

Statistical Mechanics Fermions and Bosons

The state of a many-particle system is uniquely specified by the occupancy of single-particle states (free particles are the canonical example but the considerations below work extremely well in many systems with suitable renormalization of the parameters—consider ${}^3\text{He}$ homework problem), the set $|\{n_\alpha\}\rangle$ where α denotes the quantum numbers of a single-particle state such as \vec{k} and m the z -component of the spin and n_α the number of particles in the state. The reason this is possible is, of course, that the particles are indistinguishable and the interchange of particles does not yield a new state. One can define the number operator $\hat{n}_\alpha = a_\alpha^\dagger a_\alpha$ where the creation and annihilation operators obey commutation or anti-commutation relations. The total number of particles and the total energy of the state are given by

$$N = \sum_{\alpha} n_{\alpha} \quad \text{and} \quad E = \sum_{\alpha} n_{\alpha} \epsilon_{\alpha}. \quad (1.1)$$

For fermions $n_\alpha = 0, 1$ while for bosons $n_\alpha = 0, 1, \dots, j, \dots$.

$$\mathcal{Z} = \sum_N e^{N\beta\mu} \sum_{\sum_{\alpha} n_{\alpha} = N} e^{-\beta \sum_{\alpha} \epsilon_{\alpha} n_{\alpha}} = \sum_{\{n_{\alpha}\}} e^{-\beta \sum_{\alpha} (\epsilon_{\alpha} - \mu) n_{\alpha}}. \quad (1.2)$$

In the last equality we just have an unrestricted sum over n_α ; summing with the restriction that the sum is N and then allowing N to vary over all possible values is the same as performing an unconstrained sum over all n_α . Note that you have one sum for each α and therefore we have

$$\mathcal{Z} = \prod_{\alpha} \sum_{n_{\alpha}} e^{-\beta (\epsilon_{\alpha} - \mu) n_{\alpha}}. \quad (1.3)$$

The sum for each α can be done easily and we have for fermions

$$\sum_{n_{\alpha}=0,1} e^{-\beta (\epsilon_{\alpha} - \mu) n_{\alpha}} = 1 + e^{\beta (\mu - \epsilon_{\alpha})}. \quad (1.4)$$

For bosons we have

$$\sum_{n_{\alpha}=0}^{\infty} e^{\beta (\mu - \epsilon_{\alpha}) n_{\alpha}} = \frac{1}{1 - e^{\beta (\mu - \epsilon_{\alpha})}}. \quad (1.5)$$

Thus we obtain

$$\mathcal{Z}_F = \prod_{\alpha} (1 + e^{\beta (\mu - \epsilon_{\alpha})}). \quad (1.6)$$

$$\mathcal{Z}_B = \prod_{\alpha} \frac{1}{1 - e^{\beta (\mu - \epsilon_{\alpha})}}. \quad (1.7)$$

This leads to

$$pV = k_B T \log \mathcal{Z} = \pm \sum_{\alpha} \log (1 \pm e^{\beta (\mu - \epsilon_{\alpha})}). \quad (1.8)$$

In the preceding the upper sign is for fermions and the lower for bosons. Expressing both results compactly is done in most graduate textbooks.

We can write $\log \mathcal{Z}$ as a sum convert it to an integral and analyze the behavior of thermodynamic functions. The mathematics is non-trivial and we have to develop intuition for the two cases.

The mean occupancy of a given state α can be written down easily by noting that the probability to have n_α particles in that state is proportional to $e^{\beta(\mu - \epsilon_\alpha)n_\alpha}$.

$$\langle n_\alpha \rangle_F = \frac{0 + 1 e^{-\beta(\epsilon_\alpha - \mu)}}{1 + e^{-\beta(\epsilon_\alpha - \mu)}} = \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} - 1} \quad (1.9)$$

Invent notation: $x = e^{-\beta(\epsilon_\alpha - \mu)}$. For fermions the mean number is $\frac{0+1x}{1+x} = \frac{1}{x^{-1}+1}$.

