

Thermodynamics and Statistical Mechanics Lecture 3

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Recap

We are still working with a system of N spin-1/2 particles. With $s_i = 1/2$, our energy can be represented by

$$E = -B \sum_i^N s_i = -B \frac{N_\uparrow - N_\downarrow}{2} = -BM = -nBm$$

with M being our magnetization and m being our magnetization density. Our multiplicity function can then be defined as

$$\Omega(N_\uparrow) = \frac{N!}{N_\uparrow!(N - N_\uparrow)!}$$
$$\Omega(M) = \frac{N!}{(\frac{N}{2} + M)!(\frac{N}{2} - M)!}$$

Stirling's Approximation

$$N! \approx \exp(N \ln(N) - N + O(\ln(N)))$$

We're going to go ahead and try to prove this approximation for ourselves. First we are going to take the natural logarithm of the left and see if we can get it to look like what lies within the exponential on the right side.

$$\ln(N!) = \sum_{n=1}^N \ln(n)$$

With sufficiently large N , that sum can be turned into an integral which leads us to what we want.

$$\sum_{n=1}^N \ln(n) = \int_1^N dn \ln(n) = N \ln(N) - N + O(\ln(N))$$

We can use this to get $\Omega(M)$ in a form that is easier to use.

$$\begin{aligned} \Omega(M) &= \\ \exp\left(N \ln(N) - N - \left(\frac{N}{2} + M\right) \ln\left(\frac{N}{2} + M\right) - \left(\frac{N}{2} - M\right) \ln\left(\frac{N}{2} - M\right) + \left(\frac{N}{2} + M\right) + \left(\frac{N}{2} - M\right)\right) \\ &= \exp\left(N\left(\ln(N) - \left(\frac{1}{2} + m\right) \ln\left(N\left(\frac{1}{2} + m\right)\right) - \left(\frac{1}{2} - m\right) \ln\left(N\left(\frac{1}{2} - m\right)\right)\right)\right) \\ &= \exp\left(N\left(-\left(\frac{1}{2} + m\right) \ln\left(\frac{1}{2} + m\right) - \left(\frac{1}{2} - m\right) \ln\left(\frac{1}{2} - m\right)\right)\right) \end{aligned}$$

Define Entropy

$$S(E) = k \ln(\Omega(E))$$

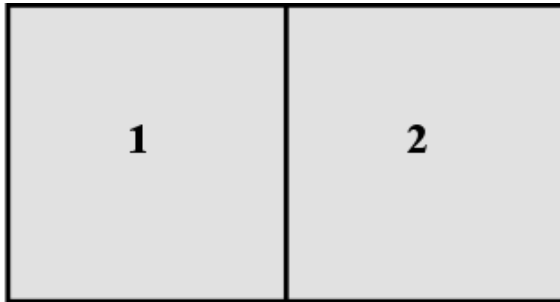


Figure 1. A system with two subsystems. Both subsystems may exchange energy, but not particles.

If we were to add up the subsystems together, with their respective micro-states and multiplicity functions, we would find that

$$\Omega_{12} = \Omega_1 \cdot \Omega_2$$

This can lead to problems since multiplication can get rather complicated very quickly. It would be a lot easier if we had some quantity that is related to the logarithm of our multiplicity functions, so our multiplication can get simplified into addition. Luckily, entropy can do exactly that.

$$S_{12} = k \ln(\Omega_{12}) = k(\ln(\Omega_1) + \ln(\Omega_2)) = S_1 + S_2$$

Using what we found earlier for Ω

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

Our probability distribution for this will be

$$P(m) = \frac{\Omega(m)}{\Omega_{tot}} = \frac{e^{S(m)/k}}{2^N}$$

We want to be able to find our mean and standard deviation so we need to find our maximum entropy.

$$\frac{dS}{dm} = 0 = -N \ln\left(\frac{\frac{1}{2} + m}{\frac{1}{2} - m}\right)$$

A quick glance at this and we can tell that we have a minimum or maximum at $m = 0$. It would be good practice to check the second derivative to make sure this isn't a minimum but that is a task for another day.

