BOOKS: ① Huang, Statistical Mechanics
② Sethna, Statistical Mechanics: Entropy, Order and Complexity
③ Kardar, Statistical Physics of Particles

Quantum Statistical Mechanics

Microstates: A microstate of a classical system of N particles can be represented by a point in a 6N-dimensional phase space $\{\{\vec{q}_i\}, \{\vec{p}_i\}\}$.

Such a description violates Heisenberg's uncertainty principle and is therefore disallowed for a quantum system.

A microstate of a quantum system can be represented by a unit vector in an infinite dimensional Hilbert space. Denoted by $|\Psi\rangle$

Evolution of microstates:

Classical:

$$\dot{q}_{i\alpha} = \frac{\partial \mathcal{H}}{\partial p_{i\alpha}} \qquad i = 1, 2, \dots, N$$

$$\dot{p}_{i\alpha} = -\frac{\partial \mathcal{H}}{\partial q_{i\alpha}} \qquad \alpha = 1, 2, 3.$$

where $\mathcal{H}$ is the Hamiltonian describing the system and is a function of all the coordinates and momenta.

Quantum mechanical:

$$i\hbar \frac{\partial |\Psi\rangle}{\partial t} = \mathcal{H} |\Psi\rangle$$

where $\mathcal{H}$ is the Hamiltonian operator describing the system.

Macrostates are described by the values of a few thermodynamic functions. A given macrostate may correspond to a large number, $\mathcal{N}$, of microstates μ_α.

Pure state: $\mathcal{N} = 1$ (microstate uniquely determined from macrostate)

Mixed state: Given a macrostate, probability that it is a result of microstate μ_α is p_α, $\alpha = 1, 2, \ldots, \mathcal{N}$.

Classical: Consider macroscopic quantity Θ. Its ensemble average is given by

$$\overline{\Theta} = \sum_\alpha p_\alpha \Theta(\mu_\alpha)$$

$$= \int d^{3N}q\, d^{3N}p\, \Theta(\{\vec{q}_i, \vec{p}_i\})\, \rho(\{\vec{q}_i, \vec{p}_i\})$$

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

$\rho(\{\vec{q}_i, \vec{p}_i\})$ is the "phase space density"

Quantum mechanical: Consider a quantum state that corresponds to states $\{|\psi_\alpha\rangle\}$ with probabilities p_α. Consider an observable described by the operator Θ.

$\{|\psi_\alpha\rangle\}$ forms an orthonormal and complete basis.

The ensemble average of its expectation value is given by.

$$\overline{\langle\Theta\rangle} = \sum_\alpha p_\alpha \langle\psi_\alpha|\Theta|\psi_\alpha\rangle$$

We introduce another complete orthonormal basis $\{|n\rangle\}$.

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

$$\because \sum_m |m\rangle\langle m| = \sum_n |n\rangle\langle n| = \mathbb{1}$$

$$= \sum_{m,n} \left[\sum_\alpha p_\alpha \langle n | \psi_\alpha \rangle \langle \psi_\alpha | m \rangle \right] \langle m | \mathcal{O} | n \rangle$$

$$= \sum_{m,n} \langle n | \rho | m \rangle \langle m | \mathcal{O} | n \rangle \quad , \quad \boxed{\rho = \sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|}$$

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

ρ is known as the "density matrix".

* For a pure state, $\rho = |\psi\rangle\langle\psi| \Rightarrow \rho^2 = |\psi\rangle\underbrace{\langle\psi|\psi\rangle}_{1}\langle\psi| = \rho$

* $\mathrm{Tr}(\rho) = \overline{\langle 1 \rangle} = 1$

* $\rho^\dagger = \rho$ (Hermitian)

* Positive definite : For any state $|\phi\rangle$,

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

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

$\Rightarrow$ All eigenvalues of ρ must be positive.

$\Rightarrow$ ρ is positive definite.

