Kardar 6.5

Quantum Macrostates

Quantum macrostates depend on a small number of thermodynamic functions, like classical macrostates.

Ensembles formed from large number $\mathcal{N}$ of microstates μ_α, corresponding to a given macrostate.

Probability of a particular microstate P_α.

Ensemble averages:

Classical: $$\overline{\mathcal{O}(\{\vec{p}_i, \vec{q}_i\})}_t = \sum_\alpha P_\alpha \mathcal{O}(\mu_\alpha(t))$$

$$= \int \prod_{i=1}^N d^3p_i\, d^3q_i\, \mathcal{O}(\{\vec{p}_i, \vec{q}_i\})\, \rho(\{\vec{p}_i, \vec{q}_i\}, t)$$

where $$\rho(\{\vec{p}_i, \vec{q}_i\}, t) = \sum_\alpha P_\alpha \prod_{i=1}^N \delta^3(\vec{q}_i - \vec{q}_i(t)_\alpha)\, \delta^3(\vec{p}_i - \vec{p}_i(t)_\alpha)$$

Mixed quantum state:

$$\overline{\langle \mathcal{O} \rangle} = \sum_\alpha P_\alpha \langle \psi_\alpha | \mathcal{O} | \psi_\alpha \rangle$$

$|\psi_\alpha\rangle$ is microstate μ_α

$$= \sum_{\alpha, m, n} P_\alpha \langle \psi_\alpha | m \rangle \langle m | \mathcal{O} | n \rangle \langle n | \psi_\alpha \rangle$$

Define the density matrix $\rho(t)$:

$$\boxed{\langle n | \rho(t) | m \rangle \equiv \sum_\alpha P_\alpha \langle n | \psi_\alpha(t) \rangle \langle \psi_\alpha(t) | m \rangle}$$

$$\boxed{\overline{\langle \theta \rangle}} = \sum_{m,n} \langle n|\rho|m\rangle\langle m|\theta|n\rangle$$

$$\boxed{= \mathrm{Tr}(\rho\,\theta)}$$

Pure state: $\rho = |n\rangle\langle n|$, prob $(|n\rangle) = 1$.

$$\rho^2 = |n\rangle\underbrace{\langle n|n\rangle}_{1}\langle n| = |n\rangle\langle n| = \rho$$

$$\boxed{\text{pure state} \iff \rho^2 = \rho.}$$

Normalization: $\boxed{\mathrm{Tr}\,\rho = 1}$

$$\langle \mathbb{1} \rangle = \mathrm{Tr}(\rho\,\mathbb{1}) = \sum_{m,n} \langle n|\rho|m\rangle\langle m|\mathbb{1}|n\rangle$$

$$= \sum_{m,n} \langle n|\rho|m\rangle\,\delta_{mn}$$

$$= \sum_{n} \langle n|\rho|n\rangle$$

$$= \sum_{\alpha,n} |\langle n|\psi_\alpha\rangle|^2 p_\alpha = \sum_\alpha p_\alpha = 1 \quad \blacksquare$$

Hermiticity: $\boxed{\rho^\dagger = \rho}$

$$\langle m|\rho^\dagger|n\rangle = \langle n|\rho|m\rangle^* = \sum_\alpha p_\alpha \langle \psi_\alpha|m\rangle^* \langle n|\psi_\alpha\rangle^*$$

$$= \sum_\alpha p_\alpha \langle m|\psi_\alpha\rangle\langle\psi_\alpha|n\rangle$$

$$= \langle m|\rho|n\rangle \quad \blacksquare$$

Positivity: $\forall\ |\phi\rangle$, $\boxed{\langle\phi|\rho|\phi\rangle \geq 0}$

$$\langle\phi|\rho|\phi\rangle = \sum_\alpha p_\alpha \langle\phi|\psi_\alpha\rangle\langle\psi_\alpha|\phi\rangle$$

$$= \sum_\alpha p_\alpha |\langle\phi|\psi_\alpha\rangle|^2 \geq 0 \quad \blacksquare$$

corrolary: $\boxed{\rho \text{ has all positive eigenvalues.}}$

For an eigenstate $|m\rangle$ of ρ s.t. $\rho|m\rangle = \rho_m |m\rangle$,

$$\langle m|\rho|m\rangle = \rho_m \langle m|m\rangle = \rho_m \geq 0 \quad \blacksquare$$

Liouville's Theorem: $\boxed{i\hbar \frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho]}$

$$i\hbar \frac{\partial}{\partial t} \langle n|\rho(t)|m\rangle = i\hbar \frac{\partial}{\partial t} \sum_\alpha p_\alpha \langle n|\psi_\alpha(t)\rangle\langle\psi_\alpha(t)|m\rangle$$

$$= \sum_\alpha p_\alpha (E_n - E_m) \langle n|\psi_\alpha\rangle\langle\psi_\alpha|m\rangle$$

[using $i\hbar \frac{\partial}{\partial t} \langle n|\psi_\alpha\rangle = E_n \langle n|\psi_\alpha\rangle$

