**Ensembles**

Now we’ll calculate the form the many body distribution function takes in different ensembles. Might look at that one file somewhere for work on directly calculating this from Random Matrix Theory. But I’ll just go the standard macroscopic route here for now. As a rule, it would be hopeless to calculate this starting from the equations of motion of all the particles. We have to employ some statistical inference about how likely the system is to be in any of its particular states {**r**i,**p**j} (classically) or |n> (quantumly).

**Microcanonical Ensemble**

We’ll start with the fundamental postulate of equilibrium statistical mechanics, regarding the distribution function feq(n). It states that in a closed system, with energy E, the system is equally likely to be in any one of its Ω(E) microstates. We’ll recall that a *macrostate* is roughly a specification of E, X, N, or some such, where E is internal energy, and X is some parameter that appears in the system’s energy levels, like V, or field if there is one. The energy levels of the system, upon solving the Schrödinger equation, would appear to be εn(X,N). So specification of E,X,N is a specification of the energy levels (via X and N), and of the energy itself εn. A microstate is any one of the states consistent with those parameters and that energy level. The degeneracy of the Hamiltonian corresponding to that eigenvalue is Ω(E), i.e., the number of microstates. The fundamental postulate of statistical mechanics is:



And so *basically*,



But properly accounting for how we count states, classically, the density matrix / distribution function in the classical and quantum situations would be as follows (presuming indistinguishable particles – otherwise no 1/N!):



And the sum in that quantum guy extends over all many-body states with energy E (and there are Ω(E) of them). Feel like pointing out that classically, Ω(E) is the density of states, i.e., the number of states between (E, E+dE), divided by dE.

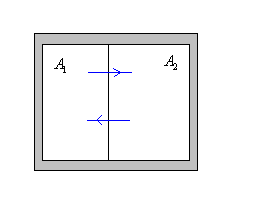
We can obtain more specific quantity averages like particle density, density fluctuations, momentum density, etc., as discussed in the prior file via:



Our result for f is somewhat inimical to our definition of f as a probability distribution of the system constructed from states of the system *actually* sampled within the time interval (t, t+τ), as our result would imply that the system must have actually visited every possible microstate exactly once (or at least the same number of times) during that interval. This can’t *literally* be true, since for instance an ideal gas restricted to a container with volume V, will not have explored the microstate whereby it momentarily confines itself to a volume V/2, say. We might imagine that this would be true if we set τ → ∞. The fact that we can *practically/conceptually* restrict τ to a small time interval, while *mathematically* using the super-large time interval result in its place is one version of the Ergodic hypothesis, I think. But it won’t always be a legit replacement – for instance meta-stable states I think.

**Relation between f and Thermodynamic Potential**

We can relate f to a thermodynamic potential as well, and along the way, obtain a mathematically precise formula for temperature, entropy, etc.. We know from thermodynamics that entropy is maximized under the same circumstances (closed to energy and particle transfer). And we can use our postulate to construct a likely candidate for the entropy.



So let’s consider two systems in thermal and particle contact. Question we’d like to address is the following: what energy, and particle number partition: E1, E2 = E0 – E1, and N1, N0 – N1 will the system A0 settle in to? From the equal a priori postulate it is the one which possesses the largest # of microstates. So what equation characterizes this situation? Well want to find the following. Maximize Ω w/r to varying E1, N1, subject to constant E0, N0. We have the two conditions:



Comparing to what we know from TD, namely that in equilibrium, two systems exchanging energies and particles will equate their temperatures and chemical potentials, this suggests the following identifications. First, that:



where k is the Boltzman constant (can take it as a definition of k I suppose). And then it follows from this (via dS = dU/T – (p/T)dV – (μ/T)dN) that:

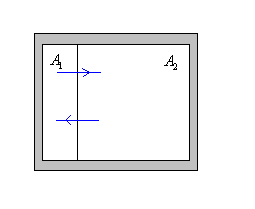


We can take the first line as the mathematical definition of temperature, by the way. Expectations of various quantities can now be obtained. If it is a thermodynamic quantity, then it can be obtained from the entropy, and other thermodynamic potentials constructed from it.

\* not sure where to put this, but I should note that the process of coming to equilibrium in a closed system requires *some* interaction between particles, even if very weak. If we had a system of truly independent particles, which never interacted with each other, then they would never exchange energy, and the system would never regress to the equilibrium distribution. Just keep in mind when doing problems involving independent particles, like ideal gas or free spins in a magnetic field.

**Canonical Ensemble**

Now let’s consider a system A1 connected to a thermal bath A2, and much smaller than it energy-wise.



