z \hat{z}$ . We assume  $\vec{B}$  to couple only to the electrons spin (neglect coupling to the translational motion): the  $g_s = 2$  degeneracy of the spin components (assumed in all problems so far) is lifted, and the Fermi gas acquires a nonzero magnetization. Denote the volume-density of magnetic moment with  $\vec{\mathcal{M}} = \mathcal{M}_z \hat{z}$ .

Recall that the gyromagnetic factor of the electron spin equals 2, and that the magnetic moment points opposite to the angular momentum component  $\pm 1/2\hbar$ :

$$\boldsymbol{\mu} = -2\mu_B \frac{\vec{S}}{\hbar}.$$

The coupling Hamiltonian

$$H_B = -\boldsymbol{\mu} \cdot \vec{B} = -\mu_z B$$

couple  $\boldsymbol{\mu}$  to the total induction field.

The resulting eigenenergy magnetic contributions are:

$$E_B(m_s) = 2\mu_B B m_s.$$

This results in two magnetic-energy levels:

$$\begin{aligned}
E_B(\uparrow) &= \mu_B B \\
E_B(\downarrow) &= -\mu_B B.
\end{aligned}$$

With  $N$  electrons,  $N = N_{\uparrow} + N_{\downarrow}$ , in a volume  $V$ , the densities of the two spin components are:

$$n_{\uparrow} = \frac{N_{\uparrow}}{V}$$

$$n_{\downarrow} = \frac{N_{\downarrow}}{V}.$$

The magnetization density amounts to

$$\mathcal{M}_z = -\frac{\mu_B}{V}(N_{\uparrow} - N_{\downarrow}) = \mu_B(n_{\downarrow} - n_{\uparrow}).$$

All these quantities fluctuate, and obviously for  $B_z = 0$ , on average,  $\mathcal{M}_z$  vanishes.

This problem asks us to compute the linear response, i.e. the proportionality coefficient in  $\mathcal{M}_z \propto B_z$ .

At  $B = 0$  the energy levels of the independent fermions are purely kinetic:

$$\mathcal{E}(k) = \frac{\hbar^2 k^2}{2m_e}$$

(In a real solid metal, this expression should be replaced with the band energy.)

For convenience, we introduce

$$\tilde{g}(\mathcal{E}) = \frac{1}{V}g(\mathcal{E}),$$

where  $g(\mathcal{E})$  is the usual total density of states for the  $B = 0$  situation (including spin).

Clearly, one can conceptually decompose this function as

$$\tilde{g}(\mathcal{E}) = \tilde{g}_{\uparrow}(\mathcal{E}) + \tilde{g}_{\downarrow}(\mathcal{E}),$$

where

$$\tilde{g}_{\uparrow}(\mathcal{E}) = \tilde{g}_{\downarrow}(\mathcal{E}) = \frac{1}{V}g_{\text{tr}}(\mathcal{E}) = \frac{1}{2}\tilde{g}(\mathcal{E}).$$

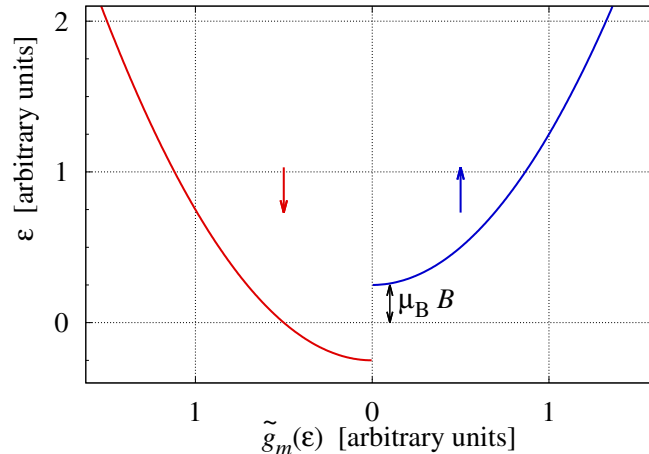
We now turn on  $B$ , which adds the magnetic eigenvalues to the kinetic energy:

$$\mathcal{E} \rightarrow \mathcal{E} + E_B(\pm 1/2) = \mathcal{E} \pm \mu_B B.$$

The effect of this addition to the energy levels shifts the density of states of the  $\uparrow$  and  $\downarrow$  electrons upward and downward respectively.

These translations can be represented by opposite-sign additions to the arguments of  $\tilde{g}_{\uparrow}(\mathcal{E})$  and  $\tilde{g}_{\downarrow}(\mathcal{E})$ :

$$\tilde{g}_{\uparrow/\downarrow}(\mathcal{E}) = \frac{1}{2}\tilde{g}(\mathcal{E} \mp \mu_B B).$$



In the limit of very weak field  $B \rightarrow 0$ , we can Taylor expand

$$\tilde{g}_{\uparrow/\downarrow}(\mathcal{E}) = \frac{1}{2}\tilde{g}(\mathcal{E} \mp \mu_B B) \simeq \frac{1}{2}\tilde{g}(\mathcal{E}) \mp \frac{1}{2}\mu_B B \tilde{g}'(\mathcal{E}) + O(B^2)$$

and truncate at first order.

With this new  $B$ -modified spectrum, at thermal equilibrium the densities of the individual spin types are:

$$n_{\uparrow/\downarrow} = \int_{-\infty}^{\infty} \tilde{g}_{\uparrow/\downarrow}(\mathcal{E}) [n_{\mathcal{E}}]_{\text{F}} d\mathcal{E} = \int_{-\infty}^{\infty} \tilde{g}_{\uparrow/\downarrow}(\mathcal{E}) f_{\text{F}}(\mathcal{E}) d\mathcal{E},$$

where

$$[n_{\mathcal{E}}]_{\text{F}} \equiv f_{\text{F}}(\mathcal{E}) = \frac{1}{e^{\beta(\mathcal{E}-\mu)} + 1}$$

is the Fermi equilibrium occupation distribution.

