

## Thermodynamic behaviour of an ideal Fermi gas

The properties of an ideal Fermi gas are strongly determined by the Pauli principle.

We shall consider the limit:

$$k_B T \ll \mu, \quad \beta \mu \gg 1$$

which defines the *degenerate Fermi gas*. In this limit, the quantum mechanical nature of the system becomes especially important, and the system has little to do with the classical ideal gas.

Since this chapter is devoted to fermions, we shall omit in the following the subscript (–) that we used for the fermionic statistical quantities in the previous chapter.

### Equation of state

Consider a gas of  $N$  non-interacting fermions, e.g., electrons, whose one-particle wave-functions  $\varphi_r(\vec{r})$  are plane-waves. In this case, a complete set of quantum numbers  $r$  is given, for instance, by the three cartesian components of the wave vector  $\vec{k}$  and the  $z$  spin projection  $m_s$  of an electron:

$$r \equiv (k_x, k_y, k_z, m_s)$$

### Spin independent Hamiltonians

We will consider only spin independent Hamiltonian operator of the type

$$\hat{H} = \sum_k \epsilon_k C_k^\dagger C_k + \int d^3r V(r) C_r^\dagger C_r$$

where the first and the second terms are respectively the kinetic and the potential energy. The summation over the states  $r$  (whenever it has to be performed) can then be reduced to the summation over states with different wavevector

where the summation over the spin quantum number  $m_s = s, s+1, \dots, s$  has been taken into account by the prefactor  $(2s+1)$ .

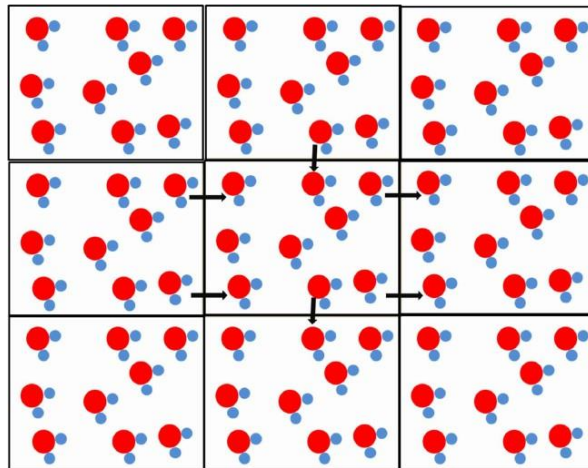
### Wavefunctions in a box. We

assume that the electrons are in a volume defined by a cube with sides  $L_x, L_y, L_z$  and volume  $V = L_x L_y L_z$ . For the one-particle wavefunction

$$\langle r | k \rangle = \varphi_k(r)$$

we use periodicity condition, here along the  $x$ -direction, at the cube's walls,

$$e^{ik_x x} = e^{ik_x x + ik_x L_x}$$



which is then translated into a condition for the allowed  $k$ -values:

$$e^{ik_x L_x} = e^{i2\pi n_x} \quad , \quad k_x = \frac{2\pi}{L_x} n_x \quad , \quad n_x \in \mathbb{Z}$$

Analogously for they - and for the  $z$  direction.

**Summation over wavevectors.** Each state has in  $k$ -space an average volume of

$$\Delta k = \frac{(2\pi)^3}{L_x L_y L_z} = \frac{(2\pi)^3}{V} .$$

For large  $V \rightarrow \infty$  we can then replace the sum  $\sum_r$  over all quantum number by

$$\sum_r \rightarrow (2S+1) \frac{1}{\Delta k} \int d^3 k = (2S+1) \frac{V}{(2\pi)^3} \int d^3 k = (2S+1) \frac{V}{(h)^3} \int d^3 p$$

Where  $k = p/\hbar$  has been used.

