Thermodynamics and Statistical Mechanics Lecture 7

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Helmholtz Free Energy

The Helmholtz Free Energy is a function that can be minimized to have thermal equilibrium at constant temperature.

$$F = E - TS$$

In the micro-canonical ensemble, entropy is a function of energy and volume. We can then rearrange our equations to get energy as a function of entropy and volume.

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV = TdS - pdV = dQ - dW$$

Let's plug this into our relation for Helmholtz free energy and see what we can find.

$$dF = dE - d(TS) = dE - TdS - SdT$$

$$= TdS - pdV - TdS - SdT$$

$$= -pdV - SdT$$

Breaking up F into its differentials we also have

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

Merging these two relationships together we find

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

We can use the fact that the order of differentiation is unimport to find

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

Canonical F

We are going to look for the entropy in our standard canonical system. The total entropy is the sum of the entropy of the reservoir and the entropy of our system.

$$S_{tot} = S_R + S = S_R(E_{tot} - E) + S(E)$$

$$S_R(E_{tot}) - \left(\frac{\partial S_R}{\partial E}\right)_V E + S(E)$$

$$= \text{constant} - \frac{E}{T} + S = \text{constant} - \frac{(E - TS)}{T}$$

$$= \text{constant} - \frac{F}{T}$$

To maximize our entropy, we need to minimize F since everything else is constant.

Example: Magnet System

We have the same magnet system we have been looking at for a minute. What we have found so far is

$$E = -NBm$$

$$m = \frac{N_\uparrow - N_\downarrow}{2N}$$

$$S(m) = kN(\left(\frac{1}{2} + m\right)\ln\left(\frac{1}{2} + m\right) + \left(\frac{1}{2} - m\right)\ln\left(\frac{1}{2} - m\right))$$

Let's solve this for our Helmholtz free energy.

$$F = E(m) - TS(m)$$

$$= -NBm - TNk(\left(\frac{1}{2} + m\right)\ln\left(\frac{1}{2} + m\right) + \left(\frac{1}{2} - m\right)\ln\left(\frac{1}{2} - m\right))$$

We can also find the Helmholtz free energy using the partition function.

$$F = E - TS$$

$$E = -\frac{\partial \ln(Z)}{\partial \beta}$$

$$S = \frac{\partial}{\partial T}(kT \ln(Z))$$

$$= kT^2 \frac{\partial}{\partial T}\ln(Z) - kT\frac{\partial}{\partial T}(T\ln(Z))$$

$$= kT(T\frac{\partial}{\partial T}(\ln(Z)) - \frac{\partial}{\partial T}(T\ln(Z))) = -kT\ln(Z)$$

Now our partition function is

$$Z = e^{S(m)}e^{-\frac{E(m)}{kt}} = e^{S(m) - \frac{E(m)}{kT}}$$

$$= e^{-\frac{F(m)}{kT}}$$

Phase Space

It can be helpful to look at systems and how the behave in phase space. Phase space is a space where each point is where momentum space and coordinate space merge. One particle in phase space can be defined by

$$\frac{1}{h^3}\int dq^3 dp^3$$

h in this case is planck's constant and we get our uncertainty relation

$$\Delta q \Delta p \geq \frac{h}{2}$$

If we have N particles our integral over phase space will be

$$\frac{1}{h^{3N}}\int \prod_{i=1}^{N} dq_i^3 dp_i^3$$

The Hamiltonian of our system is a functional in phase space and is

$$H[\{q_i, p_i\}] = \sum_i \left(\frac{p_i^2}{2m} + V(q_i)\right)$$

The partition function of an ideal gas can then be described by

$$Z = \frac{1}{h^{3N}}\int \prod_{n=1}^{N}(dq_n^3 dp_n^3)e^{-\beta \sum_i \left(\frac{p_i^2}{2m} + V(q_i)\right)}$$

There is something subtly wrong with this (It overcounts by a factor $N!$)