

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 is minimised. 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 $\beta = \frac{1}{kT}$,

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

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

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