We substitute the truncated Taylor expansion:

$$\begin{aligned} n_{\uparrow/\downarrow} &= \int_{-\infty}^{\infty} \tilde{g}_{\uparrow/\downarrow}(\mathcal{E}) f_{\text{F}}(\mathcal{E}) d\mathcal{E} = \frac{1}{2} \int_{-\infty}^{\infty} \tilde{g}(\mathcal{E} \mp \mu_B B) f_{\text{F}}(\mathcal{E}) d\mathcal{E} \\ &\simeq \frac{1}{2} \int_{-\infty}^{\infty} \tilde{g}(\mathcal{E}) f_{\text{F}}(\mathcal{E}) d\mathcal{E} \mp \mu_B B \times \frac{1}{2} \int_{-\infty}^{\infty} \tilde{g}'(\mathcal{E}) f_{\text{F}}(\mathcal{E}) d\mathcal{E}. \end{aligned}$$

The lower integration limits in the last expression can be replaced with 0 because  $\tilde{g}(\mathcal{E}) \equiv 0$  for negative energy.

In this form, it is clear that the total electron density

$$\begin{aligned} n &= n_{\uparrow} + n_{\downarrow} = \frac{1}{2} \int_0^{\infty} \tilde{g}(\mathcal{E}) f_{\text{F}}(\mathcal{E}) d\mathcal{E} + \frac{1}{2} \int_0^{\infty} \tilde{g}(\mathcal{E}) f_{\text{F}}(\mathcal{E}) d\mathcal{E} \\ &= \int_0^{\infty} \tilde{g}(\mathcal{E}) f_{\text{F}}(\mathcal{E}) d\mathcal{E}. \end{aligned}$$

The terms linear in  $B$  cancel out, and the total number of electrons remains unaffected by the magnetic field.

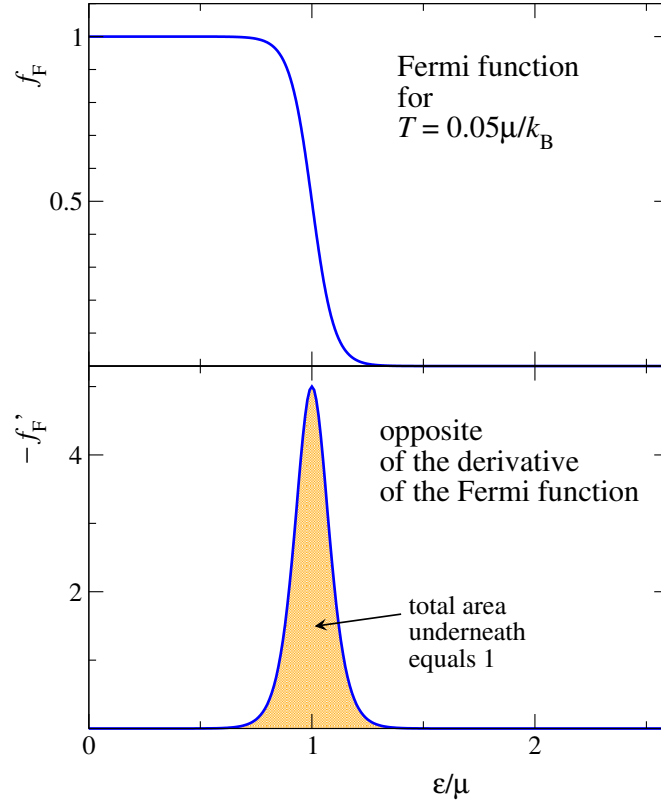
More to the point of this problem,

$$\begin{aligned} \mathcal{M}_z &= \mu_B (n_{\downarrow} - n_{\uparrow}) = \mu_B \times \left[ \frac{1}{2} \mu_B B \int_0^{\infty} \tilde{g}'(\mathcal{E}) f_{\text{F}}(\mathcal{E}) d\mathcal{E} + \frac{1}{2} \mu_B B \int_0^{\infty} \tilde{g}'(\mathcal{E}) f_{\text{F}}(\mathcal{E}) d\mathcal{E} \right] \\ &= \mu_B^2 B \int_0^{\infty} \tilde{g}'(\mathcal{E}) f_{\text{F}}(\mathcal{E}) d\mathcal{E}. \end{aligned}$$

This integration is conveniently carried out by parts:

$$\mathcal{M}_z = \mu_B^2 B \int_0^{\infty} \tilde{g}(\mathcal{E}) \left( -\frac{df_{\text{F}}}{d\mathcal{E}} \right) d\mathcal{E}.$$

The properties of the opposite of the slope of the Fermi function are clarified in the following plot:



This plot involves the rather large temperature  $T = 0.05 \mu/k_B$ . For more realistic temperatures  $T \lesssim 0.01 \mu/k_B$  the function  $-f'_F(\mathcal{E})$  turns into a very sharp peak, and approaches a Dirac-delta distribution centered at the chemical potential. Given that the density of states  $\tilde{g}(\mathcal{E})$  is a smooth function, we make a negligible error if we approximate

$$\mathcal{M}_z \simeq \mu_B^2 B \int_0^\infty \tilde{g}(\mathcal{E}) \delta(\mathcal{E} - \mu) d\mathcal{E} = \mu_B^2 B \tilde{g}(\mu) \simeq \mu_B^2 B \tilde{g}(\epsilon_F).$$

The last approximation relies on the low-temperature (Sommerfeld) expansion for the chemical potential:

$$\mu = \epsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 + \dots \right],$$

which at ordinary temperatures for ordinary metals is practically identical to  $\epsilon_F$ .

From the obtained linear-in- $B$  magnetization, one obtains a magnetic (Pauli) susceptibility

$$\chi_B = \frac{\mathcal{M}_z}{B_z} = \mu_B^2 \tilde{g}(\epsilon_F).$$

This remarkably  $T$ -independent result holds for not-too-high temperature, and for arbitrary density of states (in band metal the density of states will differ from that of free electrons, but this result will still hold!).

This equation links the magnetic susceptibility with the density of states (per unit volume) at the Fermi level.

