Lecture 34 (2-17), Apr 6, 2023

Properties of the T, V, N System

- Such systems are a lot easier to study, since keeping T constant is easier and Z is a lot easier to find than Ω
- Recall: for a T, V, N system in contact with a thermal reservoir, the probability of the system being in any microstate is given by $\dfrac{1}{Z}e^{-\beta E}$, where E is the energy of the microstate and $\beta = \dfrac{1}{kT}$
- $Z(T, V, N) = \sum e^{-\beta E}$ is called the *partition function* and plays a role analogous to the multiplicity function
- $\mathrm{d}F(T, V, N) = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N = \dfrac{\partial F}{\partial T}\,\mathrm{d}T + \dfrac{\partial F}{\partial V}\,\mathrm{d}V + \dfrac{\partial F}{\partial N}\,\mathrm{d}N$ is the thermodynamic identity for F
    - From this we get a new set of Maxwell's equations
    - Note: derivation not shown
- The probability that the system has some energy is then $P(E) = \dfrac{1}{Z}e^{-\beta E}\Omega(E) = \dfrac{1}{Z}e^{-\beta E}e^{\frac{S}{k}} = \dfrac{1}{Z}e^{-\beta(E-TS)}$
    - P is maximized when $E - TS = F$ is minimized, so we call F the free energy – the system wants to minimize F
    - F is the thermodynamic potential similar to energy except it's minimized
- At low T, $F \approx E$, so at low temperature the minimum of F is the minimum of E – the system goes to its ground state
- At high T, $F \approx -TS$, so the minimum of F is the maximum of S – the system goes to maximum entropy
- Such systems are ordered at low temperature (ground state) and unordered at high temperature (high entropy)
    - When the system heats up, the order and disorder fight
    - Phase transitions happen when one wins over the other

Partition Function of the Einstein Solid

- Recall the energy of a microstate is $-\hbar\omega(q_1 + \cdots + q_N)$
- $$\begin{aligned} Z &= \sum_{q_1=0}^{\infty} \cdots \sum_{q_N=0}^{\infty} e^{-\frac{\hbar\omega}{kT}(q_1+\cdots+q_N)} \\ &= \sum_{q_1=0}^{\infty} e^{-\frac{\hbar\omega}{kT}q_1} \cdots \sum_{q_N=0}^{\infty} e^{-\frac{\hbar\omega}{kT}q_N} \\ &= \prod_{i=1}^{N} Z_i \\ &= Z_1^N \end{aligned}$$
    - Z_1 is the partition function for a single harmonic oscillator
    - This is a general result – for systems where the energy is the sum of energies of smaller parts, the partition function factors into a product of the partition functions of the smaller parts
    - This is a useful property that the multiplicity function does not

- $Z_1 = \sum_{q=0}^{\infty} e^{-\frac{\hbar\omega q}{kT}}$
  $$= \sum_{q=0}^{\infty} \left(e^{-\frac{\hbar\omega}{kT}}\right)^q$$
  $$= \frac{1}{1 - e^{-\hbar\omega}kT}$$
  $$= \frac{1}{1 - e^{-\beta\hbar\omega}}$$
  - This gives $Z = \left(\frac{1}{1 - e^{-\beta\hbar\omega}}\right)^N$
- Let's calculate the average energy of the system as a function of temperature
- $\bar{E} = \sum P(\text{microstate}) E(\text{microstate})$
  $$= \frac{1}{Z} \sum E(\text{microstate}) e^{-\beta E(\text{microstate})}$$
  $$= \frac{1}{Z} \sum -\frac{\partial}{\partial\beta} e^{-\beta E(\text{microstate})}$$
  $$= -\frac{1}{Z}\frac{\partial}{\partial\beta} \sum e^{-\beta E(\text{microstate})}$$
  $$= -\frac{1}{Z}\frac{\partial}{\partial\beta} Z$$
  $$= -\frac{\partial}{\partial\beta} \ln Z$$
- Substitute: $\bar{E} = -\frac{\partial}{\partial\beta} \ln \left(\frac{1}{1 - e^{-\beta\hbar\omega}}\right)^N$
  $$= N\frac{\partial}{\partial\beta} \ln\left(1 - e^{-\omega\hbar\omega}\right)$$
  $$= \frac{N\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$
- $\frac{\bar{E}}{N} = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}$
  - Unlike our previous approximations this works at all temperatures
  - At low temperature, $\frac{\hbar\omega}{kT} \gg 1$ so $\frac{\bar{E}}{N} \approx \hbar\omega e^{-\frac{\hbar\omega}{kT}}$ (midterm solution)
  - At high temperature $e^{\frac{\hbar\omega}{kT}} \approx 1 + \frac{\hbar\omega}{kT}$ so $\frac{\bar{E}}{N} \approx kT$ which is equipartition!
- Note we have: $Z_1 = \sum_{q=0}^{\infty} e^{-\frac{\hbar\omega}{kT}q} = 1 + e^{-\frac{\hbar\omega}{kT}} + e^{-2\frac{\hbar\omega}{kT}} + e^{-3\frac{\hbar\omega}{kT}} + \cdots$
  - Terms with $q\hbar\omega \gg kT$ will have pretty much no contribution to Z_1, so these states with higher energy do not contribute
  - Z is called the partition function because roughly it describes the partition between states with high energy and states with low energy