This system A1 can, thanks to its ability to exchange energy with the bath A2, occupy any of its microstates with energy E1 subject to the formal constraint that E1 + E2 = E0, and we’d like to consider the probability it will do so. So consider the two systems A0 = A1 + A2 in thermal equilibrium. Again, we say A1 << A2 and E1 << E2. What is the probability A1 is in any *one* of its microstates with energy E1? We have the probability f1(E1) is:



Now take the ln of both sides and Taylor expand…



Exponentiating, we get:



And moreover, the density matrix in the quantum and classical situations would be (presuming indistinguishable particles – otherwise no 1/N!):



where the sum extends over *all* many-body states with particle number N, regardless of energy, and H is the quantum mechanical Hamiltonian operator. The first bottom row formula follows from Σe-βE\_n|ψn><ψn| = Σe-βH|ψn><ψn| = e-βH(Σ|ψn><ψn|) = e-βH, because Σ|ψn><ψn| is a resolution of identity. The formula for Z follows from Σe-βE\_n = Σ<ψn| e-βH|ψn> = Tr(e-βH). And we can obtain more specific quantity averages via:



like particle density, density fluctuations, momentum density, etc., *if* we know the many-body states associated with the microstates the system can occupy.

**Relation between f and Thermodynamic Potential**

We can use this formula to work out an expression for the free energy. So we can say, where recall Ω(E) is the number of microstates with a given energy,



Now the summand is highly peaked, in practice, about some particle energy E\*(T) [the energy at which it’s peaked will depend on what T is]. And so to very good approximation, we can just replace the sum with the value of the summand at that one particle E\*. So now we have:



where we recognize S = klnΩ. Taking ln of both sides, we have



It’s interesting to calculate the heat capacity. And we can see that it is simply a measure of the energy fluctuations about the average, i.e. the variance:





The variance/fluctuation in the energy is given by



So moments are obtained by derivatives of Z, and cumulants are obtained via derivatives of lnZ. We’ll also observe,



So interestingly, the heat capacity at constant volume measures the thermal variation in energy. Note this says relative energy fluctuations are,



This is negligible for N > 10 000 particles or so. This will in general be true regardless of the type system, as CV will always scale with N, and E2 will always scale with N2. And usually we will have something like 1023 particles, so that relative energy fluctuations will be like 1/1011. This demonstrates that in the canonical ensemble, where T is fixed, and energy allowed to vary, the energy is still *practically* constant. So whether we use the canonical ensemble or the microcanonical ensemble is user’s preference. They will give the same results (under aforementioned conditions on N). We just have to use the E associated with the given T, or vice versa. This argument also justifies our derivation of F = -kTlnZ, as the demonstrably small fluctuations in E give support to our approximation of the Z sum with the most probable value in the sum. Here’s another way to argue the same thing. Let’s go back to:



and do a Taylor series expansion of F about E\*,



F´(E\*) should be zero as it’s the peak. And let’s approximate the sum as an integral (this will mess up our units but whatever)



Now can form F = -kTlnZ,



Now we expect that in the the thermodynamic limit (large N, large V, keeping density constant), F should go as N (F being an extensive variable – see Thermodynamics Potentials stuff). E is also an extensive variable. So F´´ = d2F/dE2 should go as N/N2 = 1/N. The sizes of our terms are:



In the large N limit N >> lnN, so we are justified in saying,



Another way to look at this is to go back to:



The summand is a Gaussian distribution obviously. Comparing to the standard Gaussian form, we see the mean and variance of E are:



and in the Thermodynamic limit, these go as:



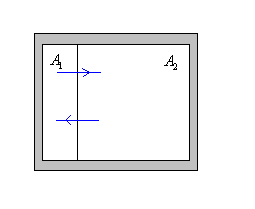
So the relative fluctuations of E will be:



So in the large N/thermodynamic limit, we can say E is a single value, E\*, and so we can skip evaluating the sum over E’s and just evaluate the summand at E\*. It’s true though that we will always claim F = -kTlnZ, regardless of N, so it might be that this is just a way to demonstrate the equality of the two in the large N limit. Whatever.

**Gibbs Ensemble (constant T and p)**

Now let’s consider a system in a thermal/volume bath, and much smaller than the bath energy/volume-wise. By this mean that A1,2 can exchange energy and volume (via a moveable partition). We’ll presume that the energy/volume exchange is small enough w/r to A2 that it retains a relatively constant temperature and pressure.



