Grand-canonical ensemble

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November 21, 2019

Contents

1 The Grand-canonical ensemble

The key behind second quantization is to remove the restriction that the number of particles is fixed. Instead, the theory is built around the idea of Fock space, where the number of particles is not fixed. This is highly advantageous when dealing with many-body systems. This same idea, when extended to finite temperatures, is what we call the **Grand canonical ensemble**. What we want is to consider some finite temperature density matrix $\rho \sim e^{-\beta H}$ where the number of particles is not fixed, but can fluctuate. However, we cannot let it fluctuate arbitrarily since that would make no physical sense.

Instead, the basic idea of the grand-canonical ensemble is to impose that **the number of particles is only fixed *on average***. That is, we impose that

$$\langle \hat{N} \rangle = N, \tag{1.1}$$

where $\hat{N}$ is the number operator and N is the number of particles in the system. In some systems, the number of particles does indeed fluctuate. This happens, for instance, in chemical solutions: if we look at a certain region of a liquid, the number of molecules there is constantly fluctuating due to molecules moving around from other parts. Of course, in many other systems on the other hand, the number of particles is fixed. However, it turns out that even in these cases, *pretending* it can may still give good answers, provided N is large (the thermodynamic limit). The reason is because, as we will show below, the variance of $\hat{N}$ scales as $\text{var}(\hat{N}) \sim N$ so that

$$\frac{\sqrt{\text{var}(\hat{N})}}{\langle \hat{N} \rangle} \sim \frac{1}{\sqrt{N}}, \tag{1.2}$$

which is thus small when N is large. Hence, when N is large, the grand-canonical ensemble will give accurate answers, even if the number of particles is not actually allowed to fluctuate. This is the idea behind **ensemble equivalence:** we are allowed to use an ensemble where the number of particles fluctuate, even though it actually doesn't, because in the thermodynamic limit the fluctuations are small.

Our focus here will be on a system described within the language of second quantization, with a Hamiltonian $\mathcal{H}$ and a number operator $\hat{N}$. We assume that

$$[\mathcal{H}, \hat{N}] = 0, \tag{1.3}$$

meaning that the number of particles is a conserved quantity. This means that $\mathcal{H}$ and $\hat{N}$ can be simultaneously diagonalized. The eigenvalues of $\hat{N}$ are all possible numbers of particles N. Thus, $\mathcal{H}$ is divided in **sectors** with well defined N; in other words, $\mathcal{H}$ is block diagonal, so there are no terms connecting sectors with different N. The eigenvalues E are thus labeled by two indices $E(N, j)$, where j labels the quantum states within each sector.

Suppose now that the system is in thermal equilibrium with exactly N particles. The corresponding canonical partition function will be

$$Z(N) = \sum_j e^{-\beta E(N,j)}. \tag{1.4}$$

This is a **constrained sum** since we are only summing over that sector that has exactly N particles. This constraint makes it notoriously difficult to compute the sum in practice.

Instead, in the grand-canonical ensemble we allow the number of particles to fluctuate but only fix them on average [Eq. (1.1)]. To summarize what we will learn below, to accomplish this we must introduce a new parameter μ, called the **chemical potential**, so that the grand-canonical equilibrium state is transformed to

$$\rho_{\text{eq}} = \frac{e^{-\beta(\mathcal{H} - \mu\hat{N})}}{Q}, \qquad Q = \text{tr}\, e^{-\beta(\mathcal{H} - \mu\hat{N})}. \qquad (1.5)$$

Here Q is the partition function; I just use a different letter to distinguish it from the canonical partition function Z. As can be seen, the chemical potential enters by shifting the Hamiltonian from

$$\mathcal{H} \to \mathcal{H} - \mu\hat{N}. \qquad (1.6)$$

The logic behind μ is twofold. When the number of particles is allowed to fluctuate, the value of μ is fixed externally (like the temperature). As a consequence the number of particles $\langle\hat{N}\rangle = N(\mu, T)$ is interpreted as a function of μ and T. Conversely, if the number of particles N is fixed, then $\mu = \mu(N, T)$ is to be interpreted as a function of N and T, which is to be determined as the solution of the implicit equation

$$\langle\hat{N}\rangle = \frac{\text{tr}\,(\hat{N} e^{-\beta(\mathcal{H} - \mu\hat{N})})}{\text{tr}\,(e^{-\beta(\mathcal{H} - \mu\hat{N})})} = N. \qquad (1.7)$$

We will explore both scenarios in a second. But before that, we still have to convince ourselves that Eq. (1.5) makes sense.

1.1 Equilibrium minimizes the thermodynamic potential

Max Ent principle for the canonical ensemble

We can make sense of Eq. (1.5) in terms of the **Max Ent** principle. When we first learned about the canonical ensemble, we learned that equilibrium was the state which minimized the free energy. In symbols, we define the free energy $F(\rho)$ associated to an arbitrary state ρ as

$$F(\rho) = \langle H \rangle_\rho - T S(\rho). \qquad (1.8)$$

Out of all states ρ, the one which minimizes $F(\rho)$ is the canonical state

$$\rho_{\text{can}} = \frac{e^{-\beta H}}{Z}. \qquad (1.9)$$

We can prove this by writing

$$F(\rho) = -T \ln Z + T S(\rho \| \rho_{\text{can}}), \qquad (1.10)$$

where $S(\rho \| \sigma) = \text{tr}(\rho \ln \rho - \rho \ln \sigma)$ is the quantum relative entropy. Since $S(\rho \| \sigma) \geq 0$ and $S(\rho \| \sigma) = 0$ iff $\rho = \sigma$, it follows that the smallest value that $F(\rho)$ can achieve is

$$F_{\text{eq}} = -T \ln Z, \qquad (1.11)$$

which occurs when $\rho = \rho_{can}$. The state with the smallest free energy is thus the thermal state (1.9).

Alternatively, we could recast the problem in terms of entropy: we write

$$F_{eq} = -T \ln Z = U_{eq} - T S_{eq}, \tag{1.12}$$

where $U_{eq} = \langle H \rangle_{th}$ and $S_{eq} = S(\rho_{can})$ are the equilibrium energies and entropies. Using this together with Eq. (1.8), we can rearrange Eq. (1.10) to read

$$S(\rho) = S_{eq} + \beta[\langle H \rangle_\rho - U_{eq}] - S(\rho \| \rho_{can}). \tag{1.13}$$

This is an identity comparing the entropy of any quantum state ρ with the entropy of the equilibrium state (1.9). Consider now the following question: *out of all states ρ having $\langle H \rangle_\rho = U_{eq}$, which has the highest entropy?* Eq. (1.13) makes the answer to this question transparent: If $\langle H \rangle_\rho = U_{eq}$ then second term vanishes. Since the first term is independent of ρ, to make $S(\rho)$ as large as possible we must minimize the second term. The minimum is thus achieved when $\rho = \rho_{can}$.

Max Ent principle for the grand-canonical ensemble

The logic we just used can now be extended to the grand-canonical ensemble. After all, if the principle works for the canonical ensemble (and we know it does because it matches experiment), then it must also work for the grand-canonical ensemble. To impose the condition (1.1), we ask

> *Out of all states ρ with fixed $\langle \mathcal{H} \rangle_\rho = U$ and $\langle \hat{N} \rangle_\rho = N$, which has the highest entropy?*

It is easy to address this question using the result from the canonical ensemble. For, as we saw in (1.6), all we need to do is replace $\mathcal{H}$ with $\mathcal{H} - \mu \hat{N}$. Eq. (1.13) then becomes

$$S(\rho) = S_{th} + \beta(\langle \mathcal{H} \rangle_\rho - U) + \beta\mu(\langle \hat{N} \rangle - N) - S(\rho \| \rho_{eq}), \tag{1.14}$$

where the relative entropy is now between the state ρ and the grand-canonical state (1.5). With this formula, we are then able to conclude that the state (1.5) is the state with the highest possible entropy, given that $\langle \mathcal{H} \rangle_\rho = U$ and $\langle \hat{N} \rangle_\rho = N$.

The thermodynamic potential

Just like we went back and forth between free energy and entropy in the case of the canonical ensemble, in the case of the grand-canonical ensemble we can move between entropy and a new thermodynamic quantity, called **thermodynamic potential** (I guess at this point people ran out of creativity for naming it). It is defined as

$$\Phi(\rho) = \langle \mathcal{H} \rangle_\rho - \mu \langle \hat{N} \rangle_\rho - T S(\rho). \tag{1.15}$$

Rearranging (1.14) we get

$$\Phi(\rho) = \Phi_{eq} + T S(\rho \| \rho_{eq}), \tag{1.16}$$

where

$$\Phi_{eq} = U_{eq} - \mu N_{eq} - T S_{eq}.$$

Eq. (1.16) allows us to conclude that the grand-canonical state (1.5) is the state minimizes the thermodynamic potential.