Time evolution of the density matrix:

We know, $i\hbar \frac{\partial}{\partial t}|\psi_\alpha\rangle = H|\psi_\alpha\rangle$

Taking Hermitian conjugate,

$$-i\hbar \frac{\partial}{\partial t}\langle\psi_\alpha| = \langle\psi_\alpha| H$$

Classical Liouville's theorem

$$\frac{d\rho}{dt} = 0 \Rightarrow \frac{\partial\rho}{\partial t} + \sum_\alpha \left(\frac{\partial\rho}{\partial q_\alpha}\dot{q}_\alpha + \frac{\partial\rho}{\partial p_\alpha}\dot{p}_\alpha\right) = 0$$

$$\Rightarrow \frac{\partial\rho}{\partial t} + \sum_\alpha \left(\frac{\partial\rho}{\partial q_\alpha}\frac{\partial H}{\partial p_\alpha} - \frac{\partial\rho}{\partial p_\alpha}\frac{\partial H}{\partial q_\alpha}\right) = 0$$

$$\Rightarrow \frac{\partial\rho}{\partial t} + \{\rho, H\} = 0$$

$$\Rightarrow \frac{\partial\rho}{\partial t} = \{H, \rho\}$$

$\{\}$: Poisson bracket

Classical to quantum correspondence:

$\{\} \leftrightarrow \frac{1}{i\hbar}[\,]$ $[\,]$: Commutator

$$\therefore\ i\hbar\frac{\partial\rho}{\partial t} = i\hbar\frac{\partial}{\partial t}\sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|$$

$$= i\hbar\sum_\alpha p_\alpha\left[\left(\frac{\partial}{\partial t}|\psi_\alpha\rangle\right)\langle\psi_\alpha| + |\psi_\alpha\rangle\left(\frac{\partial}{\partial t}\langle\psi_\alpha|\right)\right]$$

$$= \sum_\alpha p_\alpha H|\psi_\alpha\rangle\langle\psi_\alpha| - \sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| H$$

$$= H\rho - \rho H$$

$$\Rightarrow \boxed{i\hbar\frac{\partial\rho}{\partial t} = [H, \rho]}$$ Quantum Liouville's theorem

Density Matrix for the Microcanonical Ensemble

The microcanonical ensemble with energy E is ~~of~~ obtained from energy eigenstates with eigenvalues in the range $[E, E+\Delta]$. All these eigenstates are equally likely.

Thus,

$$\boxed{\rho = \sum_{E \leq \varepsilon \leq E+\Delta} \frac{|\varepsilon\rangle\langle\varepsilon|}{\Omega(E)}}$$

where $\Omega(E)$ is the number of energy eigenstates with eigenvalues in the range $[E, E+\Delta]$

Density Matrix for the Canonical Ensemble

All energy eigenstates are considered here. For temperature T, these eigenstates ~~are~~ come with probabilities proportional to $e^{-\beta \mathcal{E}}$ where $\beta = 1/k_B T$ and $\mathcal{E}$ is the energy eigenvalue.

Thus,
$$\rho = \sum_{\mathcal{E}} \frac{e^{-\beta \mathcal{E}}}{Z} |\mathcal{E}\rangle\langle\mathcal{E}| \quad , \quad Z = \sum_{\mathcal{E}} e^{-\beta\mathcal{E}} = \mathrm{Tr}\, e^{-\beta H}$$
$$= \sum_{\mathcal{E}} \frac{e^{-\beta H}}{Z} |\mathcal{E}\rangle\langle\mathcal{E}|$$
$$= \frac{e^{-\beta H}}{Z} \sum_{\mathcal{E}} |\mathcal{E}\rangle\langle\mathcal{E}|$$
$$\Rightarrow \boxed{\rho = \frac{e^{-\beta H}}{Z}} \quad \text{where } Z = \mathrm{Tr}\, e^{-\beta H}$$