Recall the result of Eq. (6):

$$g(\epsilon_F) = \frac{3N}{2\epsilon_F},$$

implying

$$\tilde{g}(\epsilon_F) = \frac{3}{2} \frac{N}{V} \frac{1}{\epsilon_F} = \frac{3}{2} \frac{n}{\epsilon_F}.$$

Therefore for the free-electron gas the magnetic susceptibility

$$\chi_B = \mu_B^2 \tilde{g}(\epsilon_F) = \frac{3}{2} \mu_B^2 \frac{n}{\epsilon_F}.$$

The Fermi energy

$$\epsilon_F = \frac{\hbar^2}{2m_e} k_F^2 = \frac{\hbar^2}{2m_e} (3\pi^2 n)^{2/3}.$$

depends on the density as  $\propto n^{2/3}$ , which means that  $\chi_B \propto n^{1/3} \propto k_F$ . This dependence indicates that just a small fraction of the electrons participate to magnetization, with most of them Pauli-principle spin-paired.

For sodium,

$$\frac{N_{\text{at}}}{V} = \frac{\rho}{M_{1 \text{ atom}}} = \frac{968 \text{ kg m}^{-3}}{23 \text{ a.m.u.}} = 2.53 \times 10^{28} \text{ m}^{-3} = \frac{N_{\text{el}}}{V} = n,$$

whence

$$\epsilon_F = 5.04 \times 10^{-19} \text{ J} = 3.146 \text{ eV},$$

and

$$\tilde{g}(\epsilon_F) = \frac{3}{2} \frac{n}{\epsilon_F} = \frac{3}{2} \frac{2.53 \times 10^{28} \text{ m}^{-3}}{5.04 \times 10^{-19} \text{ J}} = 7.542 \times 10^{46} \text{ J}^{-1} \text{ m}^{-3}.$$

The resulting numeric value of the paramagnetic susceptibility is

$$\begin{aligned} \chi_B &= \mu_B^2 \tilde{g}(\epsilon_F) = (9.274 \times 10^{-24} \text{ A m}^2)^2 \times \tilde{g}(\epsilon_F) \\ &= 8.601 \times 10^{-47} \text{ A}^2 \text{ m}^4 \times 7.542 \times 10^{46} \text{ J}^{-1} \text{ m}^{-3} = 6.4865 \text{ A}^2 \text{ J}^{-1} \text{ m} \\ &= 6.4865 \text{ A}^2 \text{ N}^{-1}. \end{aligned}$$

In practice it is more common to measure the susceptibility  $\chi_m$  relative to the *external* applied field  $\vec{H} = \epsilon_0 c^2 \vec{B}_{\text{ext}}$  (the field produced by the external currents, unrelated to the sample magnetization). The relation between  $\chi_B$  and  $\chi_m$  derives from

$$\vec{\mathcal{M}} = \chi_B \vec{B} = \chi_B \left[ \vec{B}_{\text{ext}} + \vec{B}_{\text{int}} \right] = \chi_B \left[ (\epsilon_0 c^2)^{-1} \vec{H} + (\epsilon_0 c^2)^{-1} \vec{\mathcal{M}} \right], \quad (9)$$

where we use the relation  $\vec{B}_{\text{int}} = (\epsilon_0 c^2)^{-1} \vec{\mathcal{M}}$  for the magnetic field generated by the magnetization of a uniformly magnetized material. The quantity  $(\epsilon_0 c^2)^{-1}$ , often indicated as

$$\mu_0 = (\epsilon_0 c^2)^{-1} = 1.256637 \times 10^{-6} \text{ N A}^{-2},$$

has the same physical dimensions as  $\chi_B^{-1}$ . Accordingly, the units of  $\vec{H}$  and those of  $\vec{\mathcal{M}}$  are the same, namely A/m.

We solve Eq. (9) for  $\vec{\mathcal{M}}$ :

$$\begin{aligned} \vec{\mathcal{M}} - \chi_B (\epsilon_0 c^2)^{-1} \vec{\mathcal{M}} &= \chi_B (\epsilon_0 c^2)^{-1} \vec{H}, \\ \vec{\mathcal{M}} (1 - \chi_B (\epsilon_0 c^2)^{-1}) &= \chi_B (\epsilon_0 c^2)^{-1} \vec{H}, \end{aligned}$$

obtaining

$$\vec{\mathcal{M}} = \frac{(\epsilon_0 c^2)^{-1} \chi_B}{1 - (\epsilon_0 c^2)^{-1} \chi_B} \vec{H}. \quad (10)$$

This equations defines a (dimensionless)  $H$ -susceptibility

$$\chi_m = \frac{(\epsilon_0 c^2)^{-1} \chi_B}{1 - (\epsilon_0 c^2)^{-1} \chi_B}. \quad (11)$$

In this formula for  $\chi_m$  the main ingredient is  $(\epsilon_0 c^2)^{-1} \chi_B$ . As we have calculated above, a typical value of  $\chi_B$  is in the order of a few  $\text{A}^2 \text{N}^{-1}$ . As a result,  $(\epsilon_0 c^2)^{-1} \chi_B \ll 1$ , and the denominator is very close to unity and can therefore be omitted.

As a final simplified result:

$$\chi_m \simeq (\epsilon_0 c^2)^{-1} \chi_B.$$

Its numerical value for sodium is obtained by substituting the value of  $\chi_B$  calculated above:

$$\chi_m = (\epsilon_0 c^2)^{-1} \chi_B = 1.256637 \times 10^{-6} \frac{\text{N}}{\text{A}^2} \times 6.4865 \frac{\text{A}^2}{\text{N}} = 8.15120 \times 10^{-6}.$$

This result solves the problem in full.

For the free electron gas, we can optionally estimate the expected order of magnitude of

$$\chi_m = (\epsilon_0 c^2)^{-1} \chi_B = (\epsilon_0 c^2)^{-1} \frac{3}{2} \mu_B^2 \frac{n}{\epsilon_F} = \frac{\mu_B^2}{\epsilon_0 c^2} \frac{3}{2} \frac{n}{\epsilon_F}.$$

The factor  $n/\epsilon_F$  has dimension of the inverse of (energy  $\times$  volume). As a consequence, the first fraction  $\mu_B^2/(\epsilon_0 c^2)$  must necessarily have dimensions of (energy  $\times$  volume). We should therefore be able to express the universal constant  $\mu_B^2/(\epsilon_0 c^2)$  in natural ‘‘atomic’’ units of  $E_{\text{Ha}} \times a_0^3$ .