From now on, since we will be mostly interested in equilibrium states, I will simplify the notation and write only

$$\Phi = U - \mu N - TS, \tag{1.17}$$

where it is now implied that all quantities refer to equilibrium at the state (1.5). We can also express Eq. (1.17) more simply as

$$\Phi_{\text{eq}} = -T \ln Q. \tag{1.18}$$

This is the grand-canonical analog of $F_{\text{eq}} = -T \ln Z$. In fact, if we set $\mu = 0$ we recover exactly the canonical ensemble.

If we write the eigenvalues of the Hamiltonian as $E(N, j)$, as in Eq. (1.4), then the grand-canonical partition function Q in Eq. (1.5) can be written more explicitly as

$$Q = \sum_{N,j} e^{-\beta(E(N,j)-\mu N)}.$$

We can now factor out this sum as

$$Q = \sum_{N} e^{-\beta \mu N} \sum_{j} e^{-\beta E(N,j)}.$$

The sum in j is now exactly the canonical partition function $Z(N)$ in Eq. (1.4). This therefore provides us with a link between the canonical and grand-canonical partition functions:

$$Q = \sum_{N} z^N Z(N), \qquad z = e^{-\beta \mu}, \tag{1.19}$$

where z is called the **fugacity** (a name due to historical reasons). We therefore see that $Z(N)$ is obtained from a **series expansion** of Q as a function of z. Mathematically, this transformation between $Z(N)$ and Q is called the **Z transform**; it is the discrete version of the Laplace transform.

1.2   Non-interacting Hamiltonians

We saw when we studied second quantization, that non-interacting Hamiltonians could always be written as

$$\mathcal{H} = \sum_{\alpha} \varepsilon_\alpha a_\alpha^\dagger a_\alpha, \tag{1.20}$$

where α is a set of single-particle states and the operators a_α can be either bosonic or fermionic. The number operator may be similarly written as

$$\hat{N} = \sum_{\alpha} a_\alpha^\dagger a_\alpha. \tag{1.21}$$

Thus, the grand-canonical state (1.5) becomes

$$\rho_{\text{eq}} = \frac{1}{Q} \exp\left\{ -\beta \sum_{\alpha} (\varepsilon_\alpha - \mu) a_\alpha^\dagger a_\alpha \right\}. \tag{1.22}$$

5

To compute the partition function we notice that $a_\alpha^\dagger a_\alpha$ commutes with $a_{\alpha'}^\dagger a_{\alpha'}$ for any α, α'. As a consequence, we may write

$$Q = \prod_\alpha \operatorname{tr} e^{-\beta(\varepsilon_\alpha - \mu) a_\alpha^\dagger a_\alpha}. \tag{1.23}$$

Each product can be computed independently.

For Fermions these traces generically look like

$$\operatorname{tr} e^{-\lambda a^\dagger a} = \sum_{n=0,1} e^{-\lambda n} = 1 + e^{-\lambda}, \tag{1.24}$$

where λ is any parameter. Whence,

$$Q = \prod_\alpha \left(1 + e^{-\beta(\varepsilon_\alpha - \mu)}\right), \qquad \text{(Fermions)}. \tag{1.25}$$

Conversely, for Bosons we get

$$\operatorname{tr} e^{-\lambda a^\dagger a} = \sum_{n=0}^{\infty} e^{-\lambda n} = \frac{1}{1 - e^{-\lambda}}, \tag{1.26}$$

and hence

$$Q = \prod_\alpha \left(\frac{1}{1 - e^{-\beta(\varepsilon_\alpha - \mu)}}\right), \qquad \text{(Bosons)}. \tag{1.27}$$

Occupation number

The average number of particles in state $|\alpha\rangle$ is defined as

$$\langle \hat{n}_\alpha \rangle = \operatorname{tr}\{\hat{n}_\alpha \rho_{\text{eq}}\}, \tag{1.28}$$

where $\hat{n}_\alpha = a_\alpha^\dagger a_\alpha$ is the corresponding number operator for this state. Opening this up we get

$$\langle \hat{n}_\alpha \rangle = \frac{\prod_{\alpha'} \operatorname{tr}\left(\hat{n}_\alpha e^{-\beta(\varepsilon_{\alpha'} - \mu)\hat{n}_{\alpha'}}\right)}{\prod_{\alpha'} \operatorname{tr}\left(e^{-\beta(\varepsilon_{\alpha'} - \mu)\hat{n}_{\alpha'}}\right)}.$$

Out of the product of all α', the only one which will not cancel with a corresponding term in the denominator will be that with $\alpha' = \alpha$. Whence

$$\langle \hat{n}_\alpha \rangle = \frac{\operatorname{tr}\left(\hat{n}_\alpha e^{-\beta(\varepsilon_\alpha - \mu)\hat{n}_\alpha}\right)}{\operatorname{tr}\left(e^{-\beta(\varepsilon_\alpha - \mu)\hat{n}_\alpha}\right)}.$$

For Fermions we get

$$\operatorname{tr}\left(\hat{n} e^{-\lambda \hat{n}}\right) = 0 + e^{-\lambda} = e^{-\lambda}.$$

Combining this with Eq. (1.24) leads to the **Fermi-Dirac distribution**

$$\langle \hat{n}_\alpha \rangle = \frac{1}{e^{\beta(\varepsilon_\alpha - \mu)} + 1}, \qquad \text{(Fermions)}.$$

Conversely, **for Bosons** we get

$$\operatorname{tr}\left(\hat{n}e^{-\lambda\hat{n}}\right) = \sum_{n=0}^{\infty} ne^{-\lambda n} = \frac{e^{-\lambda}}{(e^{-\lambda}-1)^2}.$$

Combining this with Eq. (1.26) yields the **Bose-Einstein distribution**

$$\langle\hat{n}_\alpha\rangle = \frac{1}{e^{\beta(\varepsilon_\alpha-\mu)}-1}, \qquad \text{(Bosons)}.$$

To summarize, in the case of **non-interacting Fermions** the thermodynamic potential $\Phi = -T\ln Q$ reads

$$\Phi = -T\sum_\alpha \ln\left(1 + e^{-\beta(\varepsilon_\alpha-\mu)}\right), \tag{1.29}$$

and the average occupation number of each state α is given by the **Fermi-Dirac distribution**

$$\langle\hat{n}_\alpha\rangle = \frac{1}{e^{\beta(\varepsilon_\alpha-\mu)}+1}. \tag{1.30}$$

Conversely, in the case of **non-interacting Bosons** we get

$$\Phi = T\sum_\alpha \ln\left(1 - e^{-\beta(\varepsilon_\alpha-\mu)}\right), \tag{1.31}$$

and the **Bose-Einstein distribution**

$$\langle\hat{n}_\alpha\rangle = \frac{1}{e^{\beta(\varepsilon_\alpha-\mu)}-1}. \tag{1.32}$$

In the case of Fermions, the value of μ can in principle be arbitrary. But for Bosons, we could have $\langle\hat{n}_\alpha\rangle < 0$, which is of course unphysical. The condition for this not to happen is to have $\mu < \varepsilon_\alpha$ for all α; or,

$$\mu < \min(\varepsilon_\alpha), \qquad \text{for Bosons}. \tag{1.33}$$

This restriction on μ in the case of Bosons has dramatic consequences, being at the core of Bose-Einstein condensation. We will study this in detail later on.

1.3 Fluctuations

Consider the thermodynamic potential $\Phi = -T\ln\operatorname{tr} e^{-\beta(\mathcal{H}-\mu\hat{N})}$. Differentiating with respect to μ, we get

$$-\frac{\partial\Phi}{\partial\mu} = \frac{\operatorname{tr}\left(\hat{N}e^{-\beta(\mathcal{H}-\mu\hat{N})}\right)}{\operatorname{tr}\left(e^{-\beta(\mathcal{H}-\mu\hat{N})}\right)}. \tag{1.34}$$

Thus we conclude that

$$\boxed{\langle\hat{N}\rangle = -\frac{\partial\Phi}{\partial\mu}} \tag{1.35}$$

This result is general, holding even in the presence of interactions. As a sanity check, differentiating Eqs. (1.29) or (1.31) with respect to μ yields

$$\langle \hat{N} \rangle = \sum_\alpha \frac{1}{e^{\beta(\varepsilon_\alpha - \mu)} \pm 1} = \sum_\alpha \langle \hat{n}_\alpha \rangle, \tag{1.36}$$

as expected. Here the + sign is for Fermions and the minus for Bosons.

