lecture 3 - 2nd law/notion of entropy

- spontaneous macroscopic processes - one way
  (irreversible)
- Kelvin statement of 2nd law
- - statistical mechanics postulate -
  $S = k_B \ln \Gamma$ - Boltzmann (microcanonical) entropy
- fundamental hypothesis of statistical mechanics
  - all states same probability -
- toy spin model, evaluation of entropy
  Gaussian distribution of probabilities

$$P_M \sim e^{-\frac{1}{2}\frac{M^2}{N}}, \quad P_m \sim e^{-\frac{Nm^2}{2}}, \quad m = M/N \tag{1}$$

  - example of central limit theorem -
  analogy to random walk
  system most of time at max entropy

- properties of entropy
  additivity
  $T \equiv \frac{\partial U}{\partial S}|_{P,V}$
  $P \equiv \frac{\partial U}{\partial V}|_{S,N}$
  $S(U, V)$ is equation of state
- thermodynamic identity

$$dU = \frac{\partial U}{\partial S}|_V dS + \frac{\partial U}{\partial V}|_S dV = TdS - PdV \tag{2}$$

  valid for any process, reversible or not

- for reversible process $dS = \frac{\delta Q}{T}, \quad \delta W = -PdV$
- thermodynamical definition of entropy, for reversible path,

$$S_2 - S_1 = \int_{(1)}^{(2)} \frac{\delta Q}{T} \tag{3}$$

- entropy of ideal gas - heuristic derivation

$$S = k_B \ln \Gamma, \quad \Gamma = cV^N U^{3N/2} \tag{4}$$

- toy spin model, $S(U, M) \to M = N\mu \tanh(\mu B/k_B T)$
  - microcanonical ensemble - fixed U, V, N

- 3rd law - Nernst - $T \to 0, \quad S \to 0$