**Independent Particles**

We’ll continue examining the various ensembles in the independent particle approximation.

**Grand Canonical Ensemble**

Now let’s move to the Grand Canonical Ensemble. And as for Ξ, first we’ll do the classical case.



where ξ = ε – μ. So we have:



and:



Another way to work that out is:



Eitherway, we can then form the Free Energy of the system, L = -kTlnΞ, which gives us:



Now let’s look at the average number of particles in the system. This is given by,



And from this we can infer the average occupation number per state is,



And consequently, we can determine the expectation of the energy, etc. from the Thermodynamic relations or from this average occupation number formula. Now consider the quantum indistinguishable situation. Suppose we have some many body system. We can parameterize a typical many body state in the following way,



where m = 1, 2, …, M label the possible quantum states |1>, |2>, …, |m>, … |M> (M could/will typically be ∞), and nm are occupation numbers. For bosons nm can range from 0 to infinity, and for fermions they can range from 0 to 1. Let’s call nmax the upper bound, whichever it is. In the Canonical Ensemble, we’d have the requirement that N = Σini. But in the Grand Canonical Ensemble, we are summing over all N as well, and so basically there is no constraint on what the ni’s can be. And let’s say our Hamiltonian is given by:



where the sum runs over all single particle quantum states, just as m did above. And more to the point we can represent the operator:



Let us calculate Ξ, and L. So the grand canonical partition function can be written as:



So we see that we’d have for bosons [using Σrn = 1/(1-r)] / fermions, the partition function



where ξ = ε – μ. We can then form the (Landau) Free Energy of the system,



So,



Now let’s look at the average number of particles in the system. This is therefore given by (see TD folder for instance),



where sum goes over all quantum states. And from this we can infer the average occupation number per energy level,



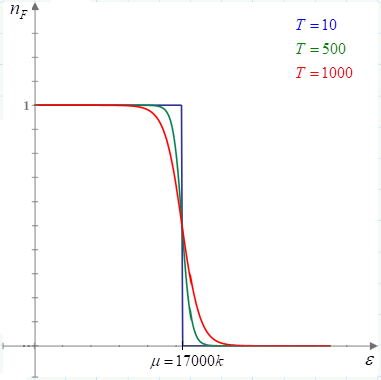
We could’ve also obtained this result if we had imagined a ‘system’ with a single level, |n>, in thermal and chemical equilibrium with the rest of ensemble. Then for that system, we could say,



and of course a derivative w/r to μ would give us our expected particle number, which would come out to be what we have above. Might notice that for ε >> kT, i.e., large energies nF/B reduces to the distinguhishable particles distribution too. So this is how we get classical statistics from quantum statistics. Often this is written,



What do these distributions look like? First we need to know typical values of z, for N large and fixed. Consider fermions first. We know (see Thermodynamics folder) that μ is basically the energy added to the system by the addition of one particle minus the heat required (to be subtracted) to keep the entropy constant. So μ ~ ΔE – TΔS. Now for a fermionic system, near T = 0, we expect ΔE to be positive due to the Fermi exclusion principle, and expect ΔS to go to zero. So μ should be some positive constant at T = 0. On the other hand, for large T we have that E ~ NT and S ~ NlnT. Therefore we expect μ to go to as T – TlnT ~ -∞ in the large T limit. For z then, we expect z = eμ/T → econst/0 → ∞ for small T and z = eμ/T → e(T-TlnT)/T → e1-ln(∞) = 0 in the large T limit. I plotted nF(ε) for an electron gas (i.e., used its density of states) with μ set so that the particle density n = N/V = ∫dερ(ε)nF(ε) is 1 per (0.5nm)3, which is somewhere around typical electron density in a metal. The requisite μ is 17000k (k = Boltzman constant) ~ 1.5eV. Note as T increases, μ is constant, but N technically decreases to keep μ the same. Still, it hardly does at all, so can treat it as constant. Can see that at T = 0 we have a box distribution – all energy states are filled up to the chemical potential. As T increases, the sharp cut-off smears out to a width ~ kT on either side. This is due to thermal energy exciting electrons below (and close to) the chemical potential to states above (and close to) the chemical potential. Thus the distribution gets depleted below μ and repleted (?) above μ. Can see though, that even past most materials’ melting points, the box-like distribution persists.



Can see that the Fermi distribution function is symmetric about the chemical potential, in the sense that, starting at ε = μ it goes down to the right as much as it goes up, to the left. In other words…

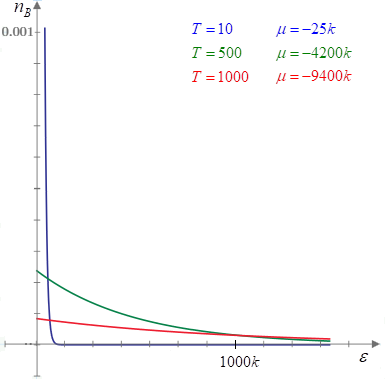


So we could approximate the distribution at the chemical potential as a straight line. The slope would be:



The distance from the μ to either nF = 1 on the left or nF = 0 on the right, is about (1/2)/(β/4) = 2kBT. So the width of the ‘window’ within which the fermions get depopulated to the left of μ, and populated to the right of μ, is about 2kBT.