Next differentiate (1.34) again with respect to μ. This leads to

$$-\frac{\partial^2 \Phi}{\partial \mu^2} = \beta \frac{\text{tr}\left(\hat{N}^2 e^{-\beta(\mathcal{H} - \mu \hat{N})}\right)}{\text{tr}\left(e^{-\beta(\mathcal{H} - \mu \hat{N})}\right)} - \beta \left[\frac{\text{tr}\left(\hat{N} e^{-\beta(\mathcal{H} - \mu \hat{N})}\right)}{\text{tr}\left(e^{-\beta(\mathcal{H} - \mu \hat{N})}\right)}\right]^2.$$

We recognize in this the variance of $\hat{N}$, $\text{var}(\hat{N}) = \langle \hat{N}^2 \rangle - \langle \hat{N} \rangle^2$. Whence,

$$\text{var}(\hat{N}) = \frac{1}{\beta} \frac{\partial \langle \hat{N} \rangle}{\partial \mu} = -\frac{1}{\beta} \frac{\partial^2 \Phi}{\partial \mu^2}. \tag{1.37}$$

This result is similar to what we found before in the canonical ensemble for the heat capacity or the susceptibility. It shows that the fluctuations are proportional to the derivative of the average with respect to μ. As a consequence, we see that since $\langle \hat{N} \rangle = N$ is the number of particles, $\text{var}(\hat{N})$ will be similarly extensive in N. This means we can write

$$\frac{\partial \langle \hat{N} \rangle}{\partial \mu} := N\kappa. \tag{1.38}$$

The constant κ is intensive and can be shown in thermodynamics to be related to the **compressibility** of the system. This therefore implies that

$$\frac{\sqrt{\text{var}(\hat{N})}}{\langle \hat{N} \rangle} = \sqrt{\frac{\kappa}{N\beta}}. \tag{1.39}$$

The relative fluctuations therefore scale proportionally to $1/\sqrt{N}$, which becomes negligible in the thermodynamic limit. This, as already discussed before, is the reason why we can use the grand-canonical ensemble even in those situations where the number of particles does not actually fluctuate.

1.4 The "classical" limit

The above results have to distinguish between Fermions and Bosons. When is this really necessary? Is it possible to have limiting cases where it does not matter if the particles are Fermions and Bosons? This is normally called the "classical" limit because it is the limit where quantum indistinguishibility no longer matters. I personally don't like this name because there are so many "classical limits" these days, you never which one people mean. In any case, if we look at Eqs. (1.30) and (1.32), we see that what distinguishes them is the ± 1 term. If this term was negligible, the results for Fermions and Bosons would be the same. The distinction between Fermions and Bosons therefore becomes irrelevant whenever

$$e^{\beta(\varepsilon_\alpha - \mu)} \gg 1. \tag{1.40}$$

When this is the case we see that $\langle \hat{n}_\alpha \rangle \simeq e^{-\beta(\varepsilon_\alpha - \mu)}$. As a consequence, the particle density in state α will be

$$\frac{\langle \hat{n}_\alpha \rangle}{\langle \hat{N} \rangle} \simeq \frac{e^{-\beta\varepsilon_\alpha}}{\sum_\alpha e^{-\beta\varepsilon_\alpha}}. \tag{1.41}$$

Notice how the chemical potential cancels out. This is nothing but the good old Maxwell-Boltzmann distribution. The left-hand side can simply be interpreted as the probability of finding a particle in a single-particle state α.

We can also do the same for the thermodynamic potential in Eqs. (1.29) and (1.31). Expanding $\ln(1 + x) \simeq x$ we get

$$\Phi \simeq -T \sum_\alpha e^{-\beta(\varepsilon_\alpha - \mu)} = -TzZ(1), \tag{1.42}$$

where $z = e^{\beta\mu}$ and $Z(1)$ is the single-particle partition function

$$Z(1) = \sum_\alpha e^{-\beta\varepsilon_\alpha}. \tag{1.43}$$

Since $\Phi = -T \ln Q$, Eq. (1.42) implies that $Q \simeq e^{zZ(1)}$. Expanding this in a Taylor series in z then yields

$$Q = \sum_{N=0}^{\infty} z^N \frac{[Z(1)]^N}{N!}. \tag{1.44}$$

Comparing with Eq. (1.19) we then reach the pretty neat conclusion that, in this limit,

$$Z(N) \simeq \frac{[Z(1)]^N}{N!} \tag{1.45}$$

The partition function of N particles is simply the partition function of a single particle to the power N. There is also a combinatorial factor of $1/N!$ to take into account the fact that the particles are still indistinguishable, so there are $N!$ equivalent ways of rearranging them. This makes sense: in the Fock representation we don't care about which particle is in which state. All we care about is **how many** particles are on a given state. Historically, this factor is usually called the **correct Boltzmann counting**.

2 Quantum gases

Let us now consider a specific case of non-interacting systems. Namely, free particles trapped in a d-dimensional box. This is what we call a Quantum Gas. We assume the box has linear dimension L with periodic boundary condition (PBC). The natural single-particle states are then of the form $|\boldsymbol{k}, s\rangle$, where $\boldsymbol{k} = (k_1, \ldots, k_d)$ are the momenta in d dimensions and $s = S, S - 1, \ldots, -S + 1, -S$ are the spin values (which can take a total of $2S + 1$ different values). I am assuming here a general spin S system just to make it slightly more general. But almost ways we either take either a spinless system ($S = 0$) or spin 1/2. Due to PBC, the k values are quantized as

$$k_i = \frac{2\pi\ell_i}{L}, \qquad \ell_i = 0, \pm 1, \pm 2, \pm 3, \ldots. \tag{2.1}$$

Moreover, the second quantized Hamiltonian is

$$\mathcal{H} = \sum_{\boldsymbol{k},s} \varepsilon_k \, a_{\boldsymbol{k},s}^\dagger a_{\boldsymbol{k},s}, \tag{2.2}$$

9

where

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m} = \frac{k_1^2 + \ldots + k_d^2}{2m}. \tag{2.3}$$

where, here, I reintroduced $\hbar$ just for completeness. Notice how the energies depend only on $k = |\boldsymbol{k}|$.

The condition (1.33) for the chemical potential in the case of Bosons becomes, in this case,

$$\mu < 0. \tag{2.4}$$

Thus, while for Fermions the chemical potential is arbitrary, for Bosons it is always negative.

2.1 The density of states

The average occupation number is given by Eqs. (1.30) or (1.32):

$$\langle \hat{\mathcal{N}} \rangle = \sum_{\boldsymbol{k},s} \frac{1}{e^{\beta(\varepsilon_k - \mu)} \pm 1}. \tag{2.5}$$

To carry out this sum, we transform it into an integral. This is justified when the box size L is large, so that the discreteness of (2.1) becomes very fine. It is actually easier to do this in a slightly more general context. Consider an arbitrary sum of the form

$$\sum_{\boldsymbol{k},s} f(k),$$

where $f(k)$ is an arbitrary function which depends only on the absolute value of k. To convert it into an integral we introduce the convenient 1:

$$1 = \left(\frac{L}{2\pi}\right)^d \Delta k_1 \ldots \Delta k_d \tag{2.6}$$

We then get

$$\sum_{\boldsymbol{k},s} f(k) = \sum_{\boldsymbol{k}} \Delta k_1 \ldots \Delta k_d f(k),$$

where we also introduced the factor $(2S + 1)$ which comes from the sum over s. Written in this way, the expression has the form of a Riemann sum. When L is large, the Δk_i become infinitesimal, so that we are allowed to convert the sum to an integral:

$$\sum_{\boldsymbol{k},s} f(k) = (2S + 1)\left(\frac{L}{2\pi}\right)^d \int \mathrm{d}^d \boldsymbol{k} \ f(k). \tag{2.7}$$

This result is already nice. It provides a recipe to go from a $\boldsymbol{k}$ sum to a $\boldsymbol{k}$ integral.

But we can also go a step further and exploit the fact that $f(k)$ depends only on $k = |\boldsymbol{k}|$. Introduce the d-dimensional solid angle $\mathrm{d}^d \boldsymbol{k} = k^{d-1} \, \mathrm{d}k \, \mathrm{d}\Omega_d$. We can then carry out the integral over $\mathrm{d}\Omega_d$. The result is the area of a d-dimensional sphere:

$$\int \mathrm{d}\Omega_d = \frac{d\pi^{d/2}}{\Gamma(\frac{d}{2} + 1)}, \tag{2.8}$$

where $\Gamma(x)$ is the Gamma function. For instance, if $d = 3$ the above expression simplifies to the familiar 4π, whereas if $d = 2$ we get 2π. With this change, Eq. (2.7) becomes

$$\sum_{k,s} f(k) = (2S + 1)\left(\frac{L}{2\pi}\right)^d \frac{d\pi^{d/2}}{\Gamma(\frac{d}{2} + 1)} \int_0^\infty \mathrm{d}k\, k^{d-1} f(k). \qquad (2.9)$$

I know this seem a bit messy. But if you think about it, everything here is just a bunch of silly numbers. These numbers represent the coefficient that you have to multiply when you want to go from a sum to an integral.

