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 (QM version)

$\boxed{\text{Classically, } \frac{\partial\rho}{\partial t} = \{H, \rho\}.}$ ← Recall

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

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

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

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

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

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 $\hat{\rho}_{eq}$: ⇕ 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.

$\Omega(E) = \mathrm{Tr}[\delta_{H,E}]$ = 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., $\mathcal{Z}(z,V,T) = \sum_{N,n} z^N e^{-\beta E_{n,N}}$.

Illustrative example

Quantum mechanical 'particle in a box' of volume V.

$$\mathcal{H} = \frac{|\vec{p}|^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \quad \text{(in coordinate basis)}$$

As, $\mathcal{H}|\vec{k}\rangle = \varepsilon(\vec{k})|\vec{k}\rangle$

The energy eigenstates are:

$$\langle \vec{x}|\vec{k}\rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{x}} \; ; \text{with, } \varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}.$$

With periodic boundary conditions, for a box of side L, the allowed values of $\vec{k}$ are $\left(\frac{2\pi}{L}\right)(n_x, n_y, n_z)$

where, n_x, n_y, n_z are integers,

Partition function for $L \to \infty$,

$$Z = \mathrm{Tr}(\rho) = \sum_{\vec{k}} \exp\left(-\beta\frac{\hbar^2 k^2}{2m}\right)$$

$$= V\int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-\beta\frac{\hbar^2 k^2}{2m}\right).$$

$$= \frac{V}{(2\pi)^3}\left(\sqrt{\frac{2\pi m k_B T}{\hbar^2}}\right)^3 = \frac{V}{\lambda^3}.$$

$$\left(\text{where, } \lambda = \frac{h}{\sqrt{2\pi m k_B T}}.\right)$$

Elements of density matrix in coordinate representation are:

$$\langle \vec{x}'|\rho|\vec{x}\rangle = \sum_{\vec{k}} \langle \vec{x}'|\vec{k}\rangle \frac{e^{-\beta\varepsilon(\vec{k})}}{Z}\langle \vec{k}|x\rangle$$

$$= \frac{\lambda^3}{V}\int \frac{V}{(2\pi)^3} d^3\vec{k}\, \frac{e^{-i\vec{k}\cdot(\vec{x}-\vec{x}')}}{V} e^{-\beta\frac{\hbar^2 k^2}{2m}}.$$

$$= \frac{1}{V}\exp\left[-\frac{m(\vec{x}-\vec{x}')^2}{2\beta\hbar^2}\right]$$

$$= \frac{1}{V}\exp\left[-\frac{\pi(\vec{x}-\vec{x}')^2}{\lambda^2}\right].$$

QM particle
$\Updownarrow$
A wave packet of size $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$

→ The diagonal elements, $\langle \vec{x}|\rho|\vec{x}\rangle = \frac{1}{V}$

(prob. for finding a particle at $\vec{x}$).

→ Off-diagonal elements $\longleftrightarrow$ no classical analogue.

Home work

(1.) Consider a single harmonic oscillator with Hamiltonian

$$\mathcal{H} = \frac{p_x^2}{2m} + \frac{m\omega^2 x^2}{2}, \quad \text{with} \quad p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

Following steps as illustrated above (for free particle)

show that : $\langle x' | \rho | x \rangle = \sqrt{\frac{m\omega^2}{2\pi k_B T}} \exp\left(-\frac{m\omega^2 x^2}{2k_B T}\right) \exp\left[-\frac{mk_BT}{2\hbar^2}(x-x')^2\right]$.

(2.) Consider a quantum rotor in two dimensions with

$$\mathcal{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\theta^2}, \quad \text{and} \quad 0 \leq \theta < 2\pi .$$

Obtain $\langle \theta' | \rho | \theta \rangle$ in a canonical ensemble at temperature T & evaluate its low- and high-temperature limits.

(3.) Read about van Leeuwen's theorem. We will discuss this later.