The grand canonical ensemble

One of the most important features of 2nd quantization and Fock states, is that deals with different particle numbers in an extremely smooth way. However, that contrasts with real experimental situations, where the total number of particles N is a fixed number.

As an example, suppose we have a lattice with L sites, described by the Fock states

$$|n_1, \ldots, n_L\rangle \tag{1}$$

If our experiment has N particles, then for us it will only be of interest to keep a subset of these states. Namely, those which satisfy $\sum_{i=1}^{L} n_i = N$. If $N = 1, 2, 3, \ldots$, then this bookeeping is manageable. But if N becomes large, it quickly gets insanely cumbersome.

In order not to deal with this, it is convenient to use a Mathematical construction called the Grand canonical ensemble. The idea is to relax the condition that N is fixed and impose instead that only $\langle \hat{N} \rangle$ is a fixed number, where

$$\hat{N} = \sum_{i=1}^{L} a_i^\dagger a_i \tag{2}$$

is the total particle number operator.

Thus, the idea is to allow for the number of particles to fluctuate, so that we can use the states (1) without any constraints. But we let them fluctuate in a such a way that

$$\langle \hat{N} \rangle = N = \text{real number of particles in the experiment} \tag{3}$$

In reality, the number of particles does not fluctuate, so what we are talking about here is only a mathematical construct. However, it can be rigorously shown that in the thermodynamic limit, this mathematical construct gives the same results as the real deal.

In order to be able to tune $\langle \hat{N} \rangle$ so that it can equal the desired value N, we must introduce a new ingredient. It is called the chemical potential and we introduce it as a Lagrange multiplier in the Hamiltonian. That is, we change H as

$$H \rightarrow H - \mu \hat{N} \tag{4}$$

where μ is the chemical potential. Hence, if a system is in thermal equilibrium, the Gibbs state should now get replaced by

$$\rho = \frac{e^{-\beta(H-\mu\hat{N})}}{Z} \qquad Z = \mathrm{tr}\left(e^{-\beta(H-\mu\hat{N})}\right) \tag{5}$$

The logic behind the chemical potential is as follows. Once we have a state like (5) we compute

$$\langle \hat{N} \rangle = \mathrm{tr}\{\hat{N}\rho\} = \frac{\mathrm{tr}\{\hat{N}\, e^{-\beta(H-\mu\hat{N})}\}}{\mathrm{tr}\{e^{-\beta(H-\mu\hat{N})}\}} \tag{6}$$

This will now be a function of μ (and other stuff). We then adjust μ in order to get $\langle \hat{N} \rangle = N$. Thus, the idea is to solve an implicit Equation

$$\boxed{\langle \hat{N} \rangle(\mu) = N \quad \rightsquigarrow \quad \mu(N, T)} \tag{7}$$

where, for completeness, I also noticed that μ will also depend on T.

We will see examples on how to apply this idea below. But before we do so I have a comment to make. Below Eq (3) I said "in reality the number of particles does not fluctuate". I lied. Most times it doesn't. But there are situations where it does.

Recall that thermal equilibrium could be viewed as the result of coupling a system to a heat bath.

The logic behind this is that the bath allows for energy to fluctuate, so that only $\langle H \rangle$ has a fixed value. In the same spirit, there are situations in which not only the energy, but also the number of particles may fluctuate. This corresponds to a bath that can exchange not only heat, but also particles with the system

This type of situation occurs in chemical solutions, for instance, where some semi-permeable membrane allows for particles to be exchanged between system and bath.

Thus, within this picture, μ is to be viewed as a property of the bath, just like temperature.

Example : 1D tight-binding chain

As an example, consider the tight-binding in 1D : including the change in Eq (4), the Hamiltonian now becomes

$$H = \sum_{i=1}^{N} (\epsilon - \mu) a_i^\dagger a_i - J \sum_{i=1}^{L} (a_i^\dagger a_{i+1} + a_{i+1}^\dagger a_i) \tag{8}$$

we already know how to diagonalize this by moving to Fourier space:

(Bosons)
$$H = \sum_k (\varepsilon_k - \mu) b_k^\dagger b_k \tag{9}$$

$$\varepsilon_k = \epsilon - 2J \cos k \tag{10}$$

of course, the same holds for Fermions, we just need to include spin

(Fermions)
$$H = \sum_{k,\sigma} (\varepsilon_k - \mu) d_{k\sigma}^\dagger d_{k\sigma} \tag{11}$$

Now we have a set of independent Bosonic or Fermionic modes. computing equilibrium properties is then very easy. Starting with (9), recall that if

$$H = \omega b^\dagger b \tag{12}$$

Then

$$\text{(Bosons)} \qquad \langle b^\dagger b \rangle = \frac{\mathrm{tr}\{ b^\dagger b\, e^{-\beta\omega b^\dagger b} \}}{\mathrm{tr}\{ e^{-\beta\omega b^\dagger b} \}} = \frac{1}{e^{\beta\omega} - 1} \tag{13}$$

which is the Bose-Einstein distribution that appeared many times before. This same structure will appear for each mode $\langle b_u^\dagger b_u \rangle$ in (9), with $\omega \to \varepsilon_u - \nu$. Thus

$$\text{(Bosons)} \qquad \boxed{\langle b_u^\dagger b_u \rangle = \frac{1}{e^{\beta(\varepsilon_u - \nu)} - 1}} \tag{14}$$

and the total number of particles, in the bosonic case, will be given by

$$\text{(Bosons)} \qquad \boxed{\langle \hat{N} \rangle = \sum_u \frac{1}{e^{\beta(\varepsilon_u - \nu)} - 1}} \tag{15}$$

