Lecture 26 (2-9), Mar 17, 2023

2 Einstein Solids

- The thermodynamic limit: in the limit as $N \to \infty, V \to \infty, E \to \infty$ (all extensive properties), but keeping the density and energy density $\frac{E}{N}, \frac{N}{V}$ fixed, the results of statistical mechanics become certainties instead of probabilistic
- Recall for the Einstein solid $E = \hbar\omega q, \Omega = \frac{(N-1+q)!}{(N-1)!q!}$
  - We keep $\frac{q}{N}$ fixed, but we could either have $\frac{q}{n} \ll 1$ or $\frac{q}{n} \gg 1$
- First consider the classical limit, where $\frac{q}{n} \gg 1$
  - For large N the multiplicity function just becomes $\frac{(N+q)!}{N!q!}$
  - $\ln \Omega = \ln(N+q)! - \ln N! - \ln q!$
  - Stirling approximation: $\ln n! \approx n \ln n$ for large n
  - $\ln \Omega \approx (N+q)\ln(N+q) - N\ln N - q\ln q = N \ln\left(q\left(1+\frac{N}{q}\right)\right) + q\ln\left(q\left(1+\frac{N}{q}\right)\right) - N\ln N - q\ln q$
  - $\ln \Omega = N\ln q + N\ln\left(1+\frac{N}{q}\right) + q\ln q + q\ln\left(1+\frac{N}{q}\right) - N\ln N - q\ln q$
  - $\ln \Omega \approx N\ln q + N\frac{N}{q} + N - N\ln N = N\ln q + N\ln e - N\ln N = \ln q^N + \ln e^N - \ln N^N$
  - $\ln \Omega = N \ln \frac{qe}{N}$ or equivalently $\Omega(q, N) = \left(\frac{qe}{N}\right)^N$
  - Entropy is $S = kN\ln\frac{qe}{N} = kN\ln\frac{Ee}{\hbar\omega N}$
  - $\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{kN}{E}$ or $\frac{E}{N} = kT$
    - This is equipartition!
  - Note the assumption that $\frac{q}{N} \gg 1 \implies kT \gg \hbar\omega$
- What about $\frac{q}{N} \ll 1$?
  - $\Omega(q, N) = \frac{(N+q)!}{N!q!}$ is symmetric with respect to switching q and N
  - This means we can do this case in exactly the same way just by swapping N and q
  - $\Omega = \left(\frac{Ne}{q}\right)^q$
  - $S = k\ln\left(\frac{Ne}{q}\right)^q = k\frac{E}{\hbar\omega}\ln\frac{Ne\hbar\omega}{E}$
  - $\frac{1}{T} = \frac{k}{\hbar\omega}\ln\left(\frac{N\hbar\omega}{E}\right)$
  - $\frac{E}{N} = \hbar\omega e^{-\frac{\hbar\omega}{kT}}$
    - Equipartition does not hold
    - If temperature is not enough to excite vibrational normal modes the energy per particle drops off exponentially

Distribution of Energies

- What is the probability of the energies of the system being different?
- Take two Einstein solids with the same N and flow
- $P(x) \sim \Omega_A\left(\frac{q}{2}-x\right)\Omega_B\left(\frac{q}{2}+x\right) = \left(\frac{\left(\frac{q}{2}-x\right)e}{N}\right)^N \left(\frac{\left(\frac{q}{2}+x\right)e}{N}\right)^N = \left(\frac{e^2}{N^2}\right)^N \left(\frac{q^2}{4}-x^2\right)^N$

- Take the ratio $\frac{P(x)}{P(0)} = \frac{\left(\frac{q^2}{4} - x^2\right)^N}{\left(\frac{q^2}{4}\right)^N} = \left(1 - \frac{qx^2}{q^2}\right)^N$
- $\ln \frac{P(x)}{P_0} = N \ln \left(1 - \left(\frac{x}{\frac{q}{2}}\right)^2\right)$
- $\frac{|x|}{\frac{q}{2}}$ is the relative energy balance
- Consider small energy balances, we can approximate it as $-N\left(\frac{x}{\frac{q}{2}}\right)^2$
- $P(x) = P_0 e^{-N\left(\frac{x}{\frac{q}{2}}\right)^2}$
- As $N \to \infty$, $P(x)$ becomes nonzero only at $x = 0$, making it a delta function, so the distribution of temperatures is now a certainty