Now a boson gas. What would its typical μ’s be? Now for a bosonic system, near T = 0, we expect ΔE to be ?? seems like it could be positive, or zero if we define the single particle ground state energy level to be 0. I’m just going to go with this option. Then the μ = 0 as T = 0. For high T, by the same arguments as the fermion gas, we have μ ~ -TlnT → -∞ as T → ∞. Then as T → 0, we have z = eβμ → e0/kT → 1, and as T → ∞, we have eβμ → e-TlnT/T = e-lnT = e-ln(∞) → 0. Our argument that z → 1 as T → 0 was a little convenient, but we can say that z can’t get larger than 1 because otherwise nB(ε) would go negative. Some typical plots. I plotted nB(ε) for a 4He gas (i.e., used same free particle density of states (e- density of states), but used 4He mass) with μ set so that the particle density n = N/V = ∫dερ(ε)nB(ε) is 1 per (0.5nm)3, which is somewhere around typical liquid 4He density, at least at really low T….whatever. The requisite μ is heavily dependent on T, unlike in the fermion case, μ ~ -0.002eV at T = 10K, and μ ~ -0.8eV at T = 1000K. As T increases, the higher energy states get more populated, and conversely as T decreases the ground state increasingly becomes the one overwhelmingly populated.



In any event, with the distributions in hand, we can determine the expectation of the energy, etc. from the thermodynamic relations or from this average occupation number formula. The distribution function is (presuming indistinguishable particles – otherwise no 1/N!):



Note N is a variable here, just as **r**, and **p** are. In practice though, N will vary only slightly around its mean value, which is set by the chemical potential. And so N is ‘practically’ a constant, just as in the Canonical ensemble, the system energy is practically a constant set by T, even though it can technically vary. Should prove sometime that for independent particles, we can write the distribution function/density matrix as:



where |ψn> are the single particle eigenstates.

**Example**

A quantum dot is constructed such that it has just three energy levels, with energies: E, 2E, and 3E. The chemical potential in the system has the value μ = 2E and the temperature is given by T = E/2kB. What will be the expected number of electrons populating the quantum dot? If the quantum dot Hamiltonian has time reversal symmetry, how does this affect the result?

So we’ll use the Fermi distribution formula:



And plug in the values,



If we have time reversal symmetry, then the energy levels must be at least two-fold degenerate. This would increase the expected value for N to at least N = 2(1.5) = 3 electrons.

**Grand Canonical Convective Ensemble**

Now let’s move to the Grand Canonical Convective Ensemble. And as for ΞC, first we’ll do the classical case.



Performing the sum, we have:



where now ξ(c) = ε – μ – **u**·**p**. We can then form the Free Energy of the system, LC = -kTlnΞC, which gives us:



Now let’s look at the average number of particles in the system. This is given by,



And from this we can infer the average occupation number per state is,



And consequently, we can determine the expectation of the energy, etc. from the Thermodynamic relations or from this average occupation number formula. But should mention that the chemical potential is now different than the non-moving chemical potential. Let U refer to the energy about the center of mass, and P be the total momentum. Then,



And filling this into ξ(c), we get:



which is just how we’d expect things to turn out for a system moving uniformly with velocity **u**. Now consider the quantum situation. Suppose we have some many body system. We can parameterize a typical many body state in the following way,



where i = 1, 2, …, M label the possible quantum states (M could/will typically be ∞), and nm are occupation numbers. For bosons ni can range from 0 to infinity, and for fermions they can range from 0 to 1. Let’s call nmax the upper bound, whichever it is. In the Canonical Ensemble, we’d have the requirement that N = Σini. But in the Grand Canonical Ensemble, we are summing over all N as well, and so basically there is no constraint on what the ni’s can be. And let’s say our Hamiltonian is given by:



where the sum runs over all single particle quantum states, just as i did above. And more to the point we can represent the K operator as:



Here we have assumed that we can diagonally represent both H and P in terms of energy eigenstates. This would only be true for free states basically, where cm = ck, the momentum annihilation operator. If that’s not possible, i.e. if we have a single particle potential, then cm and ck would just be different, but it seems we should still be able to exactly evaluate the Trace below? But there would no longer be simultaneous exact eigenstates of both H and P. Anyway, supposing it’s free, let us calculate Ξc, and Lc. So the grand convective canonical partition function can be written, where En, Nn Pn are the energy and number of particles, and momentum of particles respectively of the nth state.



So we see that we’d have for bosons [using Σrn = 1/(1-r)]/fermions, the partition function



where ξ(c)m = εm – μ – **u**·**k**m. We can then form the Free Energy of the system,



So:



Now let’s look at the average number of particles in the system. This is therefore given by (see TD folder for instance),



where sum goes over all quantum states. And from this we can infer the average occupation number per energy level,



Might notice that for E >> kT, i.e., large energies nF/B reduces to the distinguhishable particles distribution too. So this is how we get classical statistics from quantum statistics.

The distribution function is (presuming indistinguishable particles – otherwise no 1/N!):