To do so, recall that the fine-structure constant  $\alpha = e^2/(\hbar c)$ , which implies that  $c^2 = e^4/(\hbar^2 \alpha^2)$ , where  $e^2 \equiv q_e^2/(4\pi\epsilon_0)$ .

Recall also the definition of the Bohr magneton

$$\mu_B = \frac{\hbar q_e}{2m_e}.$$

Let us substitute and reorganize:

$$\begin{aligned} \frac{\mu_B^2}{\epsilon_0 c^2} &= \frac{\left(\frac{\hbar q_e}{2m_e}\right)^2}{\epsilon_0 \frac{e^4}{\hbar^2 \alpha^2}} = \frac{\left(\frac{\hbar q_e}{2m_e}\right)^2}{\epsilon_0} \frac{\hbar^2 \alpha^2}{e^4} = \frac{\hbar^2}{m_e^2} \frac{\left(\frac{q_e}{2}\right)^2}{\epsilon_0} \frac{\hbar^2 \alpha^2}{e^4} = \frac{\hbar^2}{m_e^2} \frac{q_e^2}{4\epsilon_0} \frac{\hbar^2 \alpha^2}{e^4} \\ &= \frac{\hbar^2}{m_e^2} \pi \frac{q_e^2}{4\pi\epsilon_0} \frac{\hbar^2 \alpha^2}{e^4} = \pi \frac{\hbar^2}{m_e^2} e^2 \frac{\hbar^2 \alpha^2}{e^4} = \pi \frac{\hbar^2}{m_e^2} \frac{\hbar^2 \alpha^2}{e^2} = \pi \frac{\hbar^4}{m_e^2 e^2} \alpha^2. \end{aligned}$$

The fraction factor in this formula is nothing but the natural ‘‘atomic’’ units of (energy  $\times$  volume):

$$E_{\text{Ha}} \times a_0^3 = \frac{e^2}{a_0} \times a_0^3 = e^2 a_0^2 = e^2 \left(\frac{\hbar^2}{m_e e^2}\right)^2 = \frac{\hbar^4}{m_e^2 e^2}.$$

The desired expression is then:

$$\frac{\mu_B^2}{\epsilon_0 c^2} = \pi \alpha^2 E_{\text{Ha}} a_0^3.$$

Using these observations, we can express  $\chi_m$  of the Fermi gas in terms of dimensionless ratios:

$$\begin{aligned}\chi_m &= \frac{\mu_B^2}{\epsilon_0 c^2} \frac{3}{2} \frac{n}{\epsilon_F} = \pi \alpha^2 E_{\text{Ha}} a_0^3 \times \frac{3}{2} \frac{n}{\epsilon_F} = \frac{3\pi}{2} \alpha^2 E_{\text{Ha}} a_0^3 \times \frac{n}{\epsilon_F} \\ &= \frac{3\pi}{2} \alpha^2 \times \frac{n a_0^3}{\epsilon_F/E_{\text{Ha}}}.\end{aligned}$$

Recalling the value  $\alpha = 0.007297$ , the first universal dimensionless factor  $\frac{3\pi}{2} \alpha^2 = 2.5094 \times 10^{-4}$ .

The second factor (namely the fraction) depends on the material through its electron density.

For the electron gases of ordinary metals, the density multiplied by  $a_0^3$  is of the order of 0.003–0.03. For sodium, we have a numerator  $n a_0^3 = 0.00376$ .

For these same densities, the Fermi energy ranges between 0.1–0.5 in units of  $E_{\text{Ha}}$ . For sodium, the denominator  $\epsilon_F/E_{\text{Ha}} = 0.1156$ .

Typically the fraction  $n a_0^3/(\epsilon_F/E_{\text{Ha}}) \approx 0.1$ . For sodium, this material-dependent fraction is 0.03248.

As a result the order of magnitude of is  $\chi_m \approx 10^{-5}$ , in accord with the value evaluated for sodium above.

This formulation is quite convenient to compare the Fermi-gas susceptibility with that obtained for a high-temperature gas of spin-1/2 atoms:

$$\chi_m \simeq (\epsilon_0 c^2)^{-1} \chi_B = (\epsilon_0 c^2)^{-1} \frac{N_{\text{at}}}{V} \frac{\mu_B^2}{k_B T} = \frac{\mu_B^2}{\epsilon_0 c^2} \frac{N_{\text{at}}}{V} \frac{1}{k_B T}.$$

We rewrite the universal constant factor in the same fashion as we did for the Fermi gas:

$$\chi_m = \pi \alpha^2 E_{\text{Ha}} a_0^3 \frac{N_{\text{at}}}{V} \frac{1}{k_B T} = \pi \alpha^2 \frac{\frac{N_{\text{at}}}{V} a_0^3}{k_B T/E_{\text{Ha}}}.$$

The number density multiplied by  $a_0^3$  is typically quite small. For example, an ideal gas at room conditions  $T = 300$  K and 1 bar =  $10^5$  Pa has

$$\frac{N_{\text{at}}}{V} = \frac{P}{k_B T} = 2.414 \times 10^{25} \text{ m}^{-3} = 3.5777 \times 10^{-6} a_0^{-3}$$

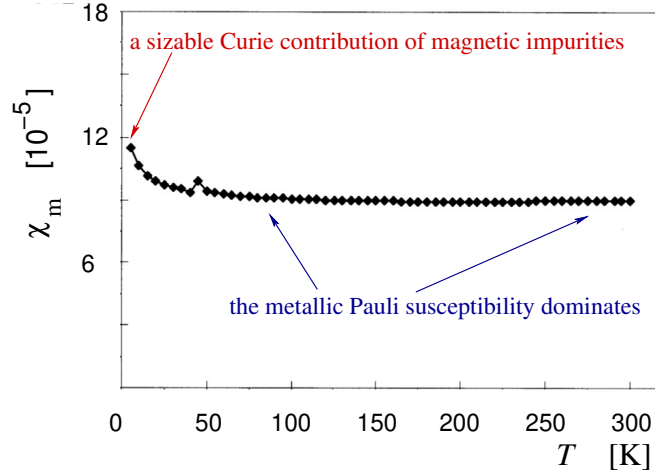
The energy ratio at the denominator is  $k_B T/E_{\text{Ha}} = 9.5004 \times 10^{-4}$ : far smaller than the corresponding quantity  $\epsilon_F/E_{\text{Ha}}$  for the electron gas, but still far larger than the density expressed in atomic units.