In the case of Fermions the situation is analogous. Except that now if

$$H = \omega d^\dagger d$$

with d being Fermionic operators, then

$$\langle d^\dagger d \rangle = \frac{\mathrm{tr}\{ d^\dagger d\, e^{-\beta\omega d^\dagger d} \}}{\mathrm{tr}\{ e^{-\beta\omega d^\dagger d} \}} = \frac{0 + (1) e^{-\beta\omega}}{1 + e^{-\beta\omega}}$$

where I used the fact that tr = sum of eigenvalues and the eigenvalues of $d^\dagger d$ are 0 and 1. Thus we find

$$\langle d^\dagger d \rangle = \frac{\mathrm{tr}\{ d^\dagger d\, e^{-\beta\omega d^\dagger d} \}}{\mathrm{tr}\{ e^{-\beta\omega d^\dagger d} \}} = \frac{1}{e^{\beta\omega} + 1} \tag{16}$$

which is the Fermi-Dirac distribution that also already appeared to us when we talked about qubits.

Again, going back now to the multimode Hamiltonian (11), we get

(Fermions)

$$\boxed{\langle d_{u\sigma}^\dagger d_{u\sigma} \rangle = \frac{1}{e^{\beta(\varepsilon_u - \mu)} + 1}} \tag{17}$$

and the total number of particles became

(Fermions)

$$\boxed{\langle \hat{N} \rangle = \sum_{u\sigma} \frac{1}{e^{\beta(\varepsilon_u - \mu)} + 1} = 2 \sum_{u} \frac{1}{e^{\beta(\varepsilon_u - \mu)} + 1}} \tag{18}$$

where in the last equality I already carried out the sum over $\sigma = \pm 1$.

Comparing Eqs (14) and (17) for Bosons and Fermions, we see there is at least one quite striking difference. In both case $\langle b_u^\dagger b_u \rangle$ and $\langle d_w^\dagger d_w \rangle$ are number operators and thus should always be strictly non-negative. In the case of fermions this will always be true, whatever is the value of μ. But for bosons this is not necessarily the case. We see that if $\varepsilon_u - \mu < 0$ then $e^{\beta(\varepsilon_u - \mu)} < 1$ and (14) will become negative. Of course, μ is a global parameter for all modes in the system, so this consistency condition should hold for all values of k. Where we arrive at

$$\boxed{\mu < \min\{\varepsilon_u\}} \qquad \text{(Bosons)} \qquad (16)$$

This is a fundamental constraint that exists only in the bosonic case. And, we will learn below, it is intimately related to the idea of Bose-Einstein condensation

Now let's discuss how to actually determine the chemical potential μ. That is done by imposing Eq (3). We first convert (15) into an integral and then equate it to N:

(Bosons)
$$\langle \hat{N} \rangle = \frac{L}{2\pi} \int_{-\pi}^{\pi} dk \, \frac{1}{e^{\beta(E_k - \mu)} - 1} = N \tag{17}$$

This is now an implicit equation for $\mu(N, T)$. It is interesting to note how μ only depends on the lattice filling $n_0 = N/L$.

(Bosons)
$$\boxed{\frac{1}{2\pi} \int_{-\pi}^{\pi} dk \, \frac{1}{e^{\beta(E_k - \mu)} - 1} = n_0} \tag{18}$$

The formula for Fermions is quite similar. Starting from (18) we get

(Fermions)
$$\boxed{\frac{2}{2\pi} \int_{-\pi}^{\pi} dk \, \frac{1}{e^{\beta(E_k - \mu)} + 1} = n_0} \tag{19}$$

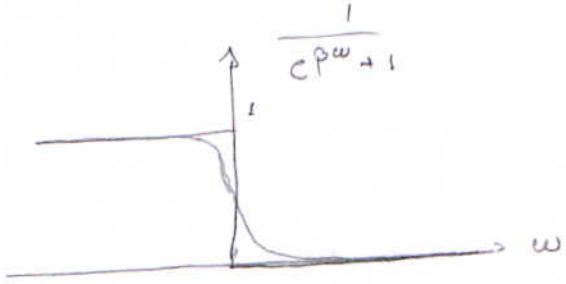
The integrals in (18) and (19) have no pretty solution, but may be expressed as an infinite series of special functions. Here we shall not take that route. Instead, let's solve it numerically.

For simplicity we set $\epsilon = 0$ and $J = 1$ in Eq (10). The former just defines an irrelevant zero of energy and the latter sets the energy scale. The only free parameters in (18) and (19) are then β and n_0. We also note that since now $\mathcal{E}_k = -2\cos k$, the condition (16) for Bosons becomes

$$\mu < -2 \tag{20}$$

The numerical analyses are shown in the accompanying Mathematica notebook

It is also fun to play with the $T=0$ limit for Fermions. The Fermi-Dirac distribution (16) has the following shape



when T is finite it goes down smoothly. But as $T \to 0$, it becomes a step function. Thus, in the limit $T \to 0$ Eq (19) becomes

$$\frac{1}{\pi}\int_{-\pi}^{\pi} dk\ \Theta(\mu - \mathcal{E}_k) = n_0 \tag{21}$$