$i\hbar \frac{\partial}{\partial t} \langle\psi_\alpha|m\rangle = -E_m \langle\psi_\alpha|m\rangle$

$$= \langle n|(\mathcal{H}\rho - \rho\mathcal{H})|m\rangle \leftarrow \text{using } \langle n|\mathcal{H} = E_n\langle n|,\ \mathcal{H}|m\rangle = E_m|m\rangle$$

$$= \langle n|[\mathcal{H}, \rho]|m\rangle$$

$\blacksquare$

Equilibrium → Time-independent averages

$$\rightarrow \frac{\partial \rho}{\partial t} = 0$$

Liouville's theorem suggests $\rho = \rho(\mathcal{H})$

[or $\rho(\mathcal{H}$, other conserved operators$)$]

operators L_α s.t. $[\mathcal{H}, L_\alpha] = 0$

<u>Microcanonical Ensemble</u>:

$$\rho(E) = \frac{\delta(\mathcal{H} - E)}{\Omega(E)}$$

$$\langle n|\rho|m\rangle = \sum_\alpha p_\alpha \langle n|\psi_\alpha\rangle\langle\psi_\alpha|m\rangle$$

$$= \begin{cases} \frac{1}{\Omega} & \text{if } \varepsilon_n = E \text{ and } m = n \\ 0 & \text{if } \varepsilon_n \neq E \text{ or } m \neq n. \end{cases}$$

$$\overline{|\langle n|\psi\rangle|^2} = \frac{1}{\Omega}$$ Equal a priori probabilities

$\langle n|\rho|m\rangle \propto \delta_{nm}$ independent random phases in the $\Omega(E)$ microstates.

$$\mathrm{Tr}\,\rho = 1 \rightarrow \Omega(E) = \sum_n \delta(E - E_n)$$

= # microstates w/ energy E.

Canonical Ensemble :

Temperature $T = 1/k_B\beta$

$$\boxed{\rho(\beta) = \frac{\exp(-\beta\mathcal{H})}{Z(\beta)}}$$

$$\mathrm{Tr}\,\rho = 1 \rightarrow Z(\beta) = \mathrm{Tr}\, e^{-\beta\mathcal{H}}$$

$$= \sum_n \langle n| e^{-\beta\mathcal{H}} |n\rangle$$

$$\boxed{Z = \sum_n e^{-\beta\varepsilon_n}}$$

Example: Single particle in a box of volume V.

$$\mathcal{H}_1 = \frac{\vec{p}^{\,2}}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \quad \text{in coordinate basis}$$

Energy eigenstates $\mathcal{H}_1 |\vec{k}\rangle = \varepsilon(\vec{k}) |\vec{k}\rangle$

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

periodic boundary condition:

allowed $\vec{k}$ are $\vec{k} = 2\pi\left(\frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z}\right)$

$L_x, L_y, L_z \to \infty$:

$$Z_1 = \mathrm{Tr}\,\rho = \sum_{\vec{k}} \exp\left(-\beta\frac{\hbar^2 k^2}{2m}\right)$$

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

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

where $\lambda = \dfrac{h}{\sqrt{2\pi m k_B T}}$

Note the factor of h in λ, justifying the classical phase space measure $\frac{d^3p\, d^3q}{h^3}$.

Density Matrix:

$$\boxed{\langle \vec{x}'|\rho|\vec{x}\rangle} = \sum_{\vec{k}} \langle \vec{x}'|\vec{k}\rangle \frac{e^{-\beta\varepsilon(\vec{k})}}{Z_1} \langle \vec{k}|\vec{x}\rangle$$

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

from $\frac{1}{Z_1}$

$$= \frac{\lambda^3}{V}\int\frac{d^3k}{(2\pi)^3}\exp\left[-\frac{\beta\hbar^2}{2m}\left(\vec{k}+\frac{i(\vec{x}-\vec{x}')m}{\beta\hbar^2}\right)^2\right]\exp\left(-\frac{|\vec{x}-\vec{x}'|^2 m}{2\beta\hbar^2}\right)$$

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

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

Diagonal elements of ρ:

$\langle \vec{x}|\rho|\vec{x}\rangle = \frac{1}{V}$ = prob density for particle at $\vec{x}$.

off-diagonal components correspond to a quantum spread of the particle over a <u>thermal wavelength</u> λ.

$T\to\infty$: $\lambda\to 0$, off-diagonal elements $\to 0 \Rightarrow$ Classical

$T\to 0$: $\lambda\to\infty$, quantum effects dominate when $\lambda\sim V$.

Grand Canonical Ensemble :

Indefinite particle number

micro states $\in$ Fock space

$$\rho(\beta,\mu) = \frac{e^{-\beta\mathcal{H}+\beta\mu N}}{Q(\beta,\mu)}$$

$$Q(\beta,\mu) = \mathrm{Tr}\left(e^{-\beta\mathcal{H}+\beta\mu N}\right) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(\beta)$$