For bosons

$$\langle n_\alpha \rangle_B = \frac{x + 2x^2 + 3x^3 + \dots}{1 + x + x^2 + \dots} = x \frac{\partial}{\partial x} \log(1 + x + x^2 + \dots) = \frac{x}{1 - x} \quad (1.10)$$

This leads to

$$\langle n_\alpha \rangle_B = \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} - 1}. \quad (1.11)$$

Thus we obtain $\boxed{\frac{1}{e^{\beta(\epsilon_\alpha - \mu)} \pm 1}}$.

Thee result for the occupancy is one of the keys to understanding quantum ideal gases.

Clearly for bosons we must have $\epsilon_\alpha > \mu$. **How is the chemical potential determined?** Experiments are done with a given number of particles or density. So we fix the mean density and determine the corresponding chemical potential. If the mean number N is known then we have

$$N = \sum_\alpha \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} \pm 1}. \quad (1.12)$$

This is an implicit relation, one of the reasons the mathematics is messy. μ is determined as a function of T , N/V and of course, the single particle energy spectrum.

Given $\epsilon = \frac{\hbar^2 k^2}{2m}$ we change variables from $\boxed{gV \int \frac{d^3k}{(2\pi)^3}}$ to an integral over ϵ . This is a very important idea. We define for the (energy) density of states, the number of states in the interval ϵ and $\epsilon + d\epsilon$ denoted by $\mathcal{D}(\epsilon)$ and defined by picking out of all the possible k states those that have the required energy

$$\mathcal{D}(\epsilon) = gV \int \frac{d^3k}{(2\pi)^3} \delta(\epsilon - \epsilon(\vec{k})). \quad (1.13)$$

In condensed matter physics $\epsilon(\vec{k})$ can be very complicated, even known only numerically. We will deal with very simple dispersion relations, non-relativistic $\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$, relativistic $\epsilon(\vec{k}) = \sqrt{\hbar^2 k^2 + m^2}$ and the massless case $\epsilon(\vec{k}) = \hbar k c$. The first case, easy to do because of isotropy, yields

$$gV \frac{1}{2\pi^2} \left. \frac{k^2}{\left| \frac{d\epsilon}{dk} \right|} \right|_{k=\sqrt{2m\epsilon}/\hbar} = \frac{gV}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}. \quad (1.14)$$

We will write the various equation in terms of the density of states. You should be very clear about the logic behind the first two equations below and be able to do it.

For compactness write $\mathcal{D}(\epsilon) = DV \sqrt{\epsilon}$ where $D \equiv \frac{g}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2}$.

$$N = \int d\epsilon \mathcal{D}(\epsilon) f_F(\epsilon) = VD \int_0^\infty d\epsilon \epsilon^{1/2} \frac{1}{e^{\beta(\epsilon-\mu)} + 1}. \quad (1.15)$$

$$U = \int d\epsilon \mathcal{D}(\epsilon) f_F(\epsilon) \epsilon = VD \int_0^\infty d\epsilon \epsilon^{3/2} \frac{1}{e^{\beta(\epsilon-\mu)} + 1}. \quad (1.16)$$

we have

$$pV = k_B T V D \int_0^\infty d\epsilon \epsilon^{1/2} \log(1 + e^{-\beta(\epsilon-\mu)}). \quad (1.17)$$

Writing $\epsilon^{1/2} = \frac{2}{3} \frac{d}{d\epsilon} \epsilon^{3/2}$ and integrating by parts we have

$$-\Omega_G = pV = \frac{2}{3} V D \int_0^\infty d\epsilon \epsilon^{3/2} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} = \frac{2}{3} U. \quad (1.18)$$

Zero temperature results

Consider fermions (think electrons) with the non-relativistic dispersion in three dimensions. At zero temperature the system is in its ground state, the lowest energy state. What is the ground state? This many-body state is obtained by filling the levels corresponding to the lowest energies (or $|\vec{k}|$) successively until we have the number of electrons N that we have specified.

