Key points lecture 02/07/2022

Canonical ensemble: connection to thermodynamics through

$$Q_N(V,T) = \exp\left(-\beta A(N,V,T)\right)$$

Helmholtz free energy

$A = U - TS$

(from thermodynamics)

it can be shown that the relation $A = U - TS$ follows from the definition of $Q_N(V,T)$

Ensemble average in canonical ensemble:

$$\langle f \rangle = \frac{\int f\, e^{-\beta \mathcal{H}}\, d^{3N}\vec{p}\, d^{3N}\vec{q}}{\int e^{-\beta \mathcal{H}}\, d^{3N}\vec{p}\, d^{3N}\vec{q}}$$

Energy fluctuation:

$$\frac{\sqrt{\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2}}{\langle \mathcal{H} \rangle} \longrightarrow \frac{1}{\sqrt{N}} \longrightarrow 0$$

numerator $= \sqrt{kT^2 C_V} \propto \sqrt{N}$

denominator $\propto N$

large N

(the "typical" scaling is indicated in red)