Quantum Statistical Mechanics

State:

$$|\psi\rangle = \sum_n |n\rangle\langle n|\psi\rangle = \sum_n \langle n|\psi\rangle\, |n\rangle$$

Normalization:

$$\langle\psi|\psi\rangle = \sum_n \langle n|\psi\rangle \langle\psi|n\rangle = \sum_n |\langle n|\psi\rangle|^2 = 1.$$

Observables:

Operators (or, matrices) $\hat{O}(\hat{q}, \hat{p})$

Classically $\{A, B\} = \sum_\alpha \frac{\partial A}{\partial q_\alpha}\frac{\partial B}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha}\frac{\partial B}{\partial q_\alpha}$

s.t., Quantum mechanically $[p_i, q_j] = -i\hbar\,\delta_{ij}$.

Expectation value $\langle\psi|O|\psi\rangle$

$$= \sum_{n,m} \langle\psi|n\rangle\langle n|O|m\rangle\langle m|\psi\rangle$$

$$= \langle\psi|O|\psi\rangle^*$$

$$\Rightarrow \langle n|O|m\rangle = \langle m|O|n\rangle.$$

$$\Rightarrow O = O^\dagger \quad : \text{Hermitian}$$

Classical time evolution : $\dot{q}_i = \frac{\partial H}{\partial p_i} = \{q_i, H\}$

$\dot{p}_i = -\frac{\partial H}{\partial q_i} = \{p_i, H\}$

Quantum time evolution :

$$i\hbar \frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle,$$

Classical macrostate (μ_α, P_α)

$$\Downarrow$$

$\rho(q_i, p_i)$.

Quantum mechanical

$$(|\Psi_\alpha\rangle, P_\alpha) \equiv \text{mixed state}$$

$$\langle O\rangle_{\text{ensemble}} = \int d\Gamma\, O(q_i, p_i)\, \rho(q_i, p_i).$$

$$\langle \hat{O}\rangle = \sum_\alpha p_\alpha \langle \Psi_\alpha|\hat{O}|\Psi_\alpha\rangle$$

$$= \sum_{\alpha, m, n} p_\alpha \langle \Psi_\alpha|m\rangle\langle m|\hat{O}|n\rangle\langle n|\Psi_\alpha\rangle$$

$$= \sum_{m,n} \langle m|\hat{O}|n\rangle \underbrace{\sum_\alpha p_\alpha \langle n|\Psi_\alpha\rangle\langle \Psi_\alpha|m\rangle}_{\langle n|\hat{\rho}|m\rangle}$$

$$= \mathrm{Tr}(\hat{\rho}\hat{O})$$

where, $\hat{\rho} = \sum_\alpha P_\alpha |\Psi_\alpha\rangle\langle\Psi_\alpha|$

(Density matrix)

Properties of Density matrix.

- Positive definite :

$$\langle \varphi | \hat{\rho} | \varphi \rangle = \sum_\alpha p_\alpha \langle \varphi | \psi_\alpha \rangle \langle \psi_\alpha | \varphi \rangle$$

$$= \sum_\alpha p_\alpha |\langle \psi_\alpha | \varphi \rangle|^2 > 0 .$$

- Hermitian :

$$\hat{\rho}^\dagger = \sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| = \hat{\rho} .$$

- Normalization :

$$1 = \mathrm{Tr}\,\hat{\rho} = \sum_{\alpha, n} p_\alpha \langle n | \psi_\alpha \rangle \langle \psi_\alpha | n \rangle$$

$$= \sum_{\alpha, n} p_\alpha \langle \psi_\alpha | n \rangle \langle n | \psi_\alpha \rangle$$

$$= \sum_\alpha p_\alpha \underbrace{\langle \psi_\alpha | \psi_\alpha \rangle}_{1}$$

$$= \sum_\alpha p_\alpha$$

$$= 1 .$$

- Liouville's theorem :

Classically , $\frac{\partial \rho}{\partial t} = \{H, \rho\}$.

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = \sum_\alpha p_\alpha \, i\hbar \frac{\partial}{\partial t} \left(|\psi_\alpha\rangle\langle\psi_\alpha| \right)$$

$$= \sum_\alpha p_\alpha \Big[\overbrace{\left(i\hbar \frac{\partial}{\partial t} |\psi_\alpha\rangle \right)}^{\hat{H}|\psi_\alpha\rangle} \langle\psi_\alpha| + |\psi_\alpha\rangle \overbrace{i\hbar \frac{\partial}{\partial t} \langle\psi_\alpha|}^{-\langle\psi_\alpha|\hat{H}} \Big] .$$

$$\left\{ \begin{array}{l} \text{But} \quad i\hbar \frac{\partial}{\partial t} |\psi\rangle = \hat{H}|\psi\rangle . \\ \Rightarrow -i\hbar \frac{\partial}{\partial t} \langle\psi| = \langle\psi|\hat{H} . \end{array} \right.$$

$$= H\left(\sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| \right) - \left(\sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| \right) \hat{H} .$$

$$= [\hat{H}, \hat{\rho}] . \qquad \Rightarrow \boxed{ i\hbar \frac{\partial \hat{\rho}}{\partial t} = [H, \hat{\rho}] . }$$

Note : $\frac{\partial \rho}{\partial t} = 0$ at equilibrium $\Rightarrow \{H, \rho\} = 0$

$\Rightarrow \rho_{eq} \equiv \rho(H) = \frac{\delta_{H,E}}{\Omega(E)}$.

Similarly, for QM case $[\hat{H}, \hat{\rho}] = 0$

for $\hat{\rho}_{eq}$: II

Equilibrium .

A. Microcanonical ensemble:

Use energy basis sets s.t., $\hat{H}|n\rangle = E_n|n\rangle$.

$$\Rightarrow \langle n|\hat{\rho}_{eq}|m\rangle = \frac{1}{\Omega(E)}\begin{cases} 1 & \text{if } E_m = E \text{ \& } m=n \\ 0 & \text{if } E_m \neq E \text{ or } m \neq n \end{cases}$$

Assumption of equal apriori probability.

$\Omega(E) = \mathrm{Tr}\left[\delta_{H,E}\right]$ = number of states of energy E.

B. Canonical ensemble

Fixed V, N and T

The density matrix is given by

$$\rho_{n,m} = \delta_{n,m}\, e^{-\beta E_n}$$

Thus, $$Z(N,V,T) = \sum_n e^{-\beta E_n} = \mathrm{Tr}\,\hat{\rho}.$$

C. Grand canonical ensemble

The density matrix acts on a Hilbert space with an indefinite number of particles.

Let $E_{n,N}$ be the n^{th} energy level for N particles. The density matrix is expressed by,

$$\rho_{n,N} = z^N e^{-\beta E_{n,N}}, \quad z = e^{\beta\mu}.$$

$$P = \frac{1}{\beta V}\ln \mathcal{Z}(z,V,T)$$

s.t., $$\mathcal{Z}(z,V,T) = \sum_{N,n} z^N e^{-\beta E_{n,N}}.$$