Lecture 9

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1 Definitions of Thermodynamic Quantities

Definition 1.1 (Entropy)**.**

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

Definition 1.2 (Temperature)**.**

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

Definition 1.3 (Pressure)**.**

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

Definition 1.4.

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

2 Stirling's Approximation

We try to approximate Ω given $q >> N$. We know

$$\Omega(q,N) = \frac{(N-1+q)!}{(N-1)!q!} \approx \frac{(N+q)!}{N!q!}$$

Then

$$\ln \Omega \approx \ln(N+q)! - \ln N! - \ln q! \approx (N+q)\ln(N+q) - N\ln N - q\ln q$$

and so

$$\ln \Omega \approx N \ln(N+q) + q \ln(N+q) - N \ln N - q \ln q$$

Note that

$$\ln(N+q) = \ln\left(q\left(1+\frac{N}{q}\right)\right) = \ln q + \ln\left(1+\frac{N}{q}\right) \approx \ln q + \frac{N}{q}$$

Substituting and cancelling the terms,

$$\ln \Omega = \ln\left(\frac{qe}{N}\right)^N$$

Then putting

$$q = \frac{E}{\hbar\omega}$$

we get

$$\frac{1}{T} = \frac{kN}{E}$$

Now for $N >> q$, we have

$$\Omega(q, N) = \ln\left(\frac{Ne}{q}\right)^q$$

So

$$\frac{1}{T} = \frac{k}{\hbar\omega} \ln \frac{N\hbar\omega}{E} \Rightarrow e^{\frac{\hbar\omega}{kT}} = \frac{N\hbar\omega}{E}$$

or

$$\frac{E}{N} = \hbar\omega e^{-\frac{\hbar\omega}{kT}}$$

Example 2.1. Consider two containers A and B placed side by side, with $q_A = \frac{q}{2} + x$ and $q_B = \frac{q}{2} - x$. We want to find the most likely value of x. Obviously, it should be 0 by intuition/symmetry. But we can also solve for this.

$$P(x) \propto \Omega_A\left(\frac{q}{2}+x, N\right)\Omega_B\left(\frac{q}{2}-x, N\right) = \left(\frac{e^2}{N^2}\right)^N \left(\frac{q}{2}-x\right)^N (\frac{q}{2}+x)^N = \left(\frac{e^2}{N^2}\right)^N \left(\left(\frac{q}{2}\right)^2 - x^2\right)^N$$

Now

$$\frac{P(x)}{P(0)} = \left(1 - \left(\frac{2x}{q}\right)^2\right)^N$$

Taking the logarithm,

$$\ln \frac{P(x)}{P(0)} = N \ln \left(1 - \left(\frac{2x}{q} \right) \right) \approx -N \left(\frac{2x}{q} \right)^2$$

So

$$P(x) \approx P(0) e^{-N \left(\frac{2x}{q} \right)^2}$$

When N is large, this is practically a delta function, and $x = 0$ is the only value where P is nonzero.