Lecture 25 (2-8), Mar 16, 2023

General Thermal Equilibrium – Statistical Definition of Temperature and Entropy

- We don't need to be restricted to the Einstein solid
- Consider a system 1 with energy E_1, system 2 with energy E_2, being brought together an allowed to reach thermal equilibrium (N, V are not exchanged)
- In TD the overall system has energy $E = E_1 + E_2$ with $E_1' = \frac{E}{2} - \Delta$ distributed to the first system, $E_2' = \frac{E}{2} + \Delta$ distributed to the second system
- The probability of having a particular Δ is $P(\Delta) = \dfrac{\Omega_1(\frac{E}{2} - \Delta)\Omega_2(\frac{E}{2} + \Delta)}{\sum_{\tilde{\Delta}=-E/2}^{E/2} \Omega_1(\frac{E}{2} - \tilde{\Delta})\Omega_2(\frac{E}{2} + \tilde{\Delta})}$
- We wish to find $\max\limits_{\Delta} P(\Delta)$
  - $\dfrac{\partial}{\partial \Delta}\Omega_1\left(\dfrac{E}{2} - \Delta\right)\Omega_2\left(\dfrac{E}{2} + \Delta\right) = 0$
  - $\dfrac{\partial \Omega_1\left(\frac{E}{2} - \Delta\right)}{\partial\left(\frac{E}{2} - \Delta\right)}(-1)\Omega_2\left(\dfrac{E}{2} + \Delta\right) + \dfrac{\partial \Omega_2\left(\frac{E}{2} + \Delta\right)}{\partial\left(\frac{E}{2} + \Delta\right)}(1)\Omega_1\left(\dfrac{E}{2} - \Delta\right) = 0$
  - $\dfrac{1}{\Omega_1\left(\frac{E}{2} - \Delta\right)}\dfrac{\partial \Omega_1\left(\frac{E}{2} - \Delta\right)}{\partial\left(\frac{E}{2} - \Delta\right)} = \dfrac{1}{\Omega_2\left(\frac{E}{2} + \Delta\right)}\dfrac{\partial \Omega_2\left(\frac{E}{2} + \Delta\right)}{\partial\left(\frac{E}{2} + \Delta\right)}$
  - $\dfrac{\partial}{\partial\left(\frac{E}{2} - \Delta\right)}\ln\Omega_1\left(\dfrac{E}{2} - \Delta\right) = \dfrac{\partial}{\partial\left(\frac{E}{2} + \Delta\right)}\ln\Omega_2\left(\dfrac{E}{2} + \Delta\right)$
  - $\dfrac{\partial}{\partial E_1'}k\ln\Omega_1(E_1') = \dfrac{\partial}{\partial E_2'}k\ln\Omega_2(E_2')$
    - The left hand side is a property of system 1, the right hand side is a property of system 2
    - This means as two bodies are brought into contact, it will change until this quantity $\dfrac{\partial}{\partial E}k\ln\Omega(E)$ becomes the same for the two bodies
  - This leads us to define $\dfrac{\partial}{\partial E_1'}k\ln\Omega_1(E_1') = \dfrac{1}{T_1(E_2', N, V)}, \dfrac{\partial}{\partial E_2'}k\ln\Omega_2(E_2') = \dfrac{1}{T_2(E_2', N, V)}$
    - Temperature is a function of E, N, V
  - We can also define entropy as $k\ln\Omega(E)$; since the macrostate that has the largest multiplicity is the most likely, this means entropy will be maximized

Definition

The *entropy* of a system is defined as

$$S(E, N, V) = k\ln\Omega(E, N, V)$$

The *temperature* of a system is defined as

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

- Since each macrostate must have $\Omega \geq 1$, we have $S \geq 0$
  - Consider the case of the electronic paramagnet, the state $N_\uparrow = N$ or $N_\uparrow = 0$ only have one microstate, so $\Omega = 1, S = 0$
    - This a very ordered system
  - If $N_\uparrow \sim \dfrac{N}{2}$ we have a lot of microstates, so we have $S \gg 1$; this is a disordered system
  - This is why entropy is sometimes referred to as the "degree of disorder"
    - In this case, "disorder" is how many microstates a macrostate can exist in

- We can also consider entropy as the inverse of how much information you have: in the $N_\uparrow = N$ state we know exactly which microstate the system is in, but in the $N_\uparrow \sim \frac{N}{2}$ state there are many microstates that the system could be in, so we have very little information about the exact microstate

- Also notice $T \geq 0$ because $\frac{\partial S}{\partial E} \geq 0$ for most "normal" systems (note this is not true for the electronic paramagnet)
  - If you heat the system, energy is introduced so there are more ways to distribute the energy, therefore entropy should also increase