At room temperature, the resulting (Curie) susceptibility

$$\chi_m(T = 300 \text{ K}) = \pi \alpha^2 \frac{3.5777 \times 10^{-6}}{9.5004 \times 10^{-4}} = 6.300 \times 10^{-7}.$$

is smaller than the Pauli susceptibility of ordinary metals (but this comparison is somewhat unfair due to the far larger density of electrons in metals!).

In solids, at lower temperature, Curie contributions (e.g. due to impurities) tend to prevail.



Coming back to the Fermi gas, since also the Fermi energy is a function of density, it is possible to express  $\chi_m$  purely in terms of  $n$ :

$$\begin{aligned}
 \chi_m &= \frac{\mu_B^2}{\epsilon_0 c^2} \frac{3}{2} \frac{n}{\epsilon_F} = \frac{\mu_B^2}{\epsilon_0 c^2} \frac{3}{2} \frac{n}{\frac{\hbar^2}{2m_e} (3\pi^2 n)^{2/3}} \\
 &= \frac{\mu_B^2}{\epsilon_0 c^2} \frac{3}{2} \frac{2m_e}{\hbar^2} \frac{n}{(3\pi^2 n)^{2/3}} = \frac{\mu_B^2}{\epsilon_0 c^2} \frac{3}{2} \frac{2m_e}{\hbar^2} \frac{(3\pi^2 n)^{1/3}}{3\pi^2} \\
 &= \frac{3}{2} \frac{2}{3\pi^2} \frac{\mu_B^2}{\epsilon_0 c^2} \frac{m_e}{\hbar^2} (3\pi^2 n)^{1/3} = \frac{1}{\pi^2} \pi \frac{\hbar^4}{m_e^2 e^2} \alpha^2 \frac{m_e}{\hbar^2} (3\pi^2 n)^{1/3} \\
 &= \frac{1}{\pi} \frac{\hbar^4}{m_e^2 e^2} \alpha^2 \frac{m_e}{\hbar^2} (3\pi^2 n)^{1/3} \\
 &= \frac{1}{\pi} \frac{\hbar^2}{m_e e^2} \alpha^2 (3\pi^2 n)^{1/3} = \frac{a_0 \alpha^2}{\pi} (3\pi^2 n)^{1/3} \\
 &= \frac{\alpha^2}{\pi} a_0 k_F \\
 &= \alpha^2 a_0 \left( \frac{3}{\pi} n \right)^{1/3}.
 \end{aligned}$$

Of course, the value obtained for sodium with this final formula is the same as the one obtained above:

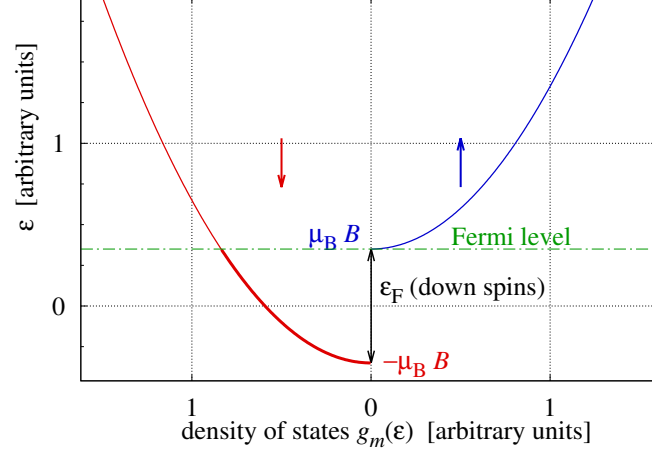
$$\chi_m = \frac{\alpha^2}{\pi} \times a_0 k_F = 1.6950 \times 10^{-5} \times 0.48088 = 8.15120 \times 10^{-6}.$$

## 16 Written test 04/03/2003, problem 3

Si consideri un gas di elettroni a temperatura nulla, e se ne trascuri l'interazione coulombiana. Si valuti la massima densità numerica  $n = N_{el}/V$  (in elettroni/m<sup>3</sup>) per cui *tutti* i momenti magnetici degli elettroni si allineano in un campo magnetico di 5 T.

### 16.1 Solution

The  $T = 0$  Fermi gas is fully polarized whenever the Fermi level strikes through the spin-down band but not the spin-up band.



As illustrated in the figure, the maximum number of electrons compatible with 100% polarization occurs when the Fermi level hits the bottom of the up-spin band.

This condition is expressed by

$$2\mu_B B = \epsilon_F(\text{down spins}).$$

We can obtain an equation for the corresponding maximum electron density, by noting that the spin degeneracy  $g_s$  for spin-down electron equals 1, rather than the usual 2.

$$2\mu_B B = \frac{\hbar^2}{2m_e} \left( \frac{6\pi^2 N_e}{g_s V} \right)^{2/3},$$

$$2\mu_B B = \frac{\hbar^2}{2m_e} \left( 6\pi^2 \frac{N_e}{V} \right)^{2/3},$$

$$2\mu_B B \frac{2m_e}{\hbar^2} = \left( 6\pi^2 \frac{N_e}{V} \right)^{2/3},$$

$$\left( 2\mu_B B \frac{2m_e}{\hbar^2} \right)^{3/2} = 6\pi^2 \frac{N_e}{V},$$

$$\frac{N_e}{V} = \frac{1}{6\pi^2} \left( 4\mu_B B \frac{m_e}{\hbar^2} \right)^{3/2} = \frac{(4m_e\mu_B B)^{3/2}}{6\pi^2 \hbar^3}.$$

Numerically:

$$\begin{aligned} \frac{N_e}{V} &= \frac{(4m_e\mu_B B)^{3/2}}{6\pi^2 \hbar^3} = \frac{(1.6891 \times 10^{-52} \text{ J kg})^{3/2}}{6.945 \times 10^{-101} \text{ J}^3 \text{ s}^3} \\ &= \frac{2.19624 \times 10^{-78} (\text{J kg})^{3/2}}{6.945 \times 10^{-101} \text{ J}^3 \text{ s}^3} = 3.16228 \times 10^{22} \text{ J}^{-3/2} \text{ kg}^{3/2} \text{ s}^{-3} \\ &= 3.16228 \times 10^{22} \text{ kg}^{-3/2} \text{ m}^{-3} \text{ s}^3 \text{ kg}^{3/2} \text{ s}^{-3} \\ &= 3.16228 \times 10^{22} \text{ m}^{-3}. \end{aligned}$$

This is a relatively small density, approximately 5 orders of magnitude smaller than regular conduction-electron densities of common metals.