The highest occupied k value is denoted by k_F the Fermi wave vector and is determined by counting the number of electrons. This is the highest occupied state and the energy to add or remove an electron is the corresponding energy, the Fermi energy ϵ_F . Clearly, ϵ_F is the zero-temperature chemical potential. We have

$$2 \times \frac{\frac{4\pi}{3} k_F^3}{(2\pi)^3} = \frac{N}{V} \Rightarrow k_F = (3\pi^2 n)^{1/3}. \quad (1.19)$$

We can define the Fermi velocity and the Fermi momentum. The total number of single particle states with energy less than or equal to ϵ is clearly given by

$$N(\epsilon) = \frac{V}{3\pi^2} \left(\frac{2m\epsilon}{\hbar^2} \right)^{3/2} \quad (1.20)$$

Make sure you can justify this. The density of states can be obtained using $\mathcal{D}(\epsilon) = \frac{dN}{d\epsilon}$. Again can you justify this result? A very useful result can be obtained from the above relationship writing

$$\frac{3}{2} \log \epsilon = \log N(\epsilon) \Rightarrow \mathcal{D}(\epsilon) = \frac{3}{2} \frac{N(\epsilon)}{\epsilon} \quad (1.21)$$

Set $\epsilon = \epsilon_F$ in the above relation. Since $N(\epsilon_F)$ is the total number of electrons the density of states (per unit volume) at the Fermi surface is 3/2 times the the total number of electrons divided by the Fermi energy. This is just dimensional analysis and allows one to find an approximate number quickly.

Expressing the density of states per unit volume we have

$$\mathcal{D} = \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{1}{2\pi^2} \sqrt{\epsilon} = 6.812 \times 10^{21} \sqrt{\epsilon(\text{in } eV)} \frac{eV}{\text{cm}^3}. \quad (1.22)$$

Cu has a Fermi energy of $7 eV$, $n = 8.45 \times 10^{22} / \text{cm}^3$, $v_F = 1.57 \times 10^8 \text{ cm/s}$ and a Fermi temperature of $81000 K$.

Note that room temperature is much smaller than T_F and a low-temperature approximation is valid.

Estimate the heat capacity: The key idea is that only electrons in a narrow energy range of $k_B T$ around the Fermi energy participate in the thermodynamics. Justify this with a qualitative argument.

So one uses the result from the classical ideal gas and replace N by N_{eff} the effective number of electrons that participate in the thermodynamics. A crude estimate is $\mathcal{D}(\epsilon_F) \times k_B T$ the number of states per unit energy interval times the width. Should it be twice $k_B T$? Well, they are not all occupied! So

$$U \approx \mathcal{D}(\epsilon_F) k_B T \frac{3}{2} k_B T \Rightarrow C_V \sim 3 \mathcal{D}(\epsilon_F) k_B^2 T \quad (1.23)$$

The exact calculation yields $\frac{\pi^2}{3} \mathcal{D}(\epsilon_F) k_B^2 T$. Pretty close, since $\pi^2/3 = 3.29$.

Na has a spherical Fermi surface *Cs* differs by about 10% and even bivalent *Be* and *Mg* have almost spherical Fermi surfaces but they extend beyond the first Brillouin zone.

One can write the density of states at the Fermi surface as

$$\mathcal{D}(\epsilon_F) = \frac{3}{2} N \frac{2m}{\hbar^2} (3\pi^2 n)^{2/3} \quad (1.24)$$

i.e., is proportional to the mass. It is conventional to write

$$\frac{\gamma_{exp}}{\gamma_{free}} = \frac{m^*}{m} \quad (1.25)$$

For Copper the ratio is around 1.5 and for Calcium 0.8 while some materials have much large effective masses of several hundreds. These are called heavy fermions. Mass renormalization is an important concept.

More useful results. We have

$$\frac{U}{V} = \frac{1}{\pi^2} \int_0^{k_F} dk k^2 \frac{\hbar^2 k^2}{2m} = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m} \quad (1.26)$$

and using $k_F^3 = 3\pi^2 N/V$ we obtain $\frac{U}{N} = \frac{3}{5} \epsilon_F$.

The pressure can be obtained from $p = \frac{2}{3} \frac{U}{V}$ and we have

$$B \equiv \frac{1}{K} = -\frac{1}{V} \frac{\partial P}{\partial V} = \frac{5}{3} p. \quad (1.27)$$

Please do this using the fact that $k_F \propto V^{-1/3}$ and therefore, U/V is proportional to $V^{-5/3}$.

