**Independent Particles**

Our results so far are general for systems. Not surprisingly, when there are no interactions between particles, our calculations simplify considerably. Well, there are *some* interactions, since otherwise our particles would not be able to exchange momentum and energy, and thereby come to thermal equilibrium. But we’ll basically assume these are just short range contact forces. A quick note. Apropos classical situations, I’ll presume a spectrum like this:



But it could very well (probably) be the case that there are internal d.o.f., like spin, vibration, etc., which I’m not taking into account, explicitly. But then we’d have:



This will change formulas below a bit if this is the case (even if εint = 0, but the internal d.o.f. persist, like for spinfull particles whose spins don’t involve themselves in the energy). For instance, we’ll see that the high T Fermi gas limit, where spin is explicitly taken into account, doesn’t match up in all respects to the classical gas case where no internal d.o.f. of freedom are presumed. I think that while the internal energy, pressure, and heat capacity match up, the chemical potential and entropy, for example, don’t. I would generally expect this to be the case – that energy considerations don’t change if the extra d.o.f. don’t have an energy component, but that entropy considerations do, since we do have extra d.o.f. Presumably our classical calculations would match up to the quantum ones entirely, in the high T limit, if we accounted for spin from the first, in our our classical approximation.

**Microcanonical Ensemble**

Here’s an interesting calculation. Let’s say we’re at high enough temperatures that we can treat our particles classically, and say we’re in the microcanonical ensemble. We can actually make some progress on calculating S in this ensemble. Consider a system of independent particles with energy,



Then (presuming indistinguishable particles – otherwise no 1/N!),



We have to introduce the inverse Laplace transform representation of the delta function,



But then this would be given by:



where we make a definition,



and then we can write:



And the entropy can be written therefore as:



Can’t really do that integral unless we know what φ(r) is. But we will do it later for special case of free gas and harmonic oscillator, though that isn’t the limit of the cases we could apply this formalism to. In the large N limit, there is probably a way to do this via the saddle-point method whereby we could get it into form that connects directly to that which we would find in the Canonical Ensemble. But I’ll leave that investigation for later. Also, we did this for classical particles, but I imagine this could be done in a suitably modified way for quantum particles, especially since we can get many of the other potentials for independent quantum particles.

**Classical single particle distribution f(r,p) by direct integration of classical many-body f(ri,pi)**

Here’s another interesting calculation. Let’s get the single particle distribution function from the many-body distribution function. From the first file, we said this would be:



And using the symmetry of the distribution function w/r to interchange of particles, we also said:



Let’s try to work this out,



which brings us to:



For our purposes, we can approximate (x) as 1 (weak potential approximation, say), as we’ll already have the φ(r) dependence we need – doing a saddle point approximation in the large N limit is probably the best way to do this. So now factor out the E-p2/2m-V(r) term from x…the limits of integration aren’t really affected since λ is an arbitrary constant somewhere to the right of the origin.



where Γ is the gamma function. Since E >> p2/2m + φ(r) (because E is the system energy while p2/2m + φ(r) is just a single particle’s energy), this affords an accurate approximation.



Now E/N should be a constant. Let’s define temperature via E = [(3/2)(N-1)-1]kBT. Then,



Now use fact that limit (1-x/n)n, as n → ∞, is e-x. So now can say,



All we’re really interested in is the r and p dependence, which lies wholly within the exponential, the rest is just a prefactor which we can determine from normalization. So we basically just get the expected distribution from the *canonical* ensemble.



where of course,



Remember β here has been ad hoc defined to match the known temperature dependence from the Canonical ensemble. But otherwise, it would just be ‘some parameter’. Obviously there is a much easier way to do to this in the Canonical Ensemble, but I think it’s cool that we can get it from the many-particle distribution function in the Microcanonical ensemble. Multiplying by N gives us the number of particles in that state:



Finally, to make contact with later stuff, observe that we can write this as:

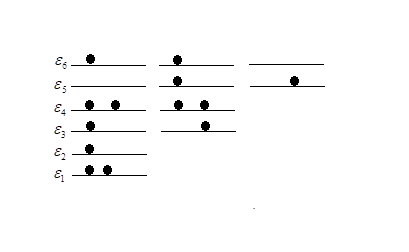


where μ is just ‘some constant’, for us, that is clearly given by: eβμ = N/Z1. μ could be otherwise ascertained by requiring the sum over states gives us the total particle number:



**Quantum single particle distribution fk by combinatorial arguments**

Let’s consider again the single particle distribution function, from a different point of view. We’ll generalize our discussion to include quantum particles (distinguishable or indistinguishable). Say we have total energy E, and N particles, each of which can occupy the single particle states with energies εj, where j ranges from say 0 to J. The εj are unique, but may comprise a degenerate subspace. Let gj be the degeneracy of that subspace/energy level. Such a setup is illustrated below; each horizontal line is a state.



We can distribute the particles subject to two requirements:



where nj is the number of particles occupying the set of states with energy εj. And if we’re dealing with Fermions, then there is the additional requirement that n for any particular single state can’t be greater than 1 (this would rule out the distribution above). We’d like to figure out what nj will be. Now according to the fundamental postulate, every allowed distribution is equally likely. But many different allowed distributions will correspond to the same set of nj’s (for instance, if dealing with Fermions, we could do n5 = 1 in three different ways, n5 = 2 in 3 different ways, and n5 = 3 in one way, and n5 = 4 in 0 ways). There will be a most probable distribution, and this will be the one with the greatest multiplicity. So we’d like to work out what the multiplicity, W, is for any given distribution. So in the classical case, we’d have:



For instance in the diagram above, the assignment to the ε4 level would be say particles (1,7,11,4), which would be considered separate from the asignment (1,7,11,5). So this multiplicity is accounted for by the N!/Πnj! term. And then the Πgjn\_j term accounts for the number of ways to distribute that set of particles to the particular states within that degenerate level, basically we have the same gj choices for each particle, as there is no limit on occupancy. And then we divide by N!, as we’re instructed to from the Gibbs Paradox thing. Then for Fermions we have:



The (1) is due to fact that they are indistinguishable so there is only 1 way to break them up into those sets. And then, considering ε5 in the diagram above, say, there are 3 choices for particle one, and then 2 choices for particle two [which translates to gj!/(gj-nj)! choices], but then we have to divide by 2! [i.e. nj!] to account for the indistinguishability of the particles]. To segue into the boson multiplicity, I’ll mention one way to look at the g!/n!(g-n)! term. If we label the states within a degenerate energy level {1,2,3,4,…,gj}, then assigning the nj particles to the states consists of constructing an nj-element subset of {1,2,3,4,…,gj}, but where once you pick a number, you can’t pick it again (so number of subsets w/o replacement). And the number of ways to do this is gj!/(gj-nj)!. And last let’s do Bosons.



The (1) is due to fact that they are indistinguishable so there is only 1 way to break them up into those sets. And then the next term is interpreted as follows. If we label the states within a degenerate energy level {1,2,3,4,…,gj}, then assigning the nj particles to the states consists of constructing an nj-element subset of {1,2,3,4,…,gj}, but unlike with the fermions, we can pick the same number again (so number of subsets w/ replacement). And the number of ways to do this is (gj+nj-1)!/n!(gj-1)!. For instance, revisiting the ε5 level. Our options are: put all two particles in either of the three states (3 options), or put them all in different states (3!/2!1! = 3 options). So there is a total of 6 options, which is the same as: (3+2-1)!/2!2! = 4!/4 = 6.