Such a small value is fully expected, given the smallness of magnetic energies compared to kinetic energies imposed by Pauli's principle.

## 17 Written test 03/11/2003, problem 4

Utilizzando il modello di fermioni non interagenti (spin- $\frac{1}{2}$ ) per  ${}^3\text{He}$  liquido, si stimi la sua pressione ed il suo calore specifico molare alla densità di  $110 \text{ kg/m}^3$  e temperatura di  $0.01 \text{ K}$ .

### 17.1 Solution

Usual technique to evaluate the number density of  ${}^3\text{He}$  atoms:

$$\frac{N}{V} = \frac{\rho}{3 \text{ a.m.u.}} = 2.2081 \times 10^{28} \text{ m}^{-3}.$$

The main thing we need keep in mind here is that the fermions in this Fermi gas are  ${}^3\text{He}$  atoms, not electrons.  ${}^3\text{He}$  atoms have electronic spin  $S = 0$  but nuclear spin  $I = 1/2$ , therefore the spin degeneracy  $g_s = 2$ , the same as for electrons. However, the mass  $M$  in the Fermi gas equations is quite different, and one should not forget to adopt the correct mass!

$$\begin{aligned} \epsilon_F &= \frac{\hbar^2}{2M_{3\text{He}}} k_F^2 = \frac{\hbar^2}{2M_{3\text{He}}} \left( \frac{6\pi^2 N}{g_s V} \right)^{2/3} \\ &= \frac{(1.055 \times 10^{-34} \text{ J s})^2}{2 \times 4.9816 \times 10^{-27} \text{ kg}} (3\pi^2 \times 2.2081 \times 10^{28} \text{ m}^{-3})^{2/3} \\ &= 1.116 \times 10^{-42} \text{ kg m}^4 \text{ s}^{-2} \times (8.6792 \times 10^9 \text{ m}^{-1})^2 \\ &= 8.4084 \times 10^{-23} \text{ J} = 0.52481 \text{ meV}, \end{aligned}$$

corresponding to a Fermi temperature

$$T_F = \frac{\epsilon_F}{k_B} = 6.090 \text{ K}.$$

With the data of this problem,  $T \ll T_F$ .

We are therefore in the degenerate-gas conditions, and we can apply the corresponding formulas:

1.

$$P(T=0) = \frac{2}{5} \frac{N}{V} \epsilon_F = \frac{2}{5} \times 2.2081 \times 10^{28} \text{ m}^{-3} \times 8.4084 \times 10^{-23} \text{ J} = 742671 \text{ Pa}.$$

The multiplicative correction due to thermal effects is

$$1 + \frac{5\pi^2}{12} \left( \frac{T}{T_F} \right)^2 = 1.000011$$

so that the pressure at  $T = 0.01 \text{ K}$  turns out

$$P(T = 0.01 \text{ K}) = 742671 \text{ Pa} \times 1.000011 = 742679 \text{ Pa},$$

almost the same: at such a low temperature, neglecting the thermal correction would not matter.

2.

$$\begin{aligned} C_{V \text{ mol}} &= N_A k_B \frac{\pi^2}{2} \frac{T}{T_F} \\ &= N_A k_B \times \frac{\pi^2}{2} \frac{0.01 \text{ K}}{6.090 \text{ K}} = N_A k_B \times 0.0081029 = 0.067371 \frac{\text{J}}{\text{mol K}}. \end{aligned}$$

## 18 Written test 15/07/2003, problem 5

La densità del rame solido è  $8960 \text{ Kg m}^{-3}$  ed il potenziale di estrazione è  $4.65 \text{ V}$ . Assumendo una banda di conduzione parabolica (elettroni liberi) occupata da un elettrone per atomo, valutare il numero medio di elettroni in un  $\text{mm}^3$  di rame che a  $1300 \text{ K}$  occupano stati ad energia sufficiente ad uscire spontaneamente dal solido con energia cinetica minore di  $10 \text{ meV}$ .

### 18.1 Solution

$$\frac{N_{\text{el}}}{V} = \frac{N_{\text{at}}}{V} = \frac{\rho}{M_{\text{Cu}}} = \frac{8960 \text{ kg m}^{-3}}{63.546 \text{ a.m.u.}} = 8.4912 \times 10^{28} \text{ m}^{-3},$$

$$\begin{aligned} \epsilon_{\text{F}} &= \frac{(1.055 \times 10^{-34} \text{ J s})^2}{2 \times 9.109 \times 10^{-31} \text{ kg}} (3\pi^2 \times 8.4912 \times 10^{28} \text{ m}^{-3})^{2/3} \\ &= 6.104 \times 10^{-39} \text{ kg m}^4 \text{ s}^{-2} \times (1.3598 \times 10^{10} \text{ m}^{-1})^2 \\ &= 1.12865 \times 10^{-18} \text{ J} = 7.04451 \text{ eV}, \end{aligned}$$

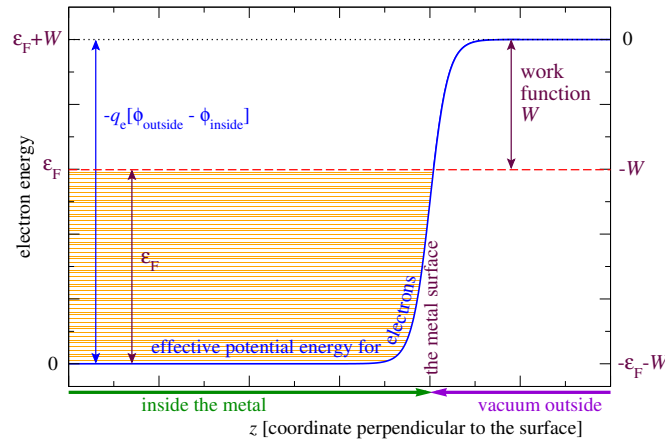
implying

$$T_{\text{F}} = \frac{\epsilon_{\text{F}}}{k_{\text{B}}} = 81748 \text{ K}.$$

At the given temperature, the chemical potential decreases to

$$\begin{aligned} \mu(T) &= \epsilon_{\text{F}} \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_{\text{F}}} \right)^2 \right] = 1.12865 \times 10^{-18} \text{ J} \times 0.999792 \\ &= 1.12842 \times 10^{-18} \text{ J} = 7.04304 \text{ eV}. \end{aligned}$$

Refer to the usual level scheme (extended to finite  $T$ ):



The electrons that the problem refers to are those in states at an energy sitting between  $0$  and  $\delta E = 10 \text{ meV}$  on the scale at the right of this diagram.

