Density Matrix

ensemble: probability distribution for microstates

Classical Mechanics

phase space: $(q_1, q_2, \dots q_N; p_1, p_2, \dots, p_N)$

$$d\omega = dq_1 dp_1\, dq_2 dp_2 \cdots dq_N dp_N$$

Hamiltonian: $H(p,q)$

ensemble: phase space distribution $\rho(p,q)$

$$\rho \geq 0, \quad \int d\omega\, \rho = 1$$

time evolution: $\frac{d}{dt}\rho = \frac{\partial}{\partial t}\rho + \{\rho, H\}$

equilibrium: $\frac{d}{dt}\rho = 0 \implies$ ρ does not depend explicitly on t
ρ is a function of H
and other conserved quantities

microcanonical ensemble: $\rho(p,q) = \frac{1}{\Omega(E)}\, \delta(H(p,q) - E)$

canonical ensemble: $\rho(p,q) = \frac{1}{Z(\beta)}\, e^{-\beta H(p,q)}$

grand canonical ensemble: $\rho(p,q;N) = \frac{1}{\mathcal{Z}(\beta,\alpha)}\, e^{-\beta H(p,q) - \alpha N}$

Quantum Mechanics

quantum states $|\psi\rangle$ form a complex vector space

can be added: $|\psi_1\rangle + |\psi_2\rangle$
can be multiplied by complex number: $\alpha|\psi\rangle$, $\alpha \in \mathbb{C}$

$\alpha|\psi\rangle$ represent same physical state as $|\psi\rangle$

inner product: $\langle\psi_1|\psi_2\rangle \in \mathbb{C}$

$\langle\psi|\psi\rangle \geq 0$ real, nonnegative
$\langle\psi|\psi\rangle = 0$ only if $|\psi\rangle = 0$

norm: $\| |\psi\rangle \| = \sqrt{\langle\psi|\psi\rangle}$

Hamiltonian operator: $\hat{H}$

hermitian: $\hat{H}^\dagger = \hat{H}$

time evolution (between measurement): $|\psi(t)\rangle$

Schroedinger equation: $i\frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$

real physical observable
is represented by hermitian operator $\hat{A}$

eigenvalues: $\hat{A}|\psi\rangle = a_i|\psi\rangle$ $\quad \hat{A}^\dagger = \hat{A} \Rightarrow a_i$ is real

quantum state can be decomposed into eigenstates of $\hat{A}$

projection operator: $\pi^2 = \pi$

projector onto eigenstates of $\hat{A}$
with eigenvalue a_i: $\pi(\hat{A}=a_i)$

completeness: $\sum_i \pi(\hat{A}=a_i) = \mathbb{1}$

sum over distinct eigenvalues

in quantum state $|\psi\rangle$, measurement of $\hat{A}$

- gives eigenvalue a_i with probability $\dfrac{\|\pi(\hat{A}=a_i)|\psi\rangle\|^2}{\||\psi\rangle\|^2}$

- collapses quantum state: $|\psi\rangle \rightarrow \pi(\hat{A}=a_i)|\psi\rangle$

measurements of $\hat{A}$ on many copies of same quantum state $|\psi\rangle$

give average value $\dfrac{\langle\psi|\hat{A}|\psi\rangle}{\langle\psi|\psi\rangle}$

<u>Quantum Mechanics</u> formulation in terms of density operator

quantum state: $|\psi(t)\rangle$

density operator: $\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|$

<u>properties</u>:

- $\hat{\rho}$ is hermitian: $\hat{\rho}^\dagger = \hat{\rho}$

$$\left(|\psi\rangle\langle\psi|\right)^\dagger = \left(\langle\psi|\right)^\dagger\left(|\psi\rangle\right)^\dagger = \left(|\psi\rangle\right)\left(\langle\psi|\right) = |\psi\rangle\langle\psi|$$

- $Tr[\hat{\rho}] = \langle\psi|\psi\rangle$

$$Tr\left(|\psi\rangle\langle\psi|\right) = \left(\langle\psi|\right)\left(|\psi\rangle\right) = \langle\psi|\psi\rangle$$

- time evolution: $\frac{d}{dt}\hat{\rho} = -\frac{i}{\hbar}[\hat{H},\hat{\rho}]$

$$i\hbar\dot{\hat{\rho}} = i\hbar\left(|\dot{\psi}\rangle\langle\psi| + |\psi\rangle\langle\dot{\psi}|\right) = \left(\hat{H}|\psi\rangle\right)\langle\psi| + |\psi\rangle\left(-\langle\psi|\hat{H}\right)$$

$$= \hat{H}|\psi\rangle\langle\psi| - |\psi\rangle\langle\psi|\hat{H} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H}$$

- $\hat{\rho}^2 = \hat{\rho}$ if $\langle\psi|\psi\rangle = 1$: $\quad \hat{\rho}^2 = \left(|\psi\rangle\langle\psi|\right)\left(|\psi\rangle\langle\psi|\right) = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = |\psi\rangle\langle\psi|$