Finally, we can also go one step further and convert the k integral into an integral over ε. To do this we change variables using Eq. (2.3):

$$\varepsilon = \frac{\hbar^2 k^2}{2m} \qquad \rightarrow \qquad \mathrm{d}\varepsilon = \frac{\hbar^2 k}{m}\, \mathrm{d}k.$$

Thus

$$\mathrm{d}k\, k^{d-1} = \frac{m}{\hbar^2} \left(\frac{2m\varepsilon}{\hbar^2}\right)^{\frac{d}{2}-1} \mathrm{d}\varepsilon.$$

Eq. (2.9) then finally becomes

$$\sum_{k,s} f(k) = (2S + 1)\left(\frac{L}{2\pi}\right)^d \frac{d\pi^{d/2}}{\Gamma(\frac{d}{2} + 1)} \frac{1}{2} \left(\frac{2m}{\hbar^2}\right)^{d/2} \int_0^\infty \mathrm{d}\varepsilon\ \varepsilon^{\frac{d}{2}-1} f(\varepsilon).$$

This still looks somewhat messy. But what we do now is to throw everything that is ugly under the carpet by defining the **density of states** (DOS)

$$D(\varepsilon) = (2S + 1)\left(\frac{L}{2\pi}\right)^d \frac{d\pi^{d/2}}{\Gamma(\frac{d}{2} + 1)} \frac{1}{2} \left(\frac{2m}{\hbar^2}\right)^{d/2} \varepsilon^{\frac{d}{2}-1}. \qquad (2.10)$$

so that our recipe finally becomes

$$\sum_{k,s} f(k) = \int_0^\infty \mathrm{d}\varepsilon\, D(\varepsilon) f(\varepsilon). \qquad (2.11)$$

The DOS therefore quantifies the weight that you get from going from a k sum to an integral in ε. With this expression, we can now write down any thermodynamic quantity we wish. For instance, the average number of particles will be

$$\langle \hat{N} \rangle = \int \mathrm{d}\varepsilon\, D(\varepsilon) \bar{n}(\varepsilon), \qquad (2.12)$$

where

$$\bar{n}(\varepsilon) := \frac{1}{e^{\beta(\varepsilon - \mu)} \pm 1}. \qquad (2.13)$$

11

Similarly, the internal energy is

$$U = \int d\varepsilon\, D(\varepsilon)\, \varepsilon\, \bar{n}(\varepsilon). \tag{2.14}$$

The DOS for $d = 1, 2$ and 3 reads

$$D(\varepsilon) = (2S + 1)\frac{L}{\sqrt{2\pi}}\sqrt{\frac{m}{\hbar^2}}\frac{1}{\sqrt{\varepsilon}}, \qquad d = 1, \tag{2.15}$$

$$D(\varepsilon) = (2S + 1)\frac{mL^2}{2\pi\hbar^2}, \qquad d = 2, \tag{2.16}$$

$$D(\varepsilon) = (2S + 1)\frac{L^3}{\sqrt{2}\pi^2}\left(\frac{m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}, \qquad d = 3. \tag{2.17}$$

What is important about these results is how $D(\varepsilon)$ depends on ε. The coefficients in front are just a bunch of numbers.

To finish, I also want to mention that there is an alternative, more elegant, way of defining the density of states. Instead of (2.11), we can define it as

$$D(\varepsilon) = \sum_{k,s} \delta(\varepsilon - \varepsilon_k). \tag{2.18}$$

Here ε is just the argument of $D(\varepsilon)$ and varies continuously; ε_k, on the other hand, are the energy eigenvalues. The reason why this definition is equivalent to Eq. (2.11) is most easily understood by doing a sort of reverse process. Consider the integral

$$\int d\varepsilon\, f(\varepsilon)D(\varepsilon) = \int d\varepsilon \sum_{k,s} f(\varepsilon)\delta(\varepsilon - \varepsilon_k).$$

We now carry out the integral over ε. The δ functions will then replace all ε with ε_k and we reach the left-hand side of Eq. (2.11). Thus, Eq. (2.18) can be viewed as a slightly more sophisticated way of defining the DOS. The reason why this is interesting is because it shows how the density of states can actually be viewed as a **comb of delta functions**. However, this comb is so finely packed together, that it forms a continuous curve, which is $D(\varepsilon)$.

2.2 Density of states and Green's functions (optional)

Consider a non-interacting system described by the single-particle Hamiltonian H (maybe I could call this H_1 to emphasize it's single particle. But I'll call it H for simplicity). We assume this Hamiltonian can be diagonalized as

$$H|k\rangle = \varepsilon_k|k\rangle, \tag{2.19}$$

where k is just a quantum number; it can mean, for instance (k, σ). But the argument I will use below is actually a bit more general. We now define the **retarded Green's function**

$$G(\epsilon) = \lim_{s \to 0} \frac{1}{\epsilon + is - H}. \tag{2.20}$$
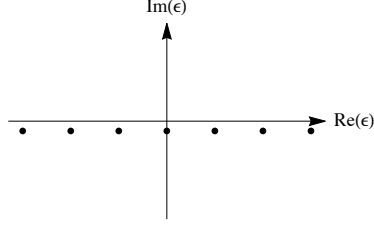
Figure 1: The poles of $\text{tr}\,G(\epsilon)$ [Eq. (2.20)] occur at $\epsilon = \varepsilon_k - is$.

Here $1/A$ is just a fancy way of writing the matrix inverse A^{-1}. This is interpreted as a continuous function of a parameter ϵ. Moreover, s is a tiny number which is left there to ensure that G never blows up when ϵ touches one of the eigenvalues ε_k. Sometimes we do not write the $\lim_{s \to 0}$ explicitly. But this limit is always there in principle.

The point I want to stress here is that the Green's function (2.20) actually contains the DOS in it. To see that, take the trace of $G(\epsilon)$ using the $|k\rangle$ basis:

$$\text{tr}\,G(\epsilon) = \sum_k \langle k | \frac{1}{\epsilon + is - H} | k \rangle$$

$$= \sum_k \frac{1}{\epsilon + is - \varepsilon_k}$$

$$= \sum_k \frac{(\epsilon - \varepsilon_k) - is}{(\epsilon - \varepsilon_k)^2 + s^2}$$

We see that $\text{tr}\,G(\epsilon)$ will have poles in the complex plane whenever $\epsilon = \varepsilon_k - is$ (see Fig. 1). Thus, by knowing the pole structure of $\text{tr}\,G(\epsilon)$ one can infer the eigenvalues of H.

Next let us focus on the imaginary part of $\text{tr}\,G(\epsilon)$:

$$\text{Im}[\,\text{tr}\,G(\epsilon)] = -\lim_{s \to 0} \sum_k \frac{s}{(\epsilon - \varepsilon_k)^2 + s^2}. \tag{2.21}$$

We now use the identity

$$\lim_{s \to 0} \frac{s}{x^2 + s^2} = \pi \delta(x), \tag{2.22}$$

which leads to

$$\text{Im}[\,\text{tr}\,G(\epsilon)] = -\pi \sum_k \delta(\epsilon - \varepsilon_k). \tag{2.23}$$

The quantity on the right-hand side is nothing but the DOS (2.18). Thus, we conclude that

$$D(\epsilon) = -\frac{1}{\pi}\text{Im}[\,\text{tr}\,G(\epsilon)] = -\frac{1}{\pi}\lim_{s \to 0}\text{Im}\sum_k \frac{1}{\epsilon + is - \varepsilon_k}. \tag{2.24}$$

This kind of relation is used to evaluate the DOS numerically in systems for which the energy levels ε_k are too complicated.

Finally, we mention that the trace in Eq. (2.24) can be taken with respect to any basis we want. This allows us to define density of states for specific **sectors**. For

13

instance, suppose we have a model where the energy eigenvalues depend on the spin projection; something like $\varepsilon_{k,\sigma}$. We can then use the basis $|k, \sigma\rangle$ to take the trace in (2.24), which allows us to decompose

$$D(\epsilon) = \sum_\sigma D_\sigma(\epsilon), \qquad D_\sigma(\epsilon) = -\frac{1}{\pi}\text{Im} \sum_k \langle k\sigma|G(\epsilon)|k\sigma\rangle. \tag{2.25}$$

The quantities $D_\sigma(\epsilon)$ can be interpreted as the density of states *within* the sector of spin σ. This kind of idea therefore allows us to address how many states are available within a given subspace.

As another example, suppose we actually have a tight-binding model where we label the position states as $|n\rangle$, with $n = 1, 2, \ldots, L$. In this case we can write (2.24) as

$$D(\epsilon) = \sum_{n=1}^{L} D_n(\epsilon), \qquad D_n(\epsilon) = -\frac{1}{\pi}\text{Im}\langle n|G(\epsilon)|n\rangle. \tag{2.26}$$

Each $D_n(\epsilon)$ therefore quantifies the density of states available at position n. It would be interesting to apply this to the Aubry-André model. I don't think anyone ever did this...

2.3 First quantum correction to the classical limit

We saw in Sec. 1.4 that the classical limit corresponds to $e^{\beta(\varepsilon_k-\mu)} \gg 1$. Since this must be true for all energies, this implies that $e^{-\beta\mu} \gg 1$. Since $\beta > 0$ we therefore see that in the classical limit $\mu < 0$. Let us now expand on this and include also the first quantum correction to this classical limit.