Now we’d want to find the {nj} – we’ll call it {nj\*} – which maximizes these W{nj}’s. It’s equivalent, and easier, to find the {nj} which maximizes S{nj} = kBlnW{nj}. Note that S{nj} is not the system’s entropy; rather, if we added up the multiplicities of each possible assignment of particles to energy levels i.e. calculated W = Σ{n\_j} W{nj}, and then took the ln of *that*, S = kBlnW, *then* we’d have the entropy. Nonetheless, it will turn out that the {nj\*} which maximizes S{nj} far surpasses all other particle assignments in its contribution to the entropy, and so it is a good approximation to say S = S{nj\*}. So let’s construct S for these guys, We’ll use Stirling’s approximation: ln(N!) = NlnN-N.



Now we want to maximize S but subject to the constraint that the energy and total particle numbers are constant. So for the classical/distinguishable case, we have:



I won’t go into it now, but we’ll see in next file we’ll see that we should interpret λ2 as β = 1/T, and λ1 as -μ/T, where T is the temperature, and μ the chemical potential. If we divide both sides by gk, and rename nk to be the number of particles in a *single* state, then we have:



This is the occupation number expectation for classically indistinguishable particles (basically the high temperature limit of quantum indistinguishable particles) To get the probability distribution, we’d just do fk = nk/N. This of course matches what we found above, except for the 1/h3 factor which just has to do with the fact a classical state has size h3. Now let’s do fermions.



If we divide both sides by gk, and rename nk to be the number of particles in a *single* state, then we have:



To get the probability distribution, we’d just do fk = nk/N. And last let’s do Bosons,



Turns out our Stirling approximation doesn’t work as well as we’d like here, and the correct result, is obtained in the gk >> 1 limit, where we can say, for the occupation number of a *single* state with energy εk,



To get the probability distribution, we’d just do fk = nk/N. Note that β and μ are ‘just parameters’ for us. But of course we know their meaning from the Canonical and Grand Canonical Ensembles. How could we determine μ for instance, and this would be done by demanding,



As seen above, this is easily done for the distinguishable particles case.



But for the other two cases, it’s harder to do that sum over k and get μ explicitly. We’ll see these results again when we look at the Grand Canonical Ensemble, where there, μ is treated as a canonical variable that will be fixed, instead of N.

**Canonical Ensemble**

Let’s consider the case of identical non-interacting particles, in say the canonical ensemble. The energy of the system would be:



And then the classical partition function would work out to:



where ε(r,p) = p2/2m + φ(r). So we have:



where,



The Free Energy follows:



The many-body distribution function would be,



where classically, ε(r,p) = p2/2m + φ(r). And we can get the single particle distribution function from f(ri,pj). Since it’s an independent product of terms, in the classical case we have:



So multiplying by N to get the occupation number, we have:



And like before, we can introduce the parameter (chemical potential of course) μ via eβμ = N/Z1 to write this as:



At least that’s one way to get it. This was a lot easier to get than in the microcanonical ensemble. We should expect this anyway; we can consider a given particle of the system to be in thermal contact with the other N-1 particles in the system at temperature T, in which case, the probability it occupies any one of its energy levels ε(r,p) is proportional to e-βε(r,p). The constant of proportionality is then 1/(2πℏ)3Z1 – in order to make distribution normalized.

What about the quantum indistinguishable particle cases? Not sure how to easily construct F in those cases. But for the single particle occupation numbers, we could do an analysis similar to what we did in the microcanonical ensemble section. Instead of finding the distribution of particles that maximizes S, we’d find the distribution which minimizes F = E – TS (since F is the potential minimized in the canonical ensemble). This is the same thing as maximizing S – E/T. Comparing our minimization calculation above to this, we see that it’s the same, just with the now explicit identification of the Lagrange multiplier λ2 as 1/T. We’d have to do this calculation w/ the constraint that particle number is conserved, and so we’ll still have our λ1 Lagrange multiplier involved, which will be ultimately identified as -μ/T again. So once again, for the quantum indistinguishable cases:



where β = 1/T. μ would still be ‘some parameter’ at this point fixed by the requirement that summing nk over all states gives us N. Of course we know from the next file that it’s the chemical potential.