Density Matrix for the Grand Canonical Ensemble

In this ensemble, both the energy and the number of particles are allowed to fluctuate. The temperature and the chemical potential are held fixed.

$$\boxed{\rho = \frac{e^{-\beta(H-\mu N)}}{Z}} \quad , \quad \text{where } N \text{ is the number operator and } Z = \mathrm{Tr}\, e^{-\beta(H-\mu N)}$$

Electron in a magnetic ~~field~~ field

An ~~Ebsa~~ electron in a magnetic field can be described by the following Hamiltonian.

$$H = -\mu_B \vec{\sigma}\cdot\vec{B}$$

where μ_B = Bohr magneton $= \frac{e\hbar}{2m_e}$ in SI units

$\vec{\sigma} = \sigma_x \hat{i} + \sigma_y \hat{j} + \sigma_z \hat{k}$

$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$= -\mu_B B \sigma_z$$

when the direction of $\vec{B}$ is chosen as the z-axis, $\vec{B} = B\hat{k}$

$$\Rightarrow H = -\mu_B B \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The density matrix, ~~$\rho = \frac{1}{Z}$~~

$$\rho = \frac{1}{Z} e^{-\beta H} \quad \text{where } Z = \mathrm{Tr}\, e^{-\beta H}$$

$$e^{-\beta H} = \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix} \Rightarrow Z = e^{\beta\mu_B B} + e^{-\beta\mu_B B} = 2\cosh(\beta\mu_B B)$$

$$\Rightarrow \rho = \frac{1}{2\cosh(\beta\mu_B B)} \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix}$$

$$\overline{\langle\sigma_x\rangle} = \mathrm{Tr}(\rho\sigma_x) = \frac{1}{2\cosh(\beta\mu_B B)} \mathrm{Tr} \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$= \frac{1}{2\cosh(\beta\mu_B B)} \mathrm{Tr} \begin{pmatrix} 0 & e^{\beta\mu_B B} \\ e^{-\beta\mu_B B} & 0 \end{pmatrix} = 0$$

Similarly, $\overline{\langle\sigma_y\rangle} = 0$

$$\overline{\langle \sigma_z \rangle} = \frac{1}{2\cosh(\beta\mu_B B)} \mathrm{Tr} \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= \frac{1}{2\cosh(\beta\mu_B B)} \mathrm{Tr} \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & -e^{-\beta\mu_B B} \end{pmatrix}$$

$$= \tanh(\beta\mu_B B)$$

Free particle in a periodic box $\qquad 0 < x, y, z < L \qquad L^3 = V$

$$H = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$$

Energy eigenstates are eigenstates of momentum (or wave-vector)

$$H|\vec{k}\rangle = \frac{\hbar^2 k^2}{2m}|k\rangle$$

In the coordinate basis,

$$\psi_{\vec{k}}(\vec{x}) = \langle \vec{x}|\vec{k}\rangle = \frac{e^{i\vec{k}\cdot\vec{x}}}{\sqrt{V}}$$

Periodic Boundary conditions $\Rightarrow \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$

$$n_x, n_y, n_z \in \mathbb{Z}$$

The density matrix, $\rho = \dfrac{e^{-\beta H}}{\mathrm{Tr}\, e^{-\beta H}}$

$$\mathrm{Tr}\, e^{-\beta H} = \sum_{\vec{k}} e^{-\beta(\hbar^2 k^2/2m)} = \frac{V}{(2\pi)^3}\int d^3k\, e^{-\beta\hbar^2 k^2/2m}$$

$$\left[\sum_{\vec{k}} \equiv \sum_{k_x}\sum_{k_y}\sum_{k_z} \; ; \quad \sum_{k_x} = \frac{1}{\Delta k_x}\int dk_x = \frac{L}{2\pi}\int dk_x \right]$$

$$\therefore \operatorname{Tr} e^{-\beta H} = \frac{V}{(2\pi)^3} \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z \, e^{-\beta\hbar^2(k_x^2+k_y^2+k_z^2)/2m}$$