In terms of the scale at the left, the relevant energy interval is  $\epsilon_{\text{F}} + W < \mathcal{E} \leq \epsilon_{\text{F}} + W + \delta E$ .

To count these electrons, the scale at the left is more convenient, because in this scale, the total density of free-electron states is

$$g(\mathcal{E}) = g_s g_{\text{tr}}(\mathcal{E}) = \frac{\sqrt{2} m_e^{3/2} V}{\pi^2 \hbar^3} \mathcal{E}^{1/2}.$$

Per unit volume, the requested number of electrons is given by

$$\begin{aligned} \frac{N(\epsilon_F + W < \mathcal{E} \leq \epsilon_F + W + \delta E)}{V} &= \int_{\epsilon_F + W}^{\epsilon_F + W + \delta E} \frac{g(\mathcal{E})}{V} f_F(\mathcal{E}) d\mathcal{E} \\ &= \frac{\sqrt{2} m_e^{3/2}}{\pi^2 \hbar^3} \int_{\epsilon_F + W}^{\epsilon_F + W + \delta E} \mathcal{E}^{1/2} \frac{1}{e^{\beta(\mathcal{E} - \mu)} + 1} d\mathcal{E} \end{aligned}$$

A primitive function for the integrand is not immediately accessible. However, note that  $\mathcal{E} - \mu \geq W$ , and therefore the argument of the exponential  $(\mathcal{E} - \mu)/(k_B T) \geq W/(k_B T) = 41.5$ , and  $e^{41.5} \simeq 10^{18} \gg 1$ . Therefore the 1 at the denominator in the Fermi function can be safely neglected for these states far above the chemical potential.

We can also rewrite the integral in dimensionless form as

$$\begin{aligned} \frac{N(\epsilon_F + W < \mathcal{E} \leq \epsilon_F + W + \delta E)}{V} &\simeq \frac{\sqrt{2} m_e^{3/2}}{\pi^2 \hbar^3} \int_{\epsilon_F + W}^{\epsilon_F + W + \delta E} \frac{\mathcal{E}^{1/2}}{e^{\beta(\mathcal{E} - \mu)}} d\mathcal{E} \\ &= \frac{\sqrt{2} m_e^{3/2}}{\pi^2 \hbar^3} \int_{\beta(\epsilon_F + W)}^{\beta(\epsilon_F + W + \delta E)} e^{\beta\mu - x} \beta^{-1/2} x^{1/2} \beta^{-1} dx \\ &= \frac{\sqrt{2} (m_e k_B T)^{3/2}}{\pi^2 \hbar^3} \int_{\beta(\epsilon_F + W)}^{\beta(\epsilon_F + W + \delta E)} e^{\beta\mu} e^{-x} x^{1/2} dx \\ &= \frac{\sqrt{2} (m_e k_B T)^{3/2} e^{\beta\mu}}{\pi^2 \hbar^3} \int_{\beta(\epsilon_F + W)}^{\beta(\epsilon_F + W + \delta E)} e^{-x} x^{1/2} dx. \end{aligned}$$

Even this integral cannot be written in terms of elementary functions, we can evaluate it approximately by numeric means.

With the paramters of the problem at hand,  $\epsilon_F + W = 1.873667 \times 10^{-18} \text{ J} = 11.695 \text{ eV}$  and  $\epsilon_F + W + \delta = 1.875269 \times 10^{-18} \text{ J} = 11.705 \text{ eV}$ .

The dimensionless integration boundaries are  $x_1 \equiv \beta(\epsilon_F + W) = 104.3917$ ,  $x_2 \equiv \beta(\epsilon_F + W + \delta) = 104.4809$ . The dimensionless integral can be evaluated approximately with the trapezoidal rule to

$$\int_{x_1}^{x_2} e^{-x} x^{1/2} dx \simeq \frac{1}{2} \left( e^{-x_1} x_1^{1/2} + e^{-x_2} x_2^{1/2} \right) (x_2 - x_1) = 4.022 \times 10^{-46}.$$

One can check that by repeting the calculation, but splitting the integral at an intermediate  $x_3 = (x_1 + x_2)/2$ , and summing the two smaller trapezoidal areas one obtains the same value to the reported digits.

The dimensional prefactor

$$\begin{aligned} \frac{\sqrt{2} (m_e k_B T)^{3/2} e^{\beta\mu}}{\pi^2 \hbar^3} &= 2.5542 \times 10^{26} \frac{\text{kg}^{3/2} \text{J}^{3/2}}{\text{J}^3 \text{s}^3} \times e^{\mu/(k_B \times 1300 \text{ K})} \\ &= 5.1453 \times 10^{53} \frac{\text{kg}^{3/2}}{\text{J}^{3/2} \text{s}^3} = 5.1453 \times 10^{53} \frac{\text{kg}^{3/2}}{\text{kg}^{3/2} \text{m}^3 \text{s}^{-3} \text{s}^3} \\ &= 5.1453 \times 10^{53} \text{m}^{-3}. \end{aligned}$$

We multiply this prefactor by the result of the integral and obtain the density of these excited electrons:

$$\begin{aligned} \frac{N(\epsilon_F + W < \mathcal{E} \leq \epsilon_F + W + \delta E)}{V} &= 5.1453 \times 10^{53} \text{m}^{-3} \times 4.022 \times 10^{-46} \\ &= 2.069 \times 10^8 \text{m}^{-3}. \end{aligned}$$

As  $V = 1 \text{ mm}^3 = 10^{-9} \text{ m}^3$ , the requested number of electrons is

$$N(\epsilon_F + W < \mathcal{E} \leq \epsilon_F + W + \delta E) = 0.2069.$$

Even if one had forgotten to take the thermal shift of the chemical potential into account, one would have obtained a quite similar value 0.2097.