## Grand canonical potential

We consider now the expression for the fermionic grand canonical potential  $\Omega(T, V, \mu)$

$$\Omega(T, V, \mu) = -k_B T \sum_r \ln [1 + e^{-\beta(\epsilon_r - \mu)}]$$

Using substitution and  $\int d^3 k = 4\pi \int k^2 dk$  we rewrite the grand canonical potential as

$$-\beta\Omega(T,V,\mu) = (2S+1) \frac{V}{(2\pi)^3} 4\pi \int k^2 dk \ln [ 1 + Ze^{-\beta\hbar^2 k^2 / (2m)} ]$$

where we used the usual expressions

for the fugacity  $z$  and for the one-particle dispersion and used an explicit expression for the one-particle energies for free electrons  $\epsilon_k$ .

**Dimensionless variables.** the above Expression is transformed by introducing with

$$X = \hbar k \sqrt{\frac{\beta}{2m}} \quad k^2 dk = \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} x^2 dx$$

a dimensionless variable  $x$ . One obtains

$$-\beta\Omega(T,V,\mu) = (2S+1) \frac{4V}{\sqrt{x}} \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} \int_0^\infty x^2 dx \ln [ 1 + Ze^{-x^2} ]$$

**De Broglie wavelengths.** By making use of the definition of the thermal de Broglie wavelength  $\lambda$ ,

$$\lambda = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$$

We then get

$$-\beta\Omega(T,V,\mu) = \frac{(2S+1)}{\lambda^3} \frac{4V}{\sqrt{\pi}} \int_0^\infty x^2 dx \ln [ 1 + Ze^{-x^2} ]$$

**Term by term integration.** We use the Taylor expansion of the logarithm,

$$\ln(1+y) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{y^n}{n}$$

in order to evaluate the integral

$$\int_0^\infty x^2 dx \ln(1 + ze^{-x^2}) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n} \int_0^\infty dx x^2 e^{-nx^2}$$

$$= \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n} \left( -\frac{d}{dn} \frac{1}{2} \sqrt{\pi} \frac{1}{\sqrt{n}} \right)$$

Term by term. The result is

$$\int_0^{\infty} x^2 dx \ln (1 + ze^{-x^2}) = \frac{\sqrt{\pi}}{4} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{5/2}}$$

**Grand canonical potential.** Defining

$$f_{5/2}(z) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{5/2}} = \frac{4V}{\sqrt{\pi}} \int_0^{\infty} x^2 dx \ln [1 + Ze^{-x^2}]$$

$$\text{We obtain } \beta (T, V, \mu) = \frac{(2s+1)}{\lambda^3} f_{5/2}(z)$$

for the grand canonical potential for an ideal Fermi gas.

**Pressure.** Our result reduces with  $\Omega = -PV$  to

which yields the pressure  $P = P(T, \mu)$ .

**Density**

$$\Omega = -k_B T \ln z = -PV \quad \frac{PV}{k_B T} = \ln z$$

We find

$$\langle \hat{N} \rangle = z \left( \frac{\partial}{\partial z} \ln z \right) = V z \left( \frac{\partial}{\partial z} \frac{PV}{k_B T} \right)$$

for the number of particles  $N$ . The density  $n(T, \mu) = \langle \hat{N} \rangle / V$  then given by

$$n = \frac{\langle \hat{N} \rangle}{V} = \frac{(2s+1)}{\lambda^3(T)} f_{3/2}(z)$$

where we have defined

$$f_{3/2}(z) = z \frac{d}{dz} f_{5/2}(z) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{3/2}}$$

**Thermal equation of state.** As a matter of principle one could solve for the fugacity  $z = z(T, n)$ , which could then be used to substitute the fugacity in for  $T$  and  $n$ , yielding such the thermal equation of state. This procedure can however not be performed in closed form.

**Rewriting the particle density.** The function  $f_{3/2}(z)$  entering the expression for the particle density may be cast into a different form. Helping is here the result for  $P(T, \mu)$ :

$$\frac{PV}{K_B T} = \frac{(2S+1)}{\lambda^3} f_{5/2}(z), \quad f_{5/2}(z) = \frac{\lambda^3}{2S+1} \frac{\ln z}{V} \quad \frac{PV}{K_B T} = \ln z$$

which leads to  $\mu nV = \frac{3}{2}PV + \frac{d}{d\beta} \ln z$

where we have used  $\ln Z/\beta = PV$ .

