Lecture 27 (2-10), Mar 20, 2023

Thermodynamic Potential

- The postulate directly implies that for a closed system that reaches thermodynamic equilibrium, it is most likely to find itself in a state of maximum S
- This can be seen as an alternative way to state the second law, that S is always increasing
- For an isolated system (constant E), we say that the entropy is the "thermodynamic potential"
  - Just like how a classical system tries to minimize its potential (e.g. a falling object), the system will try to maximize its entropy
  - Just like $\vec{F} = -\vec{\nabla} U$ is the driving force for a classical system, $\frac{1}{T} = \frac{\partial S}{\partial E}$ is the driving force for reaching thermal equilibrium
    * In equilibrium forces are in balance, just like how in thermal equilibrium the temperature must be in balance
- Since $\frac{\partial S}{\partial V}$ is the pressure and $\frac{\partial S}{\partial N}$ is the chemical potential, the partial derivatives of S determine the "force towards equilibrium"

General Properties of Entropy

- For now, only consider E
- For the Einstein solid, under $\frac{q}{N} \gg 1 \implies \frac{kT}{\hbar\omega \gg 1}$ we had $S(E) = kN \ln \frac{Ee}{N\hbar\omega}$
  - For this system and all "normal" systems, the slope of $S(E)$ to E is always positive (and so $T > 0$)
  - Additionally, this graph flattens out with increasing E; therefore $\frac{\partial^2 S}{\partial E^2}$, and so with increasing E, $\frac{\partial S}{\partial E} = \frac{1}{T}$ goes down or T goes up
    * This means that the heat capacity is positive
  - Such systems are *thermodynamically stable*
    * For systems held together by gravity (e.g. stars), this pattern is broken and the system actually cools down with more energy
- Recall that for the paramagnet $\Omega(N_\uparrow, N) = \frac{N!}{N_\uparrow!(N - N_\uparrow)!}$
  - This is not a "normal" system since it has a maximum energy
  - The plot of Ω against $N_\uparrow$ has a maximum at about $N_\uparrow = \frac{N}{2}$
  - To convert this to energy, we have to flip the graph (since $N_\uparrow = N$ has minimum energy)
  - The entropy curve is concave down with a maximum
    * In the first half of the curve between U_{min} and 0 the temperature is positive and increasing with E
    * In the second half of the curve, the temperature is negative
      - This is a metastable region that can only exist for a short amount of time
    * At the maximum, the temperature becomes infinite
  - When the total spin is maximum, we have minimum energy; as we heat up the magnet, the total spin decreases with temperature
    * The total spin at high temperature is $S \sim \frac{\mu_0 B}{kT}$ (Curie's law)