Lecture 19

Last time, introduced density matrix

$$\rho_{mn} = \frac{1}{\eta} \sum_k \langle \phi_m | \psi^k \rangle \langle \psi^k | \phi_n \rangle$$

ψ^k = quantum state of system k

$\{\phi_n\}$ = basis states

or $$\hat{\rho} = \sum_n P_n |\phi_n\rangle\langle\phi_n|$$

P_n = prob to find system in state ϕ_n

Calculate ensemble averages as

$$\langle G \rangle = \mathrm{Tr}\, \hat{\rho}\, \hat{G} \quad \text{or} \quad \frac{\mathrm{Tr}\, \hat{\rho}\, \hat{G}}{\mathrm{Tr}\, \hat{\rho}}$$

Trace = sum of diagonal elements!

Compare classical version

$$\langle G \rangle = \int G(p,q)\, \rho(p,q)\, d\omega \quad \text{or} \quad \frac{\int G \rho\, d\omega}{\int \rho\, d\omega}$$

See correspondence between classical phase space density & density matrix

And trace $\leftrightarrow$ integral over phase space

Both ways to sum over states

For canonical ensemble, use

$$\rho_{nm} = \frac{e^{-\beta E_n}}{Q_N} \delta_{nm}$$

$$= \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}$$

For grand canonical ensemble, # of particles varies

Introduce number operator $\hat{n}$

$$\hat{n} \psi^k = N_k \psi^k$$

N_k = # of particles in system k

Then take

$$\hat{\rho} \propto e^{-\beta \hat{H} - \alpha \hat{n}}$$

$$= \frac{1}{\mathcal{Q}} e^{-\beta(\hat{H} - \mu \hat{n})}$$

for $$\mathcal{Q}(\mu, V, T) = \sum_{N,r} e^{-\beta(E_r - \mu N)}$$

$$= \mathrm{Tr}\, e^{-\beta(\hat{H} - \mu \hat{n})}$$

So ensemble average is

$$\langle G \rangle = \frac{1}{\mathcal{Q}} \mathrm{Tr}\, \hat{G} e^{-\beta \hat{H}} e^{\beta \mu \hat{n}}$$

(assuming $[\hat{H}, \hat{n}] = 0$)

$$= \frac{1}{\mathcal{Q}} \sum_{N=0}^{\infty} e^{\beta \mu N} \mathrm{Tr}\, \hat{G}(N) e^{-\beta \hat{H}(N)}$$

Use $\langle G \rangle_N$ = canonical average

$$= \frac{\mathrm{Tr}\, \hat{G} e^{-\beta \hat{H}}}{Q_N}$$

and $z = e^{\beta \mu}$

So $$\langle G \rangle = \frac{1}{\mathcal{Q}} \sum_N z^N \langle G \rangle_N Q_N$$

and $$\mathcal{Q} = \sum_N z^N Q_N$$

so $$\langle G \rangle = \frac{\sum_N z^N \langle G \rangle_N Q_N}{\sum_N z^N Q_N}$$

Expression valid for both classical & quantum cases
Differ in how $\langle G \rangle_N$, Q_N computed

That's the basic framework.

Do a few examples:

Particle in a box

Say cubical box, side L

Periodic boundary conditions

Get eigenstates

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{L^{3/2}} e^{i \vec{k} \cdot \vec{r}}$$

with $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$

n_i = any integer

Energy $E_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$

Now evaluate $\hat{\rho}$ in canonical ensemble

$$\hat{\rho} = \sum_{\vec{k}} e^{-\beta E_{\vec{k}}} |\phi_{\vec{k}}\rangle\langle\phi_{\vec{k}}|$$

More meaningful to evaluate in some basis

In $\phi_{\vec{k}}$ basis, get matrix elements

$$\rho_{\vec{k}\vec{k}'} = e^{-\beta E_{\vec{k}}} \delta^3_{\vec{k}\vec{k}'}$$

Know that ρ is diagonal in energy basis, so makes sense

Lets see in position basis

$$\langle\vec{r}|\hat{\rho}|\vec{r}'\rangle = \rho(\vec{r}, \vec{r}')$$

$$= \sum_{\vec{k}} e^{-\beta E_{\vec{k}}} \underbrace{\langle\vec{r}|\phi_{\vec{k}}\rangle}_{\phi_k(\vec{r})} \underbrace{\langle\phi_k|\vec{r}'\rangle}_{\phi_k^*(\vec{r}')}$$

$$= \frac{1}{L^3} \sum_{\vec{k}} e^{-\frac{\beta\hbar^2 k^2}{2m}} e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}$$

If box is big, sum $\to$ integral

interval between k's $= \frac{2\pi}{L}$

So $\left(\frac{2\pi}{L}\right)^3 \to d^3k$

$$\rho(\vec{r},\vec{r}\,') \to \frac{1}{(2\pi)^3} \int e^{-\frac{\beta\hbar^2 k^2}{2m}} e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} d^3k$$

Fourier transform of Gaussian

$$= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} e^{-\frac{m}{2\beta\hbar^2}|\vec{r}-\vec{r}\,'|^2}$$

Recall $\Lambda = \sqrt{\frac{h^2}{2\pi mkT}} = \sqrt{\frac{2\pi\hbar^2\beta}{m}}$

$$\rho(\vec{r},\vec{r}\,') = \frac{1}{\Lambda^3} e^{-\frac{\pi}{\Lambda^2}|\vec{r}-\vec{r}\,'|^2}$$

Of course this isn't normalized.