**Caloric equation of state.** The expression for  $\mu nV = \mu N$  leads to the caloric equation of state

$$U = \frac{3}{2} PV$$

The equation  $U = 3PV/2$  is also valid for the classical ideal gas, but it is not anymore valid for relativistic fermions.

### 13.1 Classical limit

Starting from the general formulas for  $P(T, \mu)$  and for  $n(T, \mu)$ , we first investigate the classical limit (i.e. the non-degenerate Fermi gas), which corresponds to

$$n\lambda^3 \ll 1, \quad z = e^{\beta\mu} \ll 1$$

Under this condition Fermi-Dirac distribution function reduces to Maxwell - Boltzmann distribution

$$\langle \widehat{n}_r \rangle = \frac{1}{z^{-1} e^{\beta\epsilon_r} + 1} \approx z e^{-\beta\epsilon_r}$$

## Degenerated Fermi gas

In the low temperature  $T \rightarrow 0$ , the Fermi distribution function behaves like a stepfunction:

$$n_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} \begin{cases} 0 & \text{if } \epsilon_k > \mu \\ 1 & \text{if } \epsilon_k < \mu \end{cases}$$

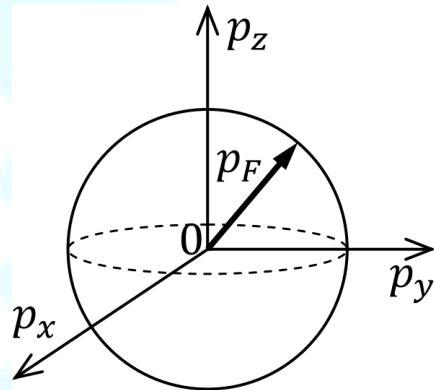
**Fermi energy.** This means that all the states with energy below the Fermi energy  $\epsilon_F$ ,

$$\epsilon_F = \mu(n, T=0),$$

are occupied and all those above are empty.

**Fermi sphere.** In momentum space the occupied states lie within the Fermi sphere of radius  $p_F$ . The system is then deep in the quantum regime.

The Fermi energy is then determined by the condition that the Fermi sphere contains the correct number of states:



$$N = \sum_{\substack{\text{states } r \\ \text{with } \epsilon_r < \epsilon_f}} 1$$

which can be written for the case of free fermions, and with

$$d^3 k / \Delta k^3 = [V / (2\pi)^3] d^3 k, \text{ as}$$

Here,  $k_f = \frac{p_f}{\hbar}$  is the Fermi wave number. We have

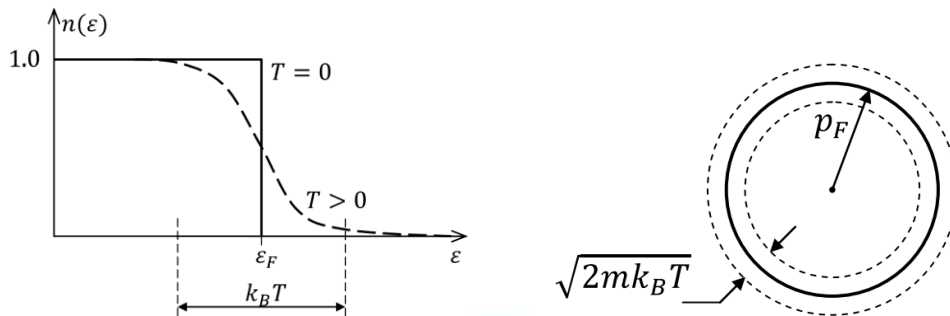
$$n = \frac{N}{V} = \frac{2s+1}{6\pi^2} k_f^3$$