For convenience, introduce a symbol

$$\zeta = \begin{cases} +1 & \text{fermions} \\ -1 & \text{bosons.} \end{cases} \tag{2.27}$$

This way we can write the occupation number as

$$\bar{n}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + \zeta}. \tag{2.28}$$

We now write this as

$$\bar{n}(\varepsilon) = e^{-\beta(\varepsilon-\mu)} \frac{1}{1 + \zeta e^{-\beta(\varepsilon-\mu)}}.$$

When $e^{-\beta(\varepsilon-\mu)} \ll 1$ we can then expand this using $(1 + x)^{-1} \simeq 1 - x$. This then yields

$$\bar{n}(\varepsilon) \simeq e^{-\beta(\varepsilon-\mu)}\left[1 - \zeta e^{-\beta(\varepsilon-\mu)}\right]. \tag{2.29}$$

For concreteness, let us now focus on the case of a quantum gas in $3D$. To be a bit more concise, let us also write the density of states, Eq. (2.17), as

$$D(\varepsilon) = \alpha V \sqrt{\varepsilon}, \qquad \alpha = (2S + 1)\frac{1}{\sqrt{2}\pi^2}\left(\frac{m}{\hbar^2}\right)^{3/2}. \tag{2.30}$$

We then get

$$\langle \hat{N} \rangle \simeq \alpha V \int\limits_0^\infty d\varepsilon \, \sqrt{\varepsilon} \Big[e^{-\beta(\varepsilon-\mu)} - \zeta e^{-2\beta(\varepsilon-\mu)} \Big]$$

$$= \alpha V \left\{ e^{\beta\mu} \int\limits_0^\infty d\varepsilon \, \sqrt{\varepsilon} \, e^{-\beta\varepsilon} - \zeta e^{2\beta\mu} \int\limits_0^\infty d\varepsilon \, \sqrt{\varepsilon} e^{-2\beta\varepsilon} \right\}$$

$$= \alpha V \left\{ e^{\beta\mu} \frac{\sqrt{\pi}}{2\beta^{3/2}} - \zeta e^{2\beta\mu} \frac{\sqrt{\pi}}{2(2\beta)^{3/2}} \right\}.$$

There are a bunch of annoying constants here.

To simplify them a bit, we introduce the **de Broglie thermal wavelength**

$$\lambda = \frac{1}{(2S+1)^{1/3}} \sqrt{\frac{2\pi\hbar^2}{mT}}. \qquad (2.31)$$

Using also the fugacity $z = e^{\beta\mu}$ we can finally write the result as

$$N = \frac{V}{\lambda^3} \left(z - \frac{\zeta z^2}{2^{3/2}} \right), \qquad (2.32)$$

where I already wrote N instead of $\langle \hat{N} \rangle$ for simplicity. I think this result ex-
plains well the idea behind the chemical potential. This is an equation relating
μ (which appears in z) with the *particle density N/V*.

Recall that in the classical limit $z = e^{\beta\mu} \ll 1$. Thus, to first order we can neglect the
term proportional to z^2, which then leads to

$$\beta\mu = \ln\left\{ \lambda^3 N/V \right\}. \qquad (2.33)$$

This yields a condition for the validity of the classical limit. Namely,

$$\frac{N}{V} \ll \frac{1}{\lambda^3}. \qquad (2.34)$$

This result is pretty neat. The quantity V/N represents roughly the average volume
occupied by each particle, whereas λ is the typical wavelength associated with the
quantum wavepackets at a temperature T. The classical limit will thus be justified when
the volume V/N they can occupy is much larger than λ^3. That is, when the confinement
of the particles is not significant so as to allow for the effects of indistinguishability to
have an effect.

Next we consider the first quantum correction, obtained by solving Eq. (2.32) with
respect to z. To do so it is useful to have an idea about **inverse series**. Eq. (2.32)
expresses $\lambda^3 N/V$ as a power series in the small parameter z. What we want is to invert
this and write z as a power series in the (also small) parameter $\lambda^3 N/V$. This can be
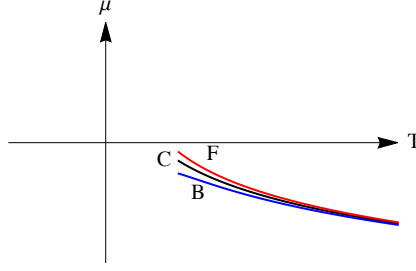
Figure 2: First quantum correction to the chemical potential, comparing the classical case (C) with that of Bosons (B) and Fermions (F). The curves were made using Eq. (2.37).

done using the following inverse series: [1]

$$y = ax + bx^2 + O(x)^3 \qquad \rightarrow \qquad x = \frac{y}{a} - \frac{by^2}{a^3} + O(y)^3. \qquad (2.35)$$

We then get

$$z = \lambda^3 N/V + \frac{\zeta}{2^{2/3}}(\lambda^3 N/V)^2. \qquad (2.36)$$

Or, in terms of the chemical potential,

$$\beta\mu = \ln\left\{\lambda^3 N/V + \frac{\zeta}{2^{2/3}}(\lambda^3 N/V)^2\right\}. \qquad (2.37)$$

The situation is depicted in Fig. 2. For very high temperatures the curves for Bosons and Fermions coincide with the classical limit [Eq. (2.33)]. As the system is cooled down, however, the quantities V/N and λ^3 start to become of the same magnitude and the indistinguishability of the particles begins to matter. As a consequence, the curves for Bosons and Fermions deviate from the classical behavior. In particular, as can be seen in Eq. (2.37), the chemical potential for Bosons ($\zeta = -1$) is always smaller than that for Fermions ($\zeta = +1$).

Next let us look at the average energy (2.14). Using again the expansion of $\bar{n}(\varepsilon)$ in Eq. (2.29) and carrying out the integrals, as before, we find

$$U = \frac{3T}{2}\frac{V}{\lambda^3}\left(z - \frac{\zeta}{2^{5/2}}z^2\right). \qquad (2.38)$$

This result is correct, but is expressed in terms of the chemical potential (in z). This is not very useful. It would be better to have the result expressed in terms of N. To do that, we can use Eq. (2.36) to get rid of z. We also need

$$z^2 = \left(\lambda^3 N/V + \frac{\zeta}{2^{2/3}}(\lambda^3 N/V)^2\right)^2 \simeq (\lambda^3 N/V)^2.$$

---

[1] This can be understood as follows. Start with $y = ax + bx^2$. We now assume that the inverse can also be expressed in a power series, as $x = cy + dy^2$, for some coefficients c and d. Plugging this ansatz in $y = ax + bx^2$ yields the equation

$$y = acy + (ad + bc^2)y^2 + O(y^3).$$

In order to satisfy this (up to second order) we must then have $c = 1/a$ and $d = -bc^2/a$, which leads to Eq. (2.35).

We then get

$$z - \frac{\zeta}{2^{5/2}}z^2 = \lambda^3 N/V + \frac{\zeta}{2^{2/3}}(\lambda^3 N/V)^2 - \frac{\zeta}{2^{5/2}}(\lambda^3 N/V)^2$$

$$= \lambda^3 N/V + \frac{\zeta}{2^{5/2}}(\lambda^3 N/V)^2.$$

Substituting this in Eq. (2.38) and simplifying a bit, we get

$$U = \frac{3}{2}NT\left(1 + \frac{\zeta}{2^{5/2}}\lambda^3 N/V\right). \tag{2.39}$$

This result is pretty cool. The value of $3NT/2$ is simply the classical internal energy of an ideal gas. When quantum corrections become important, however, we see that for Fermions the Pauli exclusion principle *increases* the energy of the gas, whereas for Bosons the energy is reduced instead. What is surprising about this is that **there are no interactions involved**; the gas is ideal and the energy is purely kinetic. A set of Bosons or Fermions at the same temperature will thus have different energies, even though they do not interact. Thus, for instance, if we have a mixture of He-3 (which are fermions) and He-4 (which are bosons), each species will have a different average energy, solely due to quantum effects.

3 Fermi gases

Let us now focus on the case of Fermions. The most important example of a Fermi gas are the electrons in a metal. The conduction electrons are only weakly bound to the atomic nuclei, so that they can pretty much more around freely. Their only constraint is that they cannot leave the metal; there is a potential barrier to do so (which is the work function for those who studied the photoelectric effect). Thus, electrons in a metal are naturally trapped in a box of length L, so that the momentum quantization rules of Sec. applies.

3.1 Ground-state

The density of states (DOS) for a 3D electron gas is given by Eq. (2.17) with $S = 1/2$; viz,

$$D(\varepsilon) = \alpha V \sqrt{\varepsilon}, \qquad \alpha = \frac{\sqrt{2}}{\pi^2}\left(\frac{m}{\hbar^2}\right)^{3/2}. \tag{3.1}$$

As our first step, let us compute the **Fermi level**. Recall that the word "Fermi" is associated with "highest filled". The Fermi level is a zero temperature property; it refers to the ground-state. We pile up the electrons, state by state, until we reach a total of N_e particles. The Fermi energy will thus be the energy of the highest filled state.

This is one of those cases where the DOS comes quite in handy. The DOS already contains all factors that come from changing from a k-sum to an integral in energy.

Thus, in terms of it, the Fermi energy ε_F is the implicit solution of

$$\int_0^{\varepsilon_F} d\varepsilon\, D(\varepsilon) = N_e. \tag{3.2}$$

Solving the integral we find

$$\alpha V \frac{2}{3} \varepsilon_F^{3/2} = N_e, \tag{3.3}$$

or

$$\varepsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n_e)^{2/3}, \tag{3.4}$$

where $n_e = N_e/V$. The Fermi energy therefore increases algebraically with the **electron density** n_e, with an exponent $2/3$.