- $\langle\psi|\hat{A}|\psi\rangle = Tr[\hat{A}\hat{\rho}]$

$$Tr[\hat{A}\hat{\rho}] = Tr[\hat{A}|\psi\rangle\langle\psi|] = \left(\langle\psi|\right)\left(\hat{A}|\psi\rangle\right) = \langle\psi|\hat{A}|\psi\rangle$$

Ensemble for macroscopic quantum system

choose complete orthonormal basis for microstates: $|\psi_r\rangle$

orthonormal: $\langle \psi_r | \psi_s \rangle = \delta_{rs}$

complete: $\sum_r |\psi_r\rangle\langle\psi_r| = \mathbb{1}$

specify probability P_r for each microstate $|\psi_r\rangle$

$$P_r \geq 0, \quad \sum_r P_r = 1$$

density matrix: $\hat{\rho} = \sum_r P_r |\psi_r\rangle\langle\psi_r|$

- $\hat{\rho}^\dagger = \hat{\rho}$
- $\mathrm{Tr}[\hat{\rho}] = 1$
- time evolution: $\frac{d}{dt}\hat{\rho} = \sum_r \dot{P}_r |\psi_r\rangle\langle\psi_r| - \frac{i}{\hbar}[\hat{H}, \hat{\rho}]$

$$\hat{\rho}^2 = \left(\sum_r P_r |\psi_r\rangle\langle\psi_r|\right)\left(\sum_s P_s |\psi_s\rangle\langle\psi_s|\right) = \sum_r\sum_s P_r P_s |\psi_s\rangle \underbrace{\langle\psi_r|\psi_s\rangle}_{\delta_{rs}} \langle\psi_s|$$

$$= \sum_r P_r^2 |\psi_r\rangle\langle\psi_r| \Longrightarrow \mathrm{Tr}[\hat{\rho}^2] = \sum_r P_r^2 \leq \sum_r P_r = 1$$

$\hat{\rho}^2 = \hat{\rho}$ only for pure state: $\hat{\rho} = |\psi\rangle\langle\psi|$

expectation value of hermitian operator $\hat{A}$

$$\langle \hat{A} \rangle \equiv \underbrace{\sum_r P_r \underbrace{\langle \psi_r | \hat{A} | \psi_r \rangle}_{\text{average from measurements in many identical copies of } |\psi_r\rangle}}_{\text{average over ensemble}}$$

$$\langle \hat{A} \rangle = \mathrm{Tr}[\hat{A}\hat{\rho}]$$

$$\mathrm{Tr}[\hat{A}\hat{\rho}] = \mathrm{Tr}\left[\hat{A}\left(\sum_r P_r |\psi_r\rangle\langle\psi_r|\right)\right]$$

$$= \sum_r P_r \, \mathrm{Tr}[\hat{A}\,|\psi_r\rangle\langle\psi_r|]$$

$$= \sum_r P_r \left(\langle\psi_r|\right)\left(\hat{A}|\psi_r\rangle\right)$$

$$= \sum_r P_r \langle\psi_r|\hat{A}|\psi_r\rangle = \langle\hat{A}\rangle$$

equilibrium density matrix: $\frac{d}{dt}\hat{\rho} = 0$

$$\frac{d}{dt}\hat{\rho} = \frac{\partial}{\partial t}\hat{\rho} - \frac{i}{\hbar}[\hat{H}, \hat{\rho}]$$

$\frac{\partial}{\partial t}\hat{\rho} = 0$ if probabilities P_r do not depend explicitly on t

$[\hat{H}, \hat{\rho}] = 0$ if $\hat{\rho}$ is a function of $\hat{H}$ and other operators that commute with $\hat{H}$

Microcanonical Ensemble with energy E

$$P_r = \frac{1}{\Omega(E)} \quad \text{if} \quad \hat{H}|\psi_r\rangle = E|\psi_r\rangle$$
$$= 0 \qquad \text{otherwise}$$

$\Omega(E) = \#$ of microstates $|\psi_r\rangle$ with $E_r = E$

$$\hat{\rho} = \frac{1}{\Omega(E)} \underbrace{\sum_{r:\, E_r = E} |\psi_r\rangle\langle\psi_r|}_{\text{projector onto states with energy } E}$$

Canonical Ensemble with temperature $T = \frac{1}{\beta}$

$$\hat{\rho} = \frac{1}{Z(\beta)} e^{-\beta\hat{H}}$$

$$Z(\beta) = \mathrm{Tr}\left[e^{-\beta\hat{H}}\right]$$

Microcanonical Ensemble with temperature $T = \frac{1}{\beta}$

chemical potential $\mu = -\alpha/\beta$

$$\hat{\rho} = \frac{1}{\mathcal{Z}(\alpha,\beta)} e^{-\beta\hat{H} - \alpha\hat{N}}$$

$$\mathcal{Z}(\alpha,\beta) = \mathrm{Tr}\left[e^{-\beta\hat{H} - \alpha\hat{N}}\right]$$