Summary : Ensembles

Ensemble	Macrostate	Probability distribution	Thermodynamics
Microcanonical	E, V, N	$P_s = \frac{1}{\Gamma(E_s)}$	$S(E, V, N) = k \log(\Gamma)$
Canonical	T, V, N	$P_s = \frac{e^{-\beta E_s}}{Q_N}$	$A(T, V, N) = -kT \log Q_N$
Grandcanonical	T, V, μ	$P_s = \frac{e^{-\beta(E_s - \mu N_s)}}{\mathcal{Q}}$	$PV = kT \log \mathcal{Q}$

P_s : probability for the system to be in microstate s

E_s : energy of system in microstate s

S : entropy

A : Helmholtz free energy

P : Pressure

$\beta = \frac{1}{kT}$

- $\Gamma(E) = \dfrac{1}{N!\,h^{3N}} \displaystyle\int_{E < \mathcal{H} < E+\Delta E} d^{3N}p \, d^{3N}q$

$\Gamma(E) = \Gamma(E, V, N)$

suppressed dependency

h: units of momentum × length

- $Q_N(T, V) = \dfrac{1}{N!\,h^{3N}} \displaystyle\int_{\text{all space}} e^{-\beta \mathcal{H}} \, d^{3N}p \, d^{3N}q$

- $\mathcal{Q}(T, V, z) = \displaystyle\sum_{N=0}^{\infty} z^N Q_N(T, V)$

<u>Ensemble average:</u>

- $\langle f \rangle = \dfrac{\frac{1}{N!\,h^{3N}} \int_{E<\mathcal{H}<E+\Delta E} f \, d^{3N}p \, d^{3N}q}{\frac{1}{N!\,h^{3N}} \int_{E<\mathcal{H}<E+\Delta E} d^{3N}p \, d^{3N}q} = \dfrac{1}{\Gamma(E)} \dfrac{1}{N!\,h^{3N}} \displaystyle\int_{E<\mathcal{H}<E+\Delta E} f \, d^{3N}p \, d^{3N}q$

- $\langle f \rangle = \dfrac{\frac{1}{N!\,h^{3N}} \int f e^{-\beta\mathcal{H}} \, d^{3N}p \, d^{3N}q}{\frac{1}{N!\,h^{3N}} \int e^{-\beta\mathcal{H}} \, d^{3N}p \, d^{3N}q} = \dfrac{1}{Q_N} \dfrac{1}{N!\,h^{3N}} \displaystyle\int f e^{-\beta\mathcal{H}} \, d^{3N}p \, d^{3N}q$

- $\langle f \rangle = \dfrac{\sum_{N=0}^{\infty} \cancel{f} \, z^N Q_N(T, V)}{\sum_{N=0}^{\infty} z^N Q_N(T, V)} = \dfrac{1}{\mathcal{Q}} \displaystyle\sum_{N=0}^{\infty} f z^N Q_N(T, V)$

$\Gamma(E)$ can be rewritten in a convenient way using the Heavy side step function:

$$\Gamma(E) = \Sigma(E+\Delta E) - \Sigma(E)$$

$$= \frac{1}{N! h^{3N}} \int_{\text{all space}} \theta\left(E + \Delta E - \mathcal{H}(\vec{p}, \vec{q})\right) d^{3N}p \, d^{3N}q$$

$$- \frac{1}{N! h^{3N}} \int_{\text{all space}} \theta\left(E - \mathcal{H}(\vec{p}, \vec{q})\right) d^{3N}p \, d^{3N}q$$