As a sanity check, we can also compute the Fermi level in a slightly more pedantic way. Recall that the k_i are discretized as in Eq. (2.1). In k-space, this leads to a grid of points like that shown in Fig. 3. We then start filling out these states, with 2 electrons in each site (because of spin). Since we must fill first states with the smallest energy, the filling is done through concentric spheres (as shown in the figure). When we reach the Fermi level we will have filled a sphere with a total volume of $4\pi k_F^3/3$.

However, this same sphere can also be picture as made up of tiny cubes of volume

$$\Delta k_x \Delta k_y \Delta k_z = \left(\frac{2\pi}{L}\right)^3.$$

And since there are N_e particles and each "cube" can take two particles, we will fill a volume of $\frac{N}{2}(2\pi/L)^3$. Since this must match $4\pi k_F^3/3$, we get

$$\frac{4\pi k_F^3}{3} = \frac{N}{2}\left(\frac{2\pi}{L}\right)^3,$$

which leads to a Fermi momentum

$$k_F = (3\pi^2 n_e)^{1/3}. \tag{3.5}$$

Plugging this in the dispersion relation $\varepsilon_k = \hbar^2 k^2/2m$ then yields the Fermi energy (3.4).

We can also compute the total ground-state energy. It is defined as

$$E_{\text{gs}} = \int_0^{\varepsilon_F} d\varepsilon\, \varepsilon D(\varepsilon). \tag{3.6}$$

Carrying out the integration we find

$$E_{\text{gs}} = \alpha V \frac{2}{5} \varepsilon_F^{5/2}.$$

We can write this in a slightly prettier way using Eq. (3.3) to eliminate the constants in front. We then get
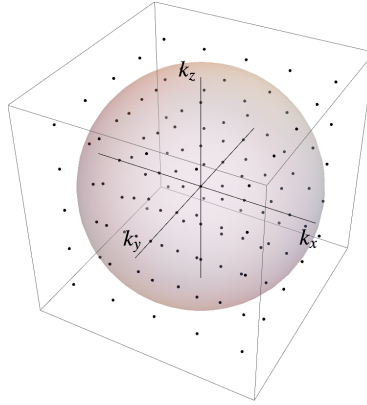
$$E_{\text{gs}} = \frac{3}{5} N \varepsilon_F. \tag{3.7}$$

18

Figure 3: Grid of available states in k-space. The Fermi energy is determined by specifying how many points lie inside a sphere of radius k_F.

The average energy per electron is therefore 3/5 of the Fermi energy. It is not exactly 1/2 because the density of states (3.1) is not uniform in ε: the higher the energy, the higher is the number of available states.

From the Fermi energy and momentum we can also compute other "Fermi" quantities. For instance, the Fermi velocity is

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}(3\pi^2 n_e)^{1/3}. \tag{3.8}$$

This yields the typical velocity of electrons around the Fermi level. The reason why this is important is because the electrons around the Fermi level are the ones which can be excited to empty states. And it is through these excitations that the physics happens. For instance, when you apply an electric potential, the electrons will begin to move around. This "moving around" means that you are exciting electrons to states above the Fermi level. The typical velocities of these electrons will therefore be of the order of v_F.

Similarly, we can also define the Fermi temperature from the relation

$$k_B T_F = \varepsilon_F, \tag{3.9}$$

where, just for now, I reinstitute Boltzmann's constant. The Fermi temperature is simply a measure of the typical energies involved in an electron gas, but measured in Kelvin instead of eV. For typical metals the Fermi energy is $\varepsilon_F \sim 1 - 10$ eV. This yields a Fermi temperature of the order of 10^4 K, a remarkably high value. This result is extremely important. It means that as far as the electron gas is concerned, room temperature (300 K) is actually a very very low temperature. Thus, the regime which matters for electron gases is actually the far opposite as that studied in the first quantum correction, Sec. 2.3. The interesting regime here is actually in the deep quantum regime, where quantum effects are very strong.

3.2 Finite temperatures

Now let us turn to the Fermi gas at finite temperatures. The Fermi-Dirac distribution

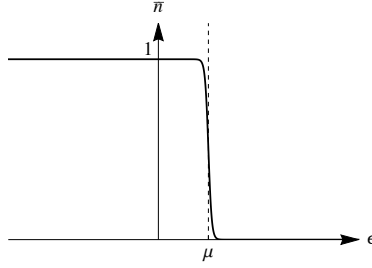$$\bar{n}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}, \tag{3.10}$$

Figure 4: Fermi-Dirac distribution (3.10) as a function of ε for low temperatures.

looks somewhat like Fig. 4 at low temperatures. It is essentially 1 when $\varepsilon < \mu$ and 0 otherwise. Indeed, in the limit where $T \to 0$ (or $\beta \to \infty$) the Fermi-Dirac function becomes the Heaviside theta function:

$$\lim_{T \to 0} \bar{n}(\varepsilon) = \theta(\mu - \varepsilon), \tag{3.11}$$

where

$$\theta(x) = \begin{cases} 1 & x > 0, \\ 0 & x < 0. \end{cases} \tag{3.12}$$

In the limit of zero temperature, all states below μ are occupied, whereas all states above μ are empty.

If we think about it for a second, we therefore conclude that at zero temperatures **the chemical potential becomes the Fermi energy**:

$$\lim_{T \to 0} \mu = \varepsilon_F. \tag{3.13}$$

The chemical potential can therefore be viewed as a sort of generalization of the notion of Fermi energy to finite temperatures. In this case the Fermionic occupations are not sharp, but instead are a bit blurred like in Fig. 4. In the vicinity of μ the different states have some finite probabilities of being occupied, which are neither 0 nor 1.

The average number of particles and average energy are computed using Eqs. (2.12) and (2.14):

$$N_e = \langle \hat{N} \rangle = \int_0^\infty d\varepsilon \, D(\varepsilon) \bar{n}(\varepsilon), \tag{3.14}$$

$$U = \langle \mathcal{H} \rangle = \int_0^\infty d\varepsilon \, D(\varepsilon) \, \varepsilon \, \bar{n}(\varepsilon). \tag{3.15}$$

As discussed in the previous section, all that matters for fermionic systems like this are very low temperatures. The integral in Eq. (3.14), for instance, will look a bit like that in Fig. 5. If we had $T = 0$ we would get exactly the integral in Eq. (3.2). Since $T \neq 0$ the integral is distorted. But since all that matters are low temperatures, the integral is not distorted too much. Only slightly. And only in the vicinity of μ. The integrals in (3.14) and (3.15) are from 0 to ∞. However, the Fermi-Dirac distribution $\bar{n}(\varepsilon)$ essentially cuts this off above μ. The cut-off is not 100% sharp, but it is pretty abrupt.
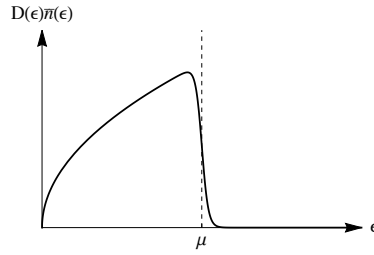
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Figure 5: The integrand in Eq. (3.14) for low temperatures.

Since these integrals cannot be computed analytically, one must resort to approximations. In the context of Fermions, the most useful one is the **Sommerfeld expansion**. It exploits the above results that the Fermi-Dirac distribution cuts-off any integrals high above μ. Given any function $g(\varepsilon)$ it reads,

$$\int\limits_0^\infty d\varepsilon \, g(\varepsilon)\bar{n}(\varepsilon) \simeq \int\limits_0^\mu d\varepsilon \, g(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 g'(\mu). \tag{3.16}$$

The first term is what would survive in the limit $T \to 0$. The second term represents the first correction, given as powers of T and depending on the derivative of g around $\varepsilon = \mu$. One can also continue the expansion and find higher order corrections. I will not derive Eq. (3.16) here. The derivation is quite boring and can be found on Wikipedia. One thing which is a bit tricky in the Sommerfeld expansion is that the right-hand side is a function of μ. Thus, for instance, the first term is still temperature-dependent, since μ is implicitly a function of T.

Finite temperature correction to the chemical potential

Let us now apply this expansion. We begin by using it in Eq. (3.14), which yields

$$N_e = \int\limits_0^\mu d\varepsilon D(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 D'(\mu). \tag{3.17}$$

To proceed from here is actually quite tricky. What we are interested in is a temperature expansion of the relevant quantities in powers of T. But in Eq. (3.17) μ is a function of temperature, so even the limit of integration is a function of T.