Now that we have our entropy, we can go ahead and see what our probability distribution looks like.

$$P(m) = 2^{-N} e^{\frac{1}{k}(S(m) + \frac{1}{2} \frac{\partial^2 S}{\partial m^2} m^2 + \dots)} = f_N e^{-Nm^2}$$

We got that end result from Taylor expanded our equation around $m = 0$. f_N is our way of normalizing our distribution and will be as follows.

$$f_N = \left(\int_{-\infty}^{\infty} dm e^{-Nm^2} \right)^{-1} = \sqrt{\frac{N}{\pi}}$$

This gives us a really pretty equation for our probability.

$$P(m) = \frac{N}{\pi} e^{-Nm^2}$$

From this equation, we can quickly pull out the standard deviation and the mean for our case where $B = 0$.

$$\begin{aligned} \langle m \rangle &= 0 \\ \sigma &= \frac{1}{\sqrt{2N}} \end{aligned}$$

Thermal Contact

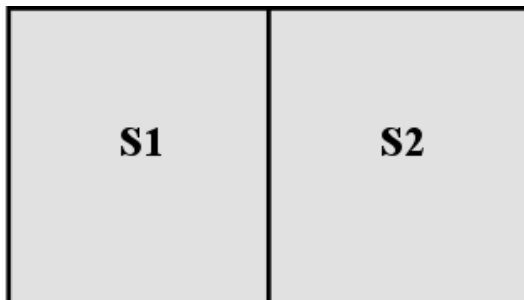


Figure 2. A system with two subsystems. Both subsystems may exchange energy, but not particles.

We are going to play with the same type of system but now look at it from a perspective that takes into account temperature and our own intuition on how it behaves. Both E_1 and E_2 are free to change but the overall energy of our system E cannot. This enables us to name a new variable that give us a way to tell when our system is in equilibrium.

$$E_- = E_1 - E_2$$

We will be in equilibrium when $E_- = 0$. We want to differentiate our entropy in respect to energy, but now we have a lot of different energies to look at. Which one do we use? The energy we will want to look at is the new energy variable we just defined.

$$\begin{aligned} \frac{\partial S}{\partial E_-} = 0 &= \left(\frac{\partial S_1}{\partial E_-} \right)_{E,N} + \left(\frac{\partial S_2}{\partial E_-} \right)_{E,N} = \frac{\partial S_1}{\partial E_1} \frac{\partial E_1}{\partial E_-} + \frac{\partial S_2}{\partial E_2} \frac{\partial E_2}{\partial E_-} \\ &= \left(\frac{\partial S_1}{\partial E_1} \right)_{E_1, N_1} - \left(\frac{\partial S_2}{\partial E_2} \right)_{E_2, N_2} = 0 \end{aligned}$$

This is a pretty cool result and gives us a relationship we have for temperature T and how it relates to entropy and energy.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{E,N}$$

There are a couple of situations we can find ourselves in. **a)** $T_1 = T_2$ This system will be in thermal equilibrium so $\delta S = 0$.

b) $T_1 > T_2$ This system is not in thermal equilibrium but we can figure out what is going on with the energy exchange fairly easily.

$$\delta S = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta E_-$$

Since we know δS must be positive due to the second law of thermodynamics, and that out temperature term is negative, we know $\delta E_- < 0$. This tells us that E_2 will increase and E_1 will decrease which is just as we would expect.

Let's take a look at our entropy in regards to energy.

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

Differentiating this in respect to E we find the following equation.

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{-k}{B} \ln \left(\frac{\frac{1}{2} + \frac{E}{BN}}{\frac{1}{2} - \frac{E}{BN}} \right)$$

Unfortunately, it is impossible, or in the very least extremely difficult, to measure entropy directly. Fortunately for us, there is a way around it using **Heat Capacity** which is easily measurable and can be as follows.

$$C_V(T) = \left(\frac{\partial E}{\partial T} \right)_{N,V}$$