Thermodynamics and Statistical Mechanics Lecture 6

Todd Hirtler

03Feb20

Canonical Partition Function

$$Z = \sum_n e^{-\beta E_n}$$

With

$$\beta = \frac{1}{kT}$$

The probability distribution will then be

$$P_n = \frac{1}{Z} e^{-\beta E_n}$$

Average Energy

The average energy of our system will be

$$\langle E \rangle = \sum_n E_n P_n = \frac{1}{Z} \sum_n E_n e^{-\beta E_n} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln(Z)$$

We can find the dispersion, or variance of our energy using

$$(\Delta E)^2 = \left\langle (E - \langle E \rangle)^2 \right\rangle = \left\langle E^2 \right\rangle - \langle E \rangle^2 = \sigma^2$$

We can use the partition function to easily find our variance of energy.

$$\sigma_E^2 = \frac{\partial^2}{\partial \beta^2}\ln(Z) = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = -\frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$$

$$= -\langle E \rangle + \frac{1}{Z}\sum_n E_n^2 e^{-\beta E_n} = \left\langle E^2 \right\rangle - \langle E \rangle^2$$

Looking deeper into different forms of the energy variance gives us

$$\sigma_E^2 = -\frac{\partial}{\partial \beta}\langle E\rangle = -\frac{\partial T}{\partial \beta}\Big(\frac{\partial E}{\partial T}\Big)_{V,N} = kT^2 C_v$$

$$\boxed{\sigma_E^2 = kT^2 C_v}$$

There are two different interpretations of this equation.

1) It is a special case of the **Fluctuation Dissipation Theorem**. The LHS is fluctuations in the equilibrium and the RHS is a **response function**. A small change of the equilibrium is used to see how the energy responds.

2) The variance is proportional to the size N of the system as C_v scales with size. This might seem like a problem since it diverges, but we can solve that problem by looking at relative fluctuations.

$$\frac{\Delta E}{\langle E\rangle} \propto \frac{\sqrt{N}}{N} \propto \frac{1}{\sqrt{N}}$$

This relative energy fluctuation vanishes as N increases. This can be considered the thermodynamic limit.

Example: Two State System

We return to our spin-1/2 system with energy

$$E = -\sum_{i=1}^{N} \frac{\epsilon}{2}\sigma_i$$

with $sigma_i = \pm 1$. Our partition function for this system, assuming each particle's spin is independent of the others is

$$Z_N = (Z_1)^N$$

$$Z_1 = e^{-\beta E_\uparrow} + e^{-\beta E_\downarrow} = e^{-\frac{\beta\epsilon}{2}} + e^{\frac{\beta\epsilon}{2}} = 2\cosh\left(\frac{\beta\epsilon}{2}\right)$$

$$Z^N = 2^N \cosh^N(\frac{\beta\epsilon}{2})$$

Let's manipulate this partition function to give us our average energy and specific heat.

$$\ln(Z_N) = N\ln(2) + N\ln\left(\cosh\left(\frac{\beta\epsilon}{2}\right)\right)$$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln(Z) = -\frac{N\epsilon}{2}\tanh\left(\frac{\beta\epsilon}{2}\right)$$

$$C_v = \Big(\frac{\partial\langle E\rangle}{\partial T}\Big)_N = -\frac{1}{kT^2}\frac{\partial E}{\partial\beta} = \frac{\epsilon}{2kT^2}\frac{1}{\sinh^2(\frac{\beta\epsilon}{2})}$$

Gibb's Entropy

We can make M copies of the system with M sufficiently large and each copy is in the state n. The probability distribution of our system can be any arbitrary P_n. P_nM are in state n. Our multiplicity function will be

$$\Omega_M = \frac{M!}{\prod(P_nM)!}$$

We can find the entropy to be

$$\begin{aligned} S_M &= k\ln(\Omega_M) \\ &= k(M\ln(M) - M - \sum_n (MP_n\ln(MP_n) - MP_n)) \\ &= -kM\sum P_n\ln(¶_n) \end{aligned}$$

Our Gibb's Entropy will then be

$$\boxed{S = -k\sum P_n\ln(P_n)}$$

With the micro-canonical ensemble probability being

$$P_n = \frac{1}{|omega}$$

We can plug that into our Gibb's Entropy equation to get

$$S = k\ln\left(\sum\frac{1}{\Omega}\ln(\Omega)\right) = k\ln(\Omega)$$

Which exactly what we expect.

Canonical Entropy

We can use Gibb's Entropy with the canonical ensemble as well.

$$\begin{aligned} S &= -k\sum_n \frac{1}{Z}e^{-\beta E_n}\ln\left(\frac{1}{Z}e^{-\beta E_n}\right) \\ &= \frac{k\beta}{Z}\sum_n E_n e^{-\beta E_n} + \frac{k}{Z}\sum_n e^{-\beta E_n}\ln(Z) \\ &= k\beta\langle E\rangle + k\ln(Z) = \frac{\partial}{\partial T}(kT\ln(Z)) \end{aligned}$$