We will learn in a second that the first correction to μ is of order T^2, so that we may expand

$$\mu \simeq \varepsilon_F - \eta(k_B T)^2, \tag{3.18}$$

where η is a constant to be determined. If we then restrict ourselves only to terms at most of order T^2, we can simplify the last term in Eq. (3.17) as

$$\frac{\pi^2}{6}(k_B T)^2 D'(\mu) \simeq \frac{\pi^2}{6}(k_B T)^2 D'(\varepsilon_F). \tag{3.19}$$

As for the first term, we split the integral as

$$\int_0^\mu \mathrm{d}\varepsilon D(\varepsilon) = \int_0^{\varepsilon_F} \mathrm{d}\varepsilon D(\varepsilon) - \int_\mu^{\varepsilon_F} \mathrm{d}\varepsilon D(\varepsilon). \tag{3.20}$$

The first integral already appeared before in [Eq. (3.2)] and reads

$$\int_0^{\varepsilon_F} \mathrm{d}\varepsilon \, D(\varepsilon) = N_e. \tag{3.21}$$

This result continues to hold, irrespective of whether we are at finite temperatures or not; it is merely a definition of ε_F.

The last term in Eq. (3.20) can be expanded in a power series because μ and ε_F are very close to each other. This leads to

$$\int_\mu^{\varepsilon_F} \mathrm{d}\varepsilon D(\varepsilon) \simeq (\varepsilon_F - \mu) D\left(\frac{\varepsilon_F + \mu}{2}\right)$$

$$= \eta (k_B T)^2 D\left(\varepsilon_F - \frac{\eta}{2}(k_B T)^2\right)$$

$$\simeq \eta (k_B T)^2 \left[D(\varepsilon_F) - \frac{\eta}{2}(k_B T)^2 D'(\varepsilon_F) \right].$$

The last term is already of order T^4 and may thus be neglected. We therefore conclude that

$$\int_\mu^{\varepsilon_F} \mathrm{d}\varepsilon D(\varepsilon) = (\varepsilon_F - \mu) D(\varepsilon). \tag{3.22}$$

Plugging this in Eq. (3.20) yields an approximation for the integral involving μ in the limits of integration. I will write down the result for a generic function $g(\varepsilon)$, since this will appear again in a second:

$$\boxed{\int_0^\mu \mathrm{d}\varepsilon \, g(\varepsilon) \simeq \int_0^{\varepsilon_F} \mathrm{d}\varepsilon \, g(\varepsilon) + (\mu - \varepsilon_F) g(\varepsilon_F).} \tag{3.23}$$

In the particular case of $g(\varepsilon) = D(\varepsilon)$ we get, using also Eq. (3.21),

$$\int_0^\mu \mathrm{d}\varepsilon D(\varepsilon) \simeq N_e + (\mu - \varepsilon) D(\varepsilon_F). \tag{3.24}$$

Finally, plugging this back in Eq. (3.17) and using also Eq. (3.19) we find

$$N_e = N_e + (\mu - \varepsilon) D(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 D'(\varepsilon_F),$$

Solving for μ:

$$\mu = \varepsilon_F - \frac{\pi^2}{6}(k_B T)^2 \frac{D'(\varepsilon_F)}{D(\varepsilon_F)}. \tag{3.25}$$

This gives the chemical potential as a function of T and N_e (which is encoded in ε_F). The chemical potential is lowered with respect to ε_F due to thermal fluctuations, by a factor proportional to the sensitivity of $D(\varepsilon_F)$ around the Fermi level.

One thing which you may not have noticed is that in deriving Eq. (3.25) nowhere did we use the actual form of the density of states. This result is therefore general and holds for any kind of non-interacting Fermi gases. All that is going to change is the shape of $D(\varepsilon)$.

Energy and heat capacity

Let us now repeat the steps for the internal energy (3.15). Using the Sommerfeld expansion (3.16) we find

$$U = \simeq \int_0^\mu \mathrm{d}\varepsilon\, D(\varepsilon)\varepsilon + \frac{\pi^2}{6}(k_B T)^2 \Big[D(\mu) + \mu D'(\mu) \Big]. \tag{3.26}$$

Using the same logic as in Eq. (3.19) we can simplify the last term by simply replacing μ with ε_F. As for the first term, we use Eq. (3.23) with $g(\varepsilon) = \varepsilon D(\varepsilon)$, which yields up to order T^2,

$$U \simeq \int_0^{\varepsilon_F} \mathrm{d}\varepsilon\, D(\varepsilon)\varepsilon + (\mu - \varepsilon_F)\varepsilon_F D(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 \Big[D(\varepsilon_F) + \varepsilon_F D'(\varepsilon_F) \Big].$$

The first term is nothing but the ground-state energy E_{gs} in Eq. (3.7). As for the remaining terms, there turns out to be a cancelation when we substitute Eq. (3.25) for μ:

$$\varepsilon_F \Big\{ (\mu - \varepsilon_F)D(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 D'(\varepsilon_F) \Big\} = 0.$$

Whence, we are left only with

$$U = \frac{3}{5}N\varepsilon_F + \frac{\pi^2}{6}(k_B T)^2 D(\varepsilon_F). \tag{3.27}$$

The heat capacity is therefore

$$C = \frac{\partial U}{\partial T} = N\gamma T, \qquad \gamma = \frac{\pi^2 k_B^2}{3}D(\varepsilon_F). \tag{3.28}$$

The heat capacity of an electron gas is therefore linear in temperature; the coefficient γ is called the **Sommerfeld coefficient** and is very frequently measured in the lab. By determining the Sommerfeld coefficient one can extract information about the density of states at the vicinity of the Fermi level, $D(\varepsilon_F)$. If you think about it, this is somewhat remarkable: from the heat capacity, which is a very bulky thermal-ish property, one can actually learn something valuable

about the electronic structure of the material. This is not the only situation where this happens. I'm always amazed by how much information is contained in C.

4 Bose gases and Bose-Einstein condensation

We next turn to a more detailed analysis of a Bose gas. For simplicity, I will assume that the Bosons have spin 0. This doesn't change anything. Just avoids having to include a sum over s. The thermodynamic potential and the Bose-Einstein occupation number are

$$\Phi = T \sum_{\boldsymbol{k}} \ln \left\{ 1 - e^{-\beta(\varepsilon_k - \mu)} \right\}, \tag{4.1}$$

and

$$\bar{n}_k = \frac{1}{e^{\beta(\varepsilon_k - \mu)} - 1}, \tag{4.2}$$

with the dispersion relation $\varepsilon_k = \hbar^2 k^2 / 2m$.

As already discussed before, $\bar{n}_k$ must be non-negative by construction. And since this must be true for all ε_k, we see that this constraints the allowed values of μ to

$$\mu < 0. \tag{4.3}$$

No such constraint exists in the case of Fermions. And, as we will see, it leads to dramatic consequences; namely, Bose-Einstein condensation (BEC).

Before delving into the full Bose gas, it is therefore useful to emphasize once again why this kind of constraint exists. Consider a system with only one single-particle state available, with Hamiltonian

$$\mathcal{H} = \varepsilon a^\dagger a. \tag{4.4}$$

The partition function in the grand-canonical ensemble is

$$Q = \operatorname{tr} e^{-\beta(\epsilon - \mu)\hat{n}} = \sum_{n=0}^{\infty} e^{-\beta(\varepsilon - \mu)n}.$$

This is a geometric series $\sum_{n=0}^{\infty} x^n$, with $x = e^{-\beta(\varepsilon - \mu)}$. Such a sum only converges if $|x| < 1$, which imposes the constraint that $\mu < \varepsilon$. This is what is happening in (4.3), except that there, $\mu < \varepsilon_k$ for all energies ε_k. Thus

$$\mu < \min_k \varepsilon_k = 0.$$

Another way of seeing this is by looking at what happens if we take the limit of $T \to 0$. In this case the system should tend to the ground-state. But we are in the grand-canonical ensemble, so this is the ground-state in Fock space, where the number of particles can vary. One should, therefore, find the configuration for which

$$\mathcal{H} - \mu \hat{N} = (\varepsilon - \mu)\hat{n},$$

has the smallest possible energy. If $\varepsilon - \mu > 0$, this will be a configuration with zero particles. But if $\varepsilon - \mu < 0$ we can minimize the energy more and more by just putting more and more particles in that state. The ground-state would therefore be **thermodynamically unstable** in the sense that we could always make the energy smaller and smaller, as we wish. This is why we must have $\varepsilon - \mu > 0$.

Ok. Now let's go into the actual Bose gas. The total number of particles is

$$N = \sum_{\boldsymbol{k}} \bar{n}_k. \tag{4.5}$$

We could convert this to an integral using the density of states. If we assume our gas is again in 3D (with spin 0) then the DOS reads [Eq. (2.17)]:

$$D(\varepsilon) = \alpha V \sqrt{\varepsilon}, \qquad \alpha = \frac{1}{\sqrt{2}\pi^2} \left(\frac{m}{\hbar^2} \right)^{3/2} ., \tag{4.6}$$

In the case of a Bose gas, however, there is something tricky about converting the sum to an integral.

Recall that the DOS is defined from the general recipe

$$\sum_{\boldsymbol{k}} f(\varepsilon_k) = \int \mathrm{d}\varepsilon \, f(\varepsilon) D(\varepsilon).$$

Now, this recipe assumes that the function $f(\varepsilon_k)$ is a **smooth function** of ε. I mean, of course: if $f(\varepsilon)$ is a super weird function, with discontinuities and divergences and etc., then we cannot expect that the integral (which is a smooth guy) will capture the ruggedness of the sum.

