Thermodynamics and Statistical Mechanics Lecture 5

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Micro-canonical Ensemble Summary

In a closed system, the energy is fixed. $\Omega(E, X)$ is the number of microstates with energy E and other macro-observables X.

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

Ergodic Hypothesis: all micro-states are equally probable.
Equilibrium: Variable X adjusts to the most probable state (maximum entropy)

$$p = T\left(\frac{\partial S}{\partial V}\right)_E$$
$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$
$$T_1 = T_2$$
$$P_1 = P_2$$

Discrete Energy

At this time it might be weird seeing some type of differential of energy while knowing that the energy levels of a quantum system are discrete. Let's look into why we can treat the energy like it is continuous.

$$\Omega_{\delta E}(E) = D(E)\delta E$$
$$S(E) = k \ln(\Omega(E)) = k \ln(D(E)) + k \ln(\delta E)$$

$D(E)$ is our density of states and in this case can de described by

$$D(E) = \frac{2^N}{BN}$$

Plugging this into our equation for entropy

$$S(E) = k\ln\left(\frac{2^N}{BN}\right) + k\ln(\delta E)$$
$$= kN\ln(2) - k\ln(BN) + k\ln(\delta E)$$
$$= kN\ln(2) + k\ln\left(\frac{\delta E}{BN}\right) = kN\ln(2) - k\ln\left(\frac{BN}{\delta E}\right)$$

The second term is a lot smaller than the first term, and can be neglected, so the discreteness of the energy really doesn't matter much with large ensembles.

There are problems with the micro-canonical ensemble, however. Most systems are not closed and it is difficult and tedious to count states of fixed energy.

Canonical Ensemble

We want to look at a system of a large reservoir and a smaller subsystem. The reservoir is sufficiently large so that the temperature is fixed.

$$\langle X \rangle = \sum_n P_n X_n$$

$$P_n = \frac{\Omega_R(E_{tot} - E_n)}{\Omega_{tot}}$$

$$P_n = \frac{1}{\Omega_{tot}} e^{\frac{1}{k}S_R(E_{tot}-E_n)}$$

Since $E_n << E_{tot}$, we can use a taylor expansion to simplify this mess.

$$P_n \approx \frac{1}{\Omega_{tot}} e^{(\frac{1}{k}S_R(E_{tot}) - \frac{1}{k}(\frac{\partial S_R}{\partial E})E_n)}$$
$$= \frac{1}{\Omega_{tot}} e^{\frac{1}{k}S_R(E_{tot}) - \frac{E_n}{kT}}$$
$$= \frac{1}{Z} e^{\frac{-E_n}{kT}} = \frac{1}{Z} e^{-\beta E_n}$$

with $\beta = \frac{1}{kT}$ being the **inverse temperature** and Z being our **partition function**. The exponential is called the **Boltzmann Factor**.

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

The partition function normalizes our probability distribution. The partition function also is multiplicative when adding multiple systems, much like the multiplicity function.