Temperature, Pressure, and Entropy

Temperature

From classical thermo we understand that heat will flow from a hot object to a neighboring cold object until they reach the same temperature.

In stat mech, we insist that the distribution of heat between two objects is determined by the microcanonical assumption that all possible states, of fixed energy E, are equally likely.

Here, we'll connect these two descriptions by defining temperature in terms of phase space volume $\Omega(E)\delta E$. From this description, we'll see entropy makes a natural appearance.

- First, consider two subsystems, 1 and 2, each of which have fixed volume V and fixed N. We connect them and assume that they are weakly connected energetically.

By "weak connection", we mean that the system volume is very large compared to the interface between 1 and 2. Interaction energy is only important near the surface, which is a negligible fraction of volume.

Ok, now, a simple question: What is the probability density for subsystem 1 to have energy E_1?

$$\rho(E_1) = \frac{\text{Phase space volume having } E_1 \text{ and } E_2 = E - E_1}{\text{Total Phase space volume}}$$

Since the states are now coupled, we must always consider E_1 and $E_2 = E - E_1$

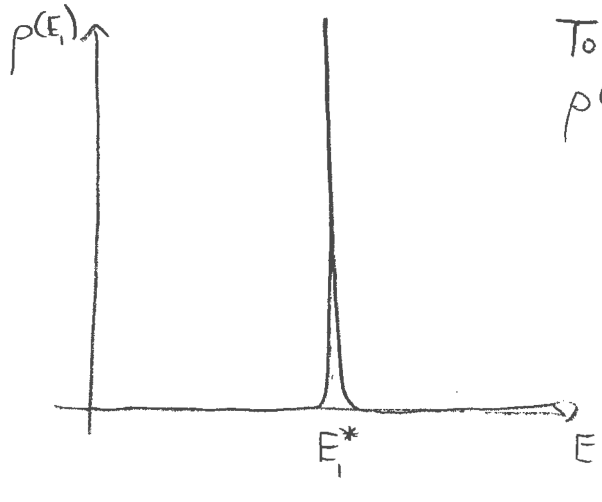
$$\rho(E_1) = \frac{\Omega(E_1)\Omega_2(E-E_1)}{\Omega(E)}$$

Notice this is the integrand of $\Omega(E)$ normalized by $\Omega(E)$, i.e.

$$\rho(E_1) = \frac{1}{\Omega(E)} \frac{\partial \Omega(E)}{\partial E_1}$$

When N is large, fluctuations are small ($\sim 1/\sqrt{N}$) and $\rho(E_1)$ is VERY sharply peaked.

Therefore, in equilibrium, the energy of subsystem 1 is given by the maximum in the integrand $\Omega_1(E_1)\Omega_2(E-E_1)$



To find E_1^*, we find the maximum in $\rho(E_1)$

$\Rightarrow$ Take the derivative & set to zero!

$$\frac{d\rho}{dE_1} = \frac{1}{\Omega(E)} \frac{d}{dE_1}\left(\Omega_1(E_1)\Omega_2(E-E_1)\right)\Big|_{E_1=E_1^*} = \frac{d\Omega_1}{dE_1}\Big|_{E_1=E_1^*}\Omega_2 + \Omega_1 \frac{d\Omega_2}{dE_1}\Big|_{E_1=E_1^*} = 0$$

Now, since

$$E_2 = E - E_1$$
$$dE_2 = -dE_1$$

$$\Rightarrow \frac{dp}{dE_1} = \frac{d\Omega_1}{dE_1}\Omega_2 - \Omega_1 \frac{d\Omega_2}{dE_2}\bigg|_{E_2 = E - E_1^* = E_2^*} = 0$$

$$\therefore \boxed{\frac{1}{\Omega_1}\frac{d\Omega_1}{dE_1}\bigg|_{E_1 = E_1^*} = \frac{1}{\Omega_2}\frac{d\Omega_2}{dE_2}\bigg|_{E_2 = E_2^*}}$$

This condition will give us the value of E_1 that maximizes $p(E_1)$. In other words, the most likely value of E_1 is found when the above holds.

Notice each side looks like a logarithmic derivative:

$$\frac{d}{dx}\ln f(x) = \frac{1}{f(x)}\frac{df(x)}{dx}$$

This suggests we define a function like $\ln \Omega(E)$... let's call it S:

$$S \sim \log(\Omega(E))$$

Multiply by a fudge factor to make units work out (as we'll see later)

$$S = k_B \log(\Omega(E))$$

This is the entropy! This equation is written on Ludwig Boltzmann tombstone.

Then

$$\frac{dS}{dE} = k_B \frac{1}{\Omega} \frac{d\Omega}{dE}$$

So

$$\frac{dS_1}{dE_1} = k_B \frac{1}{\Omega_1} \frac{d\Omega_1}{dE_1} \quad , \quad \frac{dS_2}{dE_2} = k_B \frac{1}{\Omega_2} \frac{d\Omega_2}{dE_2}$$

So our condition that gives the value of E_1 that maximizes $\rho(E_1)$ is:

$$\frac{d}{dE_1}\left[S_1(E_1) + S_2(E - E_1)\right] = \left.\frac{dS_1}{dE_1}\right|_{E_1^*} - \left.\frac{dS_2}{dE_2}\right|_{E_2^*} = 0$$

Therefore the most likely value of E_1 is where the entropy is maximized!

Simply stated: The condition that a maximum occurs in $\rho(E_1)$ is that the entropy $S_1 + S_2$ is maximized, and, as we will see, that the temperatures are equal.

Again, the condition is

$$\left.\frac{dS_1}{dE_1}\right|_{E_1^*} = \left.\frac{dS_2}{dE_2}\right|_{E_2^* = E - E_1^*}$$