Lecture 17

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1 Boltzmann Distribution

In a thermostat (T, V, N), the probability of a microstate is given by

$$P(\text{microstate}) = \frac{1}{z}e^{-\frac{E}{kT}}$$

And the probability of a system with energy E is

$$P(\text{energy}) = P(\text{microstate})\Omega(E) = \frac{1}{z}e^{-\frac{E-TS(E)}{kT}}$$

The most likely energy is where the numerator of the exponent. Defining the free energy

$$F = E - TS(E)$$

we can simply look for the minimum free energy. Note that

$$dF = -SdT - pdV + \mu dN$$

The proof is left as an exercise for the reader. Now given F, we see for a low T, F is dominated by the E term, so the lowest energy arrangement is the most likely. Similarly, for a high T, F is dominated by the $-TS$ term, so the arrangement where S is maximised is the most likely. This is the **order disorder** transition.

2 Working with z

$$\begin{aligned} z &= \sum_{q_1=0}^{\infty}\sum_{q_2=0}^{\infty}\cdots\sum_{q_N=0}^{\infty} e^{-\frac{\hbar\omega}{kT}q_1} e^{-\frac{\hbar\omega}{kT}q_2} \times \cdots \times e^{-\frac{\hbar\omega}{kT}q_N} \\ &= \left(\sum_{q_1=0}^{\infty} e^{-\frac{\hbar\omega}{kT}q_1}\right)\left(\sum_{q_2=0}^{\infty} e^{-\frac{\hbar\omega}{kT}q_2}\right) \times \cdots \times \left(\sum_{q_N=0}^{\infty} e^{-\frac{\hbar\omega}{kT}q_N}\right) \\ &= (z_1)^N \end{aligned}$$

Now z_1 itself is a geometric series, so

$$z = (z_1)^N = \left(\frac{1}{1 - e^{-\hbar\omega/kT}}\right)^N$$

We attempt to find the average energy. Now letting $\beta = \frac{1}{kT}$,

$$\begin{aligned} E_{\text{avg}} &= \sum_{\text{microstate}} EP \\ &= \sum_{\text{microstate}} -\frac{1}{z}\frac{\partial}{\partial\beta}e^{-\beta E} \\ &= -\frac{1}{z}\frac{\partial}{\partial\beta}\left(\sum e^{-\beta E}\right) \\ &= -\frac{1}{z}\frac{\partial z}{\partial\beta} \\ &= -\frac{\partial}{\partial\beta}\ln z \\ &= N\frac{\partial}{\partial\beta}\ln\left(1 - e^{-\beta\hbar\omega}\right) \\ &= \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1} \end{aligned}$$

Now at high T, we approximate $e^x - 1 \approx x$, so that gives us

$$\overline{E} \approx NkT$$