Should divide by $Q_1 = \mathrm{Tr}\,\hat{\rho} = \sum_{\vec{k}} e^{-\beta E_k}$

$$= \int d^3r\, \rho(\vec{r},\vec{r})$$

$$= \frac{V}{\Lambda^3}$$

So normalized $\boxed{\rho = \frac{1}{V} e^{-\frac{\pi}{\Lambda^2}|\vec{r}-\vec{r}\,'|^2}}$

See: $\rho(\vec{r},\vec{r}) = \frac{1}{V}$ = density

So $\rho(\vec{r},\vec{r})\,d^3r$ = probability to find particle at $\vec{r}$

Again see diagonal elements of ρ give probabilities

Here see off-diagonal elements $\rho(\vec{r},\vec{r}')$

$\rightarrow 0$ as $|\vec{r}-\vec{r}'| \gg \Lambda$

Recall Λ = thermal de Broglie wavelength

$\sim$ typical de Broglie wavelength for

$E \sim k_B T$

$\sim$ extent of wavefunction $\psi(\vec{r})$

So $\rho(\vec{r},\vec{r}')$ is large if particle has quantum amplitude to be found at both $\vec{r}$ + $\vec{r}'$ at same time

small if not

Say $\rho(\vec{r},\vec{r}')$ describes quantum coherence between points at $\vec{r}$, $\vec{r}'$

Like optical coherence:

If we sent our particle through a pair of slits, need slit spacing $\lesssim \Lambda$ to observe interference.

Note, we can work in any basis we want

For instance, can calculate energy

$$\langle H \rangle = \mathrm{Tr}\, \hat{H}\hat{\rho}$$

$$= \frac{1}{Q_1} \sum_{\vec{k}} E e^{-\beta E_k}$$

$$\rightarrow \frac{1}{Q_1} \left(\frac{L}{2\pi}\right)^3 \int d^3k \, \frac{\hbar^2 k^2}{2m} e^{-\beta \frac{\hbar^2 k^2}{2m}}$$

$$= \frac{3}{2\beta}$$

or $$\langle H \rangle = \int d^3r \left(-\frac{\hbar^2}{2m}\nabla_r^2\right)\left(\frac{1}{V} e^{-\frac{\pi |\vec{r}-\vec{r}'|}{\Lambda^3}}\right)\Bigg|_{\vec{r}=\vec{r}'}$$

$$= \frac{3}{2\beta}$$

or just $$\langle H \rangle = -\frac{\partial}{\partial\beta} \ln Q_1 = \frac{3}{2\beta}$$

One more example:

Two level system

Specifically, electron in magnetic field B_z

Eigenstates $|m=+\frac{1}{2}\rangle$, $|m=-\frac{1}{2}\rangle$

or just $|\uparrow\rangle$ $|\downarrow\rangle$

Then $\hat{\rho} \rightarrow 2\times 2$ matrix $\begin{bmatrix} \langle\downarrow|\rho|\downarrow\rangle & \langle\uparrow|\rho|\downarrow\rangle \\ \langle\downarrow|\rho|\uparrow\rangle & \langle\uparrow|\rho|\uparrow\rangle \end{bmatrix}$

Consider ensemble where $|\uparrow\rangle$ & $|\downarrow\rangle$ equally likely

$$P_\uparrow = P_\downarrow = \frac{1}{2}$$

Then $$\hat{\rho} = \frac{1}{2}|\uparrow\rangle\langle\uparrow| + \frac{1}{2}|\downarrow\rangle\langle\downarrow|$$

So $$\langle\uparrow|\rho|\uparrow\rangle = \langle\downarrow|\rho|\downarrow\rangle = \frac{1}{2}$$
$$\langle\uparrow|\rho|\downarrow\rangle = \langle\downarrow|\rho|\uparrow\rangle = 0$$

$$\rho \rightarrow \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{bmatrix}$$

Compare ensemble where spin always points in $+x$ direction

Recall $$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_z\rangle + |\downarrow_z\rangle\right) = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle + |\downarrow\rangle\right)$$

So $$\hat{\rho} = \frac{1}{2}\left(|\uparrow\rangle + |\downarrow\rangle\right)\left(\langle\uparrow| + \langle\downarrow|\right)$$
$$= \frac{1}{2}\left(|\uparrow\rangle\langle\uparrow| + |\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|\right)$$

So matrix $$= \begin{bmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{bmatrix}$$

See that diagonal terms same either way

Off-diagonal terms describe quantum coherence that makes this a pure state