The whole point about Bose gases is that the sum (4.5) is *not* smooth. We can convince ourselves of that by looking at the ground-state when $T \to 0$. Since the bosons do not satisfy the Pauli exclusion principle, the ground-state will simply correspond to putting all N particles in the state with $\boldsymbol{k} = 0$. Thus, in the ground-state we will have $\bar{n}_0 = N$ and $\bar{n}_k = 0$ for all $\boldsymbol{k} \neq 0$. This is definitely very very far from "smooth". Even if the temperature is small, but not exactly zero, we should still have a very high concentration of particles around $k = 0$, which goes down very quickly as we increase $\boldsymbol{k}$. Of course, for high values of $\boldsymbol{k}$ the function $\bar{n}_k$ should once again be pretty smooth. After all, there are tons and tons of k values, all very finely spaced. The only real problem is for $k = 0$ and $\boldsymbol{k}$ very very small.

The idea, therefore, is that we *can* convert Eq. (4.5) into an integral. But before doing that, we should separate the part of N which is not smooth. Something like

$$N = \sum_{\boldsymbol{k}\text{'s close to } 0} \bar{n}_k + \sum_{\text{other } \boldsymbol{k}\text{'s}} \bar{n}_k. \tag{4.7}$$

The first term contains the non-smooth parts; we will simply call it N_0. Of course, we do not know the value of N_0 yet. Perhaps it can even turn out that $N_0 = 0$. But we already know that, at least for $T \to 0$, N_0 should be non-zero. So we will leave N_0 here hanging as one of the variables of the problem. Henceforth we shall refer to it as the **condensate fraction** because N_0/N represent the fraction of particles which have "condensed" in the $\boldsymbol{k} \sim 0$ states.

The last term in Eq. (4.7), on the other hand, is a smooth sum and can thus be converted to an integral:

$$\sum_{\text{other } \boldsymbol{k}\text{'s}} \bar{n}_k \simeq \int_0^{\infty} \mathrm{d}\varepsilon D(\varepsilon) \bar{n}(\varepsilon).$$

Rigorously speaking, the integral should not start at zero. But it will start somewhere so close to zero, that it doesn't matter. Setting the lower limit of integration to zero will

not make a difference. We therefore conclude that

$$N = N_0 + \int_0^\infty d\varepsilon D(\varepsilon)\bar{n}(\varepsilon). \tag{4.8}$$

4.1 Solving for the chemical potential

Eq. (4.8) should be viewed as an implicit equation for $\mu(N, T)$ and $N_0(N, T)$. We try to find a value of μ which gives us the correct N. If that cannot be done, then we use N_0 to compensate. You will see how it works. It's kind of fun.

First, we make the equation more explicit. Using Eq. (4.6) and setting $x = \beta\varepsilon$, we get

$$\alpha V \int_0^\infty d\varepsilon \frac{\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)} - 1} = \frac{1}{\sqrt{2}\pi^2} \left(\frac{m}{\hbar^2}\right)^{3/2} V T^{3/2} \int_0^\infty dx \frac{\sqrt{x}}{z^{-1}e^x - 1},$$

where $z = e^{\beta\mu}$. Introducing again the De Broglie thermal wavelength

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mT}}, \tag{4.9}$$

yields

$$\alpha V \int_0^\infty d\varepsilon \frac{\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)} - 1} = \frac{2V}{\sqrt{\pi}\lambda^3} \int_0^\infty dx \frac{\sqrt{x}}{z^{-1}e^x - 1}.$$

Plugging this in Eq. (4.8) we then field

$$n = n_0 + \frac{2}{\sqrt{\pi}\lambda^3} \int_0^\infty dx \frac{\sqrt{x}}{z^{-1}e^x - 1}, \tag{4.10}$$

where $n = N/V$ and $n_0 = N_0/V$.

The integral on the right-hand side of Eq. (4.10), is a function only of z. Let us call it

$$g(z) = \frac{2}{\sqrt{\pi}} \int_0^\infty dx \frac{\sqrt{x}}{z^{-1}e^x - 1}. \tag{4.11}$$

Eq. (4.10) is then written more simply as

$$g(z) = \lambda^3(n - n_0). \tag{4.12}$$

It is kind of nice that we were able to write this integral in this way. It is a pity that the integral cannot be solved analytically, but at least we converted it into a function of a *single* parameter z. This makes it much easier to analyze it. A plot of this function is shown in Fig. 6. As can be seen, it is always positive. At the point $z \to 1$ (i.e. $\mu \to 0$) it has the value

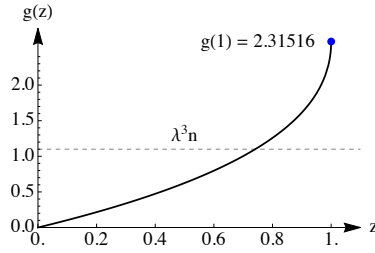$$g(1) = \zeta(3/2) \simeq 2.31516, \tag{4.13}$$

Figure 6: The function $g(z)$ in Eq. (4.11). Since $z = e^{\beta \mu}$, the point $z = 1$ corresponds to $\mu = 0$. The horizontal line represents the typical solution of Eq. (4.14).

where $\zeta(x)$ is the Riemann zeta function.

We now try to solve Eq. (4.10). Fix n at some value (the experimentally determined particle density in the gas). Moreover, let us first look for solutions which have $n_0 = 0$. The equation then becomes

$$g(z) = \lambda^3 n. \tag{4.14}$$

We then start to change the temperature T (which enters into λ) and try to find the value of z which solves this equation. This is tantamount to drawing a horizontal line in the plot of $g(z)$, as depicted in Fig. 6.

If we decrease T (cool down) we increase λ [Eq. (4.9)]. The horizontal line therefore goes up. But eventually a limiting value is reached because the function $g(z)$ stops at $g(1) = 2.31516$. If $\lambda^3 n$ is increased above that, it is impossible to find a z which solves (4.14). This special point therefore defines the **critical temperature for the BEC**,

$$'g(1) = \lambda^3(T_c)n. \tag{4.15}$$

Using Eq. (4.9),

$$\left(\frac{2\pi\hbar^2}{mT_c}\right)^{3/2} n = \zeta(3/2),$$

or

$$\boxed{T_c = 3.3125\frac{\hbar^2}{m}n^{2/3}.} \tag{4.16}$$

The critical temperature occurs at $z = 1$ or $\mu = 0$. A plot of the chemical potential as a function of T will therefore look like that in Fig. 7. For large temperatures $\mu < 0$. As we cool down, it starts going up and then eventually reaches $\mu = 0$ exactly at $T = T_c$.

4.2   Physics below T_c

What happens below T_c? Well, Fig. 6 graphically shows us that it is impossible to find a value of z (or μ) which will solve Eq. (4.11). The only solution, therefore, is to look for solutions which have $n_0 \neq 0$. Below T_c the only solutions are those in which the condensate fraction is non-zero. This is the Bose-Einstein condensation. As the system is cooled sufficiently, a transition occurs at a sharp value T_c, where particles begin to accumulate in the $k = 0$ state. Bose-Einstein condensation is therefore not a condensation in real space; it is a **condensation in momentum space**. The zero
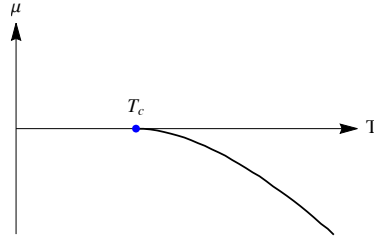
Figure 7: The chemical potential as a function of temperature. Obtained from the numerical solution of Eq. (4.14).
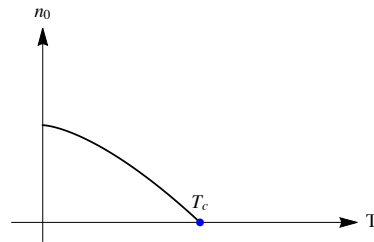

Figure 8: The condensate fraction n_0 as a function of temperature, Eq. (4.18).

momentum state is completely delocalized in space, so the particles are not within the same region of space.

Below T_c, we must therefore return to Eq. (4.12). Now the chemical potential is fixed at $\mu = 0$ and we must instead solve for n_0. That is, we find

$$g(1) = \lambda^3(n - n_0). \tag{4.17}$$

It is convenient to use Eq. (4.15) to substitute $g(1)$:

$$n\lambda^3(T_c) = \lambda^3(T)(n - n_0).$$

Using Eq. (4.9) we can write this more neatly as

$$n_0 = n\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right]. \tag{4.18}$$

This gives the fraction n_0/n of particles which are in the condensate state. When $T \to 0$ this fraction tends to 1: at zero temperature all particles condensed onto the ground-state. As T increases, however, this fraction goes down until reaching zero at $T = T_c$. Of course, please note that it is not n_0 which tends to zero specifically; it is the *fraction n_0/n*. What I am trying to say is that the remarkable feature of $T < T_c$ is that the occupation n_0 is macroscopically large. Above T_c all momentum states have some degree of occupation. But no state concentrates so many particles, so as to have a macroscopic occupation.