For Copper the contribution of the bulk modulus $63.8 \times 10^{10} \text{ dynes/cm}^2$ while the actual value is 134.3. More than half the resistance to compression comes from the degeneracy pressure.

It is wildly optimistic to apply free electron theory to a metal with Coulomb interactions but amazingly it work well in many cases. Discuss reasons in class qualitatively.

Extra Comments We have used the so-called *independent electron approximation* one neglects the Coulomb repulsion between electrons. Clearly from elementary quantum mechanics such an interaction will lead to decay of single-particle states; they are no longer stationary states (eigenstates of the Hamiltonian). Next quarter we may discuss why this is not fatal!

Free electron approximation: We have also neglected the periodic potential of the ions that are located at the sites of the crystalline lattice. If the electrons obey a single particle Schrödinger equation in the periodic potential of the ions they are called Bloch electrons. Note that our framework in terms of single-particle states continues

to be useful when we include electron- ion interaction. (The density of states will be drastically altered.)

Felix Bloch: “*By straight Fourier analysis I found to my delight that the wave differed from a plane wave of free electron only by a periodic modulation.* ””

Pauli susceptibility

Recall the derivation of the susceptibility of a single spin with moment μ_B in a field H that can assume an up and a down value. We have

$$Z = e^{\beta\mu_B H} + e^{-\beta\mu_B H} \quad (1.28)$$

and the magnetization per spin is

$$M = p_+(\mu_B) + p_-(-\mu_B) = \mu_B \tanh(\beta\mu_B H) \approx \frac{\mu_B^2 H}{k_B T} \quad (1.29)$$

and therefore the susceptibility of N independent spins is given by $\chi_C = \frac{N\mu_B^2}{k_B T}$. The inverse temperature behavior of the susceptibility is known as the *Curie Law*. Usually $k_B T \chi$ is plotted from experimental data. Using our usual arguments about the effective number of free electrons $\mathcal{D}_0(\epsilon_F) \times k_B T$ we obtain the Pauli result $\chi_{pauli} \approx \mu_B^2 \mathcal{D}_0(\epsilon_F)$.

Argue that this contribution is much smaller.

For Lithium the measured result is 2.09/0.81 and can be attributed to interaction effects. This was measured by Slichter and Schumacher.

A more complete derivation is given below:

The up spins have a lower energy and the down spins a higher energy. The density of states becomes

$$\mathcal{D}_{\pm}(\epsilon) = \frac{1}{2} \mathcal{D}_0(\epsilon \mp \mu_B H). \quad (1.30)$$

Draw a figure.

The number of electrons per unit volume is given by

$$n_{\pm} = \int d\epsilon \mathcal{D}_{\pm}(\epsilon) f(\epsilon) \quad (1.31)$$

where f is the Fermi function:

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}. \quad (1.32)$$

The chemical potential is determined and eliminated by fixing the number density of electrons as usual. We can write

$$\mathcal{D} \pm (\epsilon) = \frac{1}{2} (\mathcal{D}_0(\epsilon) \pm (\mu_B H) \mathcal{D}'(\epsilon)) . \quad (1.33)$$

Using

$$n = n_+ + n_- = \int d\epsilon \mathcal{D}_0(\epsilon) f(\epsilon) \quad (1.34)$$

we see that to this order the chemical potential is unaltered. The magnetization (per unit volume) is give by

$$M = \mu_B (n_+ - n_-) = \mu_B^2 H \int d\epsilon \mathcal{D}'_0(\epsilon) f(\epsilon) \quad (1.35)$$

At zero temperature we know that

$$\mathcal{D}'_0(\epsilon) = -\delta'(\epsilon - \epsilon_F) \quad (1.36)$$

and thus integrating by parts we obtain

$$M = \mu_B^2 \mathcal{D}_0(\epsilon_F) H \quad (1.37)$$

and the Pauli susceptibility is $\boxed{\mu_B^2 \mathcal{D}_0(\epsilon_F)}$.