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

$$= \frac{V}{(2\pi)^3} \left(\frac{2\pi m}{\beta\hbar^2} \right)^{3/2} \qquad \because \int_{-\infty}^{\infty} dx \, e^{-x^2/2\sigma^2} = \sqrt{2\pi\sigma^2}$$

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

$$= \frac{V}{\lambda^3} \quad \text{where} \quad \boxed{\lambda \equiv \sqrt{\frac{2\pi\hbar^2}{m k_B T}} \quad \text{Thermal de Broglie wavelength}}$$

Thus, $\rho = \frac{\lambda^3}{V} e^{-\beta H}$

Matrix elements of the density matrix in the coordinate basis:

$$\langle \vec{x}' | \rho | \vec{x} \rangle = \frac{\lambda^3}{V} \langle \vec{x}' | e^{-\beta H} | \vec{x} \rangle$$

$$= \frac{\lambda^3}{V} \sum_{\vec{k}} \langle \vec{x}' | e^{-\beta H} | \vec{k} \rangle \langle \vec{k} | \vec{x} \rangle$$

$$= \frac{\lambda^3}{V} \frac{V}{(2\pi)^3} \int d^3k \, e^{-\beta\hbar^2 k^2/2m} \underbrace{\langle \vec{x}' | \vec{k} \rangle}_{\frac{e^{i\vec{k}\cdot\vec{x}'}}{\sqrt{V}}} \underbrace{\langle \vec{k} | \vec{x} \rangle}_{\frac{e^{-i\vec{k}\cdot\vec{x}}}{\sqrt{V}}}$$

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

$$= \frac{\lambda^3}{(2\pi)^3 V} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dk_x \, dk_y \, dk_z \, e^{-\frac{\beta\hbar^2(k_x^2+k_y^2+k_z^2)}{2m}} \times e^{-i[k_x(x-x') + k_y(y-y') + k_z(z-z')]}$$

$$\Rightarrow \langle \vec{x}'|\rho|\vec{x}\rangle = \frac{\lambda^3}{(2\pi)^3 V} \prod_{u=x,y,z} \left[\int_{-\infty}^{\infty} dk_u \, e^{-\frac{\beta\hbar^2 k_u^2}{2m} - ik_u(u-u')} \right]$$

$$-\frac{\beta\hbar^2 k_u^2}{2m} - ik_u(u-u') = -\frac{\beta\hbar^2}{2m}\left(k_u^2 + \frac{2im}{\beta\hbar^2} k_u(u-u')\right)$$

$$= -\frac{\beta\hbar^2}{2m}\left(k_u + \frac{m(u-u')i}{\beta\hbar^2}\right)^2 - \frac{(u-u')^2 m}{2\beta\hbar^2}$$

$$\Rightarrow \int_{-\infty}^{\infty} dk_u \, e^{-\frac{\beta\hbar^2 k_u^2}{2m} - ik_u(u-u')} = e^{-\frac{m(u-u')^2}{2\beta\hbar^2}} \int_{-\infty}^{\infty} dk_u \, e^{-\frac{\beta\hbar^2}{2m}\left(k_u + \frac{im(u-u')}{\beta\hbar^2}\right)^2}$$

$$= e^{-\frac{\cancel{\beta} m(u-u')^2}{2\beta\hbar^2}} \sqrt{\frac{2\pi m}{\beta\hbar^2}}$$

$$= \frac{2\pi}{\lambda} e^{-m(u-u')^2/2\beta\hbar^2}$$

$$\therefore \langle \vec{x}'|\rho|\vec{x}\rangle = \frac{1}{V} e^{-\frac{m}{2\beta\hbar^2}\left[(x-x')^2 + (y-y')^2 + (z-z')^2\right]}$$

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

Probability density of finding the particle at $\vec{x}$ is

$\langle \vec{x}|\rho|\vec{x}\rangle = 1/V$ (as expected)