These values indicate that, on average, one electron every approximately  $5 \text{ mm}^3$  is ready to leave the copper sample at any time.

This spontaneous thermal emission of electrons out of solids is called thermoelectric effect.

## 19 Written test 24/09/2020, problem 2

Un ipotetico cristallo bidimensionale di potassio abbia reticolo quadrato di lato  $a = 310 \text{ pm}$ . Nello spazio  $(k_x, k_y)$  dei vettori d'onda, si disegni la prima zona di Brillouin (1BZ) e se ne descrivano la forma e le dimensioni in non più di 10 parole. Gli elettroni di conduzione si muovono seguendo la legge di dispersione:

$$\varepsilon(k_x, k_y) = -A - B [\cos(k_x a) + \cos(k_y a)],$$

dove  $A = 3.9 \text{ eV}$  e  $B = 3.1 \text{ eV}$ , su una scala dove lo 0 di energia è all'infinito lontano dal cristallo. All'interno della 1BZ si disegni la linea equienergia  $\varepsilon(k_x, k_y) = -A$ . Valutando la frazione di area della 1BZ corrispondente a stati con  $\varepsilon(k_x, k_y) \leq -A$ , si dimostri che proprio le soluzioni di  $\varepsilon(k_x, k_y) = -A$  costituiscono la superficie – in questo caso linea – di Fermi. Da questa osservazione si deduca il valore della funzione lavoro di questo ipotetico cristallo. [Si ricorda che  $\cos(-\alpha) = \cos(\alpha)$  e che  $\arccos(-u) = \pi - \arccos(u)$ .]

### 19.1 Solution

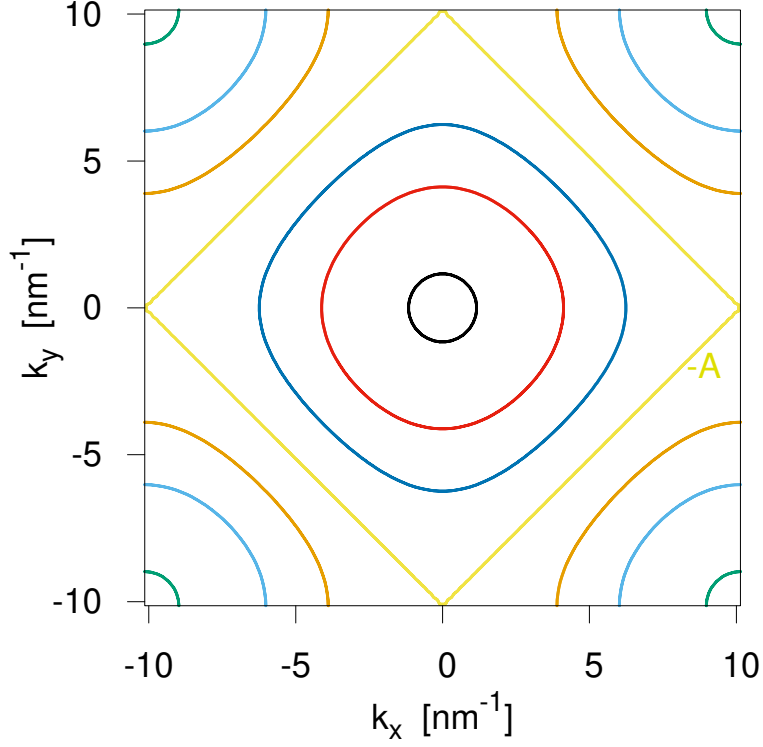
The 1BZ is clearly a square of side  $2\pi/a$ , centered around  $\vec{k} = \vec{0}$ .

In other terms

$$-\frac{\pi}{a} < k_{x/y} \leq \frac{\pi}{a}.$$

Here, for the first time, we encounter an energy dispersion which does not depend on  $|\vec{k}|$  only: the energy depends explicitly on the direction of  $\vec{k}$ .

In the following plot, we report the contour levels of this dispersion at 2 eV energy intervals, including the value  $-A$  (yellow level):



The contour level at energy  $-A$  is especially simple, because it solves

$$\varepsilon(k_x, k_y) = -A - B [\cos(k_x a) + \cos(k_y a)] = -A,$$

i.e.

$$-B [\cos(k_x a) + \cos(k_y a)] = 0,$$

namely

$$\cos(k_x a) + \cos(k_y a) = 0,$$

or

$$\cos(k_x a) = -\cos(k_y a).$$

Cosines of different angles are mutually opposite

$$\cos(\alpha) = -\cos(\beta),$$

for

$$|\alpha| = \pi \pm \beta + n2\pi,$$

where  $n$  is an arbitrary integer. This solution generates angles  $\alpha$  of both signs, because cosine is an even function.

In terms of  $k_{x/y}$  in the 1BZ this translates into:

$$k_y = \frac{\pi}{a} \pm k_x,$$

and

$$k_y = -\frac{\pi}{a} \pm k_x.$$

This accounts for the yellow square in figure.

Potassium has a density of 1 conduction electron per atom, i.e. 1 electron per cell.

For a  $N_x \times N_y$  macroscopically repeated crystal, the allowed  $\vec{k}$  points are

$$k_{x/y} = \frac{n_{x/y}}{N_{x/y}} \frac{2\pi}{a}.$$

The number of these  $\vec{k}$  points is  $N_x \times N_y$  inside the 1BZ.

The number of electrons is also  $N_x \times N_y$ . Therefore, one half of the  $\vec{k}$  points has to be filled with 2 electrons, and consequently the remaining half remains empty.

As the area inside the yellow square is indeed 50% of the area of the 1BZ, this proves that the yellow square is the Fermi “surface” (or rather line) separating filled (inside) from empty (outside) states.

As a result the work function

$$W = A = 3.9 \text{ eV}.$$