Canonical Ensemble

consider macroscopic system in thermal contact
with much larger energy reservoir

energy of system : E

" reservoir : E_{res} $\qquad E_{res} >> E$

thermal contact : system and reservoir can exchange energy
but total energy is conserved

$$E + E_{res} = E_{tot}$$

microcanonical ensemble for system + reservoir
with total energy E_{tot}

# of microstate in which system has energy E

$$\Omega(E) \times \Omega_{res}(E_{tot} - E)$$

$\log \Omega_{res}(E_{tot} - E) = S_{res}(E_{tot} - E)$ can be expanded in powers of E

$$S_{res}(E_{tot} - E) = S_{res}(E_{tot}) + \frac{\partial S_{res}}{\partial E_{res}}(E_{tot})(-E) + \cdots$$

$$= S_{res}(E_{tot}) - \frac{1}{T_{res}} E + \cdots$$

$S_{res}(E_{tot})$ is extensive in size of reservoir, $-\frac{1}{T_{res}} E$ is intensive,
higher term go to 0 as size of reservoir goes to ∞

$$\Omega(E) \times \Omega_{res}(E_{tot} - E) \simeq \Omega(E) \times \exp\left(S_{res}(E_{tot}) - \beta E\right)$$

$$= \Omega_{res}(E_{tot}) \times \Omega(E)\, e^{-\beta E}$$

where $\beta = \frac{1}{T_{res}}$

<u>canonical ensemble</u> with temperature T

microstates: r with energy E_r

probability distribution: $P_r = \frac{1}{Z} e^{-\beta E_r}$ $\quad \beta = \frac{1}{T}$

where $Z = \sum_r e^{-\beta E_r}$

thermal equilibrium with reservoir

$\Longrightarrow$ $\beta = 1/T$, T = temperature of system

average energy: $U \equiv \langle E_r \rangle = \frac{1}{Z} \sum_r e^{-\beta E_r} E_r$

$$\boxed{U = -\frac{\partial}{\partial \beta} \log Z}$$

information entropy:

$$S = -\sum_r P_r \log P_r = -\sum_r \frac{1}{Z} e^{-\beta E_r} \left(-\beta E_r - \log Z\right)$$

$$= \beta \frac{1}{Z} \sum_r e^{-\beta E_r} E_r + \log Z\, \frac{1}{Z} \sum_r e^{-\beta E_r} = \beta U + \log Z$$

compare with Helmholtz free energy

$$F = U - TS$$

$$\beta F = \beta U - S$$

$$\Longrightarrow \boxed{F = -\frac{1}{\beta} \log Z}$$

partition function: $Z = \sum_r e^{-\beta E_r}$

determine other thermodynamic variables most easily
using thermodynamic relation for F

$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$\mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}$$

Classical ideal gas

N particles in volume V

Hamiltonian: $H = \sum_{n=1}^{N} \frac{1}{2m} \vec{p}_n^{\,2}$

probability density $\propto e^{-\beta H} d\omega$, $\quad d\omega = \prod_{n=1}^{N} d^3x_n \, d^3p_n$

partition function

$$Z_N = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int e^{-\beta H} d\omega$$

$$\int e^{-\beta H} d\omega = \int e^{-\beta \sum_{n=1}^{N} \vec{p}_n^{\,2}/2m} \prod_{n=1}^{N} d^3x_n \, d^3p_n$$

$$= \prod_{n=1}^{N} \int e^{-\beta \vec{p}_n^{\,2}/2m} d^3x_n \, d^3p_n$$

$$= \left(\int e^{-\beta \vec{p}_1^{\,2}/2m} d^3x_1 \, d^3p_1 \right)^N$$

$$Z_N = \frac{1}{N!} Z_1^N, \quad \text{where } Z_1 = \frac{1}{(2\pi\hbar)^3} \int e^{-\beta p^2/2m} d^3x \, d^3p$$

Z_1 = partition function for 1 particle
in thermal contact
with reservoir of temperature $T = \frac{1}{\beta}$

$$Z_1 = \frac{1}{(2\pi\hbar)^3}\int e^{-\beta\vec{p}^2/2m}\, d^3x\, d^3p$$

$$= \frac{V}{(2\pi\hbar)^3}\int e^{-\beta(p_x^2+p_y^2+p_z^2)/2m}\, dp_x\, dp_y\, dp_z$$

$$= \frac{V}{(2\pi\hbar)^3}\left(\int_{-\infty}^{\infty} e^{-\beta p_x^2/2m}\, dp_x\right)^3$$

$$= \frac{V}{(2\pi\hbar)^3}\left(\sqrt{\frac{2\pi m}{\beta}}\right)^{3/2}$$

$$= V\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2}$$

partition function: $Z_N = \frac{1}{N!} V^N \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3N/2}$

$$\log(N!) \simeq N(\log N - 1)$$

$$\log Z_N \simeq N\left[\log\left(\frac{V}{N}\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2}\right) + 1\right]$$

total energy: $U = -\frac{\partial}{\partial\beta}\log Z_N$

$$= -N\left(-\frac{3}{2}\frac{1}{\beta}\right) = \frac{3}{2}NT$$

free energy: $F = -\frac{1}{\beta}\log Z_N$

$$= -NkT\left[\log\left(\frac{V}{N}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right) + 1\right]$$