The fermi energy is then

$$\epsilon_f = \frac{\hbar^2 k_f^2}{2m}$$

## Fermi temperature

At low but a finite temperature, the Fermi distribution function  $\langle \hat{n}_r \rangle = n(\epsilon)$  for the occupation number smooths out around the Fermi energy



Such an evolution of  $n(\epsilon)$  with increasing temperature is due to the excitation of fermions within a layer beneath the Fermi surface to a layer above. “Holes” are left beneath the Fermi surface

**Fermi temperature.** We define the *Fermi temperature*  $T_F$  as

$$\epsilon_F = k_B T_F$$

- $T \ll T_f$

For low temperatures  $T \ll T_f$  the Fermi distribution deviates from that at  $T=0$  mainly in the neighborhood of  $\epsilon_F$  in a layer of thickness  $k_B T$ . Particles at energies of order  $k_B T$  below the Fermi energy are excited to energies of order  $k_B T$  above the Fermi energy.

- $T \gg T_F$

The Fermi distribution approaches the Maxwell-Boltzmann distribution. The quantum nature of the constituent particles becomes irrelevant.

**Specific heat.** Since the average excitation energy per particle is  $k_B T$ , the internal energy of the system is of order

$$U = U_0 + \left(\frac{T}{T_f}\right) N k_B T$$

Where  $U_0$  is the ground-state energy. The specific heat capacity  $C_V$  is then of the order of

$$\frac{C_V}{N k_B} \sim \frac{T}{T_f}$$

The electronic contribution to the specific heat vanishes linearly with  $T \rightarrow 0$ . The room-temperature contribution of phonons (lattice vibrations) to  $C_V$  is therefore in general dominant.

## Low temperature expansion

In this section we will derive the scaling relations together with their respective prefactors.

### Density of states

We will work from now on with density of state per volume  $D(E) = \Omega(E)/V$ , which is defined as the derivative of the integrated phase space per volume,

$$\varphi(E) = \Phi(E)/V:$$

$$D(E) = \frac{\partial \varphi(E)}{\partial E}, \quad \varphi(E) = \frac{1}{V} \int \frac{d^3 k}{\Delta k^3}, \quad E = \frac{\hbar^2 k_E^2}{2m}$$

The spin degeneracy factor  $2s+1$  will be added further below.

**Fermi sphere.** With the phase space being isotropic we may write the volume of the Fermi sphere as

$$(V \Delta k^3) \varphi(E) = \frac{4}{3} \pi k_E^3 = \frac{4\pi}{3} \left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

Introducing the spin degeneracy factor  $2s+1$  we then obtain



$$D(E) = \begin{cases} A\sqrt{E} & \text{if } E \geq 0 \\ 0 & \text{otherwise} \end{cases}$$

$$A = \frac{2s+1}{(2\pi)^2} \left( \frac{2m}{\hbar^2} \right)^{3/2}$$

Since we did not use any special properties of a fermionic system, this expression is also valid for bosons. For both type of systems  $D(E)$  shows a  $\sqrt{E}$  dependence.

### Energy and particle density.

The energy density  $U/V$  is given by

$$\frac{U(T, \mu)}{V} = \int_{-\infty}^{+\infty} dE E n(E) D(E), \quad n(E) = \frac{1}{e^{\beta(E-\mu)} + 1}$$

Where  $n(E)$  is the Fermi distribution as a function of the energy.

**Specific heat.** Assuming a constant density of states  $D(E) \approx D(\epsilon_F)$  close to the Fermi energy  $\epsilon_F$  we find

$$c_V = \frac{C_V}{V} = \frac{1}{V} \frac{\partial U}{\partial T} \quad c_V \approx \frac{\pi^2}{3} (k_B^2 T) D(\epsilon_F)$$

for the intensive specific heat. A trademark of a fermionic gas is that  $c_V$  is linear in the temperature.

The heat capacity per volume saturates however for  $T \rightarrow \infty$ , where it becomes identical with the ideal gas value

$$C_V/V = 3nk_B/2$$

