Physics 112 : Lecture 14

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel
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1   Chemical Potential

Recall from last time that we derived the chemical potential for a gas to be:

$$M_{\text{int}} = \tau \ln\left(\frac{n}{n_Q}\right)$$

Suppose now that the particles have a magnetic moment, and are placed in a magnetic field of strenght B in the 'up' direction. Then, our chemical potential is altered for spin up and spin down particles:

$$M_{\text{tot}}(\uparrow) = \tau \ln\left(\frac{n}{n_Q}\right) - mB$$

$$M_{\text{tot}}(\uparrow) = \tau \ln\left(\frac{n}{n_Q}\right) + mB$$

In equilibrium, we must have that these two chemical potentials are equal. Setting these equal, we find that:

$$\frac{n_\uparrow}{n_\downarrow} = e^{2mB/\tau}$$

Now, from our earlier equations, we also have that:

$$\frac{n_\uparrow}{n_Q} = e^{(M(\uparrow)+mB)/\tau}$$

If we enforce that $n_\uparrow + n_\downarrow = n_0$ at $B = 0$, then we can solve for n_Q in terms of n_0, and subsituting back in and solving the equation:

$$n_\uparrow(B) = \frac{n_0}{2}e^{mB/\tau}; \qquad n_\downarrow(B) = \frac{n_0}{2}e^{-mB/\tau}$$

so now, adding the two equations together, we find that:

$$n(B) = n_\uparrow(B) + n_\downarrow(B) = n_0 \cosh(mB/\tau)$$

In the limit where mB/τ is very small, we have that:

$$n(B) \approx n_0\left(1 + \frac{1}{2}\left(\frac{mB}{\tau}\right)^2\right)$$

Let's come back to the theory for a while. For now, our working definition of chemical potential is:

$$M = \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$$

we know a relationship between entropy and free energy though, $F = U - \tau\sigma$, so we'd like to substitute this in to find a relationship between the chemical potential and the entropy of a system. Note that we also have:

$$\left(\frac{\partial \sigma}{\partial N}\right)_{\tau V} = \left(\frac{\partial \sigma}{\partial U}\right)_{V,N}\left(\frac{\partial U}{\partial N}\right)_{\tau,V} + \left(\frac{\partial \sigma}{\partial V}\right)_{U,N}\left(\frac{\partial V}{\partial N}\right)_{\tau,V} + \left(\frac{\partial \sigma}{\partial N}\right)_{U,V}$$

We can clean this formula up by realising $\partial\sigma/\partial U = 1/\tau$, $\partial\sigma/\partial V = 0$ (Not doing any work on the system). Hence, if we substitute all of this into our formula for the chemical potential, we find that:

$$M = -\tau\left(\frac{\partial \sigma}{\partial N}\right)_{U,V}$$

Or, if we wanted to hold entropy constant, we also have:

$$M = \left(\frac{\partial U}{\partial N}\right)_{\sigma,V}$$

Now, returning to our formula for an infinitessimal in entropy, we have:

$$d\sigma = \left(\frac{\partial \sigma}{\partial U}\right)_{V,N}dU + \left(\frac{\partial \sigma}{\partial V}\right)_{U,N}dV + \left(\frac{\partial \sigma}{\partial N}\right)_{U,V}dN$$

subsituting in our known quantities:

$$\left(\frac{\partial \sigma}{\partial U}\right)_{V,N} = \frac{1}{\tau}; \qquad \left(\frac{\partial \sigma}{\partial V}\right)_{U,N} = \frac{p}{\tau}; \qquad \left(\frac{\partial \sigma}{\partial N}\right)_{U,V} = \frac{-M}{\tau}$$

so finally we have:

$$\tau d\sigma = dU + p\,dV - M\,dN$$

rearranging, we have:

$$dU = \tau d\sigma - p\,dV + M\,dN$$

which holds for a reversible process. Now, remember that we derived the partition function in the case where the system was in contact with a thermal resevoir, but was *not* allowed to exchange particles. Now, let's free ourselves from that constraint! Suppose we have a system connected to a big reservoir, so that the entropy of the system is just given

by the entropy of the reservoir. Now, the probability of a state occuring is proportional to the multiplicity of that state, so we have:

$$\frac{P(N_1, \epsilon_1)}{P(N_2, \epsilon_2)} = \frac{e^{\sigma(N_0 - N_1, U_0 - \epsilon_1)}}{e^{\sigma(N_0 - N_2, U_0 - \epsilon_2)}} = e^{\Delta\sigma}$$

Now, to first order, we have that:

$$\Delta\sigma = -(N_1 - N_2)\left(\frac{\partial\sigma}{\partial N_0}\right)_{U_0} - (\epsilon_1 - \epsilon_2)\left(\frac{\partial\sigma}{\partial U_0}\right)_{N_0} = \frac{(N_1 - N_2)M}{\tau} - \frac{(\epsilon_1 - \epsilon_2)}{\tau}$$

So now we have derived the Gibbs factor, (the analog for the boltzmann factor in the case where particles can be exchanged):

$$\frac{P(N_1, \epsilon_1)}{P(N_2, \epsilon_2)} = \frac{e^{(N_1 M - \epsilon_1)/\tau}}{e^{(N_2 M - \epsilon_2)/\tau}}$$

Now, just as before where we got the Partition Function by summing over the Boltzmann Factors, we can form the Gibbs Sum (some call it the "Grand Sum"):

$$\zeta(M, \tau) = \sum_{N=0}^{\infty} \sum_{S(N)} e^{(NM - \epsilon_S(N))/\tau}$$

where the $S(N)$ denotes the possible energy states for a particle number N. This serves the exact same thing as the Partition function, so we might as well throw that idea out. Now, we have that the probability of finding ourselves in a state:

$$P(N_1, \epsilon_1) = \frac{e^{(N_1 M - \epsilon_1)/\tau}}{\zeta}$$

We can calculate averages the usual way, now that we have a probability distribution. Some results are nice though, for instance:

$$\langle N \rangle = \frac{\sum N e^{(NM - \epsilon)/\tau}}{\zeta} = \tau \frac{\partial \ln \zeta}{\partial M}$$