So A1 can now occupy any of its microstates with any volume, and we’d like to consider the probability it will do so. So consider two systems A0 = A1 + A2 in thermal and ‘volume’ equilibrium. Let’s say A1 << A2 and E1 << E2, and V1 << V2 What is the probability A1 is in any *one* of its microstates with energy E1, and volume V1? Then we have:



Now take the ln of both sides and Taylor expand…



(we know that S = klnΩ and that since dS = (dE + pdV - μdN)/T, it follows that ∂lnΩ/∂V = βp --- or we can adapt the analysis we did in the microcanonical ensemble to identify β and μ, this time replacing μ,N with p,V). Exponentiating, we get:



And moreover, the density matrix in the quantum and classical situations would be (presuming indistinguishable particles – otherwise no 1/N!):



where the sum extends over all many-body states with any energy or volume. And for what it’s worth, generic averages in this ensemble would be given by:



**Relation between f and Thermodynamic Potential**

We can use our result to work out an expression for the Gibbs free energy. Using manipulations similar to the canonical ensemble:



where V´, E´, are an allowed volume and energy the system may have, and Ω(V´,E´) the number of microstates with that volume and energy. Then like above we can say that there will be one volume, V, and energy, E, overwhemingly more probable than the others. And this allows us to approximate the sum with just that one term,



Of course klnΩ = S. And so we have:

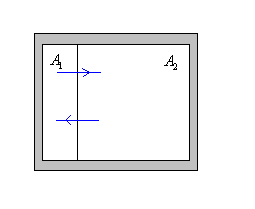


Thus,



**Grand Canonical Ensemble**

Now let’s consider a system in a thermal/particle bath, and much smaller than the bath energy/particle-wise.



This system can now occupy any of its microstates with any particle #, and we’d like to consider the probability it will do so. So consider two systems A0 = A1 + A2 in thermal and chemical equilibrium. Let’s say A1 << A2 and E1 << E2, and N1 << N2 What is the probability A1 is in any *one* of its microstates with energy E1, N1? Then we have:



Now take the ln of both sides and Taylor expand…



Exponentiating, we get:



And moreover, the density matrix in the quantum and classical situations would be (presuming indistinguishable particles – otherwise no 1/N!):



(and Trace would extend over all many-body states, |Ψn>, of any particle number). And we can obtain more specific quantity averages via:



like particle density, density fluctuations, momentum density, etc., *if* we know the many-body states associated with the microstates the system can occupy. Also, note that the distribution functions would be normalized according to:



And the trace (Tr) is taken over all states with any particle number.

**Relation between f and Thermodynamic Potential**

We can use our result to work out an expression for the Landau free energy. Making manipulations similar to before,



And so we have:



Now let’s look at a few derivatives. We can get energy expectation directly from Ξ, but it’s a little more complicated now. So for instance,



and so,



Let that suffice for E. And then also,



So again, moments are given by derivatives of Ξ, and cumulants by derivatives of L (lnΞ). In the canonical, grand canonical ensembles, fluctuations of E and N about their averages are small and we can, as we did in the canonical ensemble, associate these average quantities with the actual values of the internal energy and particle number of the sytem. Interestingly, we can relate the thermal compressibility with fluctuations in particle number (this is shown, at least, for fermionic system near T = 0 in the Condensed Matter/Interacting Electrons/Compressibility, etc. file).



In the Thermodynamics folder, the isothermal compressibility was defined as (‘twas called β back then) = ….



For an ideal gas, this would be:



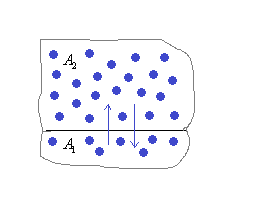
From these, we can solve for the particle fluctuations,



So we see that they are negligible in fact, for systems with more than, say, 10 000 particles. By similar arguments we can see that the relative energy fluctuations are ~ 1√N. And these arguments justify our derivation of L = -kTlnΞ where we approximated the sum in Ξ with the sum’s most probable value.

**Grand convective canonical ensemble (constant T, μ, and u)**

Now let’s consider another case where we have two sets of particles traveling to the right and exchanging energy, particles and momentum (the latter via collisions, just as with energy). It’s easiest to suppose the two sets of particles are not necessarily enclosed in compartments, and that the bath, A2, is much larger, and at energy E2, particle number N2, and momentum P2 (and temperature T, chemical potential μ, and velocity **u** = <**P**2>/<M2>) The subsystem A1 will have values E1, N1, and P1. Of course we presume A1 << A2.



The system A1 can now occupy any of its microstates with any energy, particle #, and momentum and we’d like to consider the probability it will do so. So consider the two systems A0 = A1 + A2 in thermal, chemical, and ‘translational’ equilibrium. Let’s say A1 << A2 and E1 << E2, N1 << N2, and P1 << P2. What is the probability A1 is in any *one* of its microstates with energy E1, N1, P1? Then we have:



Now take the ln of both sides and Taylor expand…



where **u** is the velocity **u** = **P**/M of system two (can make this identification by looking at the thermodynamic potentials file in case of moving system). Exponentiating, we get:



And moreover, the density matrix in the quantum and classical situations would be (presuming indistinguishable particles – otherwise no 1/N!):



where the sum/trace in the last line runs over quantum states with all particles numbers, and all energy eigenstates pertaining to those particle numbers. P(pj) would of course be (p1+p2+…+pN), and would be equivalent operator version.