Phys. 528 Lecture 11

Quantum Statistics (cont.)

1) Statistical ensembles

To describe a stationary (steady state) ensemble with $\dot{\hat{\rho}} = 0$, we require $\hat{\rho}$ to be a function of a constant of the motion. e.g.,

$$\hat{\rho} = \hat{\rho}(\hat{A}) \quad , \quad [\hat{A}, \hat{H}] = 0$$

Then $[\hat{\rho}, \hat{H}] = 0$ so $\dot{\hat{\rho}} = 0$.

This implies that the density matrix describing a system in a steady state (even a nonequilibrium steady state) must be <u>diagonal</u> in the <u>energy</u> basis.

2) microcanonical esemble

For equilibrium systems, typically $\hat{\rho} = \hat{\rho}(\hat{H})$. In the energy basis, the microcanonical esemble is described by the density matrix

$$\rho_{nm} = \begin{cases} \frac{1}{\Omega}\delta_{nm}, & E - \frac{\Delta}{2} \le E_n \le E + \frac{\Delta}{2} \\ 0, & \text{otherwise} \end{cases}$$

with $\mathrm{Tr}\,\hat{\rho} = 1$.

3) Canonical esemble

$$\rho_{nm} = C\, e^{-\beta E_n}\, \delta_{nm}$$

$$C = \frac{1}{Z_N(\beta)}$$

$$\hat{\rho} = \sum_n |n\rangle \frac{e^{-\beta E_n}}{Z_N(\beta)} \langle n|$$

$$= \frac{e^{-\beta \hat{H}}}{Z_N(\beta)} \sum_n |n\rangle\langle n|$$

$$= \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\{e^{-\beta \hat{H}}\}} \quad , \quad Z_N(\beta) = \mathrm{Tr}\{e^{-\beta H}\}$$

$$E = \langle \hat{H} \rangle = \mathrm{Tr}\{\hat{\rho}\, \hat{H}\} = \frac{\mathrm{Tr}\{\hat{H} e^{-\beta \hat{H}}\}}{\mathrm{Tr}\{e^{-\beta \hat{H}}\}}$$

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

4) <u>Grand canonical ensemble</u>

$$\hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\mathrm{Tr}\{e^{-\beta(\hat{H}-\mu)\hat{N}}\}} \quad , \quad [\hat{H}, \hat{N}] = 0$$

$$\rho_{nm} = \langle n|\hat{\rho}|m\rangle = \frac{e^{-\beta(E_n - \mu N_n)}}{\mathcal{Z}}\delta_{nm}$$

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

5) Examples

i) Two-level system

$$\hat{H} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

A mixed state

$$\hat{\rho} = \begin{pmatrix} \rho_1 & 0 \\ 0 & \rho_2 \end{pmatrix}$$

e.g., canonical ensemble with $\rho_i = \dfrac{e^{-\beta E_i}}{Z}$

is stationary $\dot{\rho}_{nm} = 0$.

A pure state

$$\hat{\rho} = |\psi\rangle\langle\psi| \quad \text{with} \quad |\psi\rangle = \frac{|1\rangle + e^{i\theta}|2\rangle}{\sqrt{2}}$$

has
$$\hat{\rho}(0) = \begin{pmatrix} \frac{1}{2} & \frac{1}{2}e^{-i\theta} \\ \frac{1}{2}e^{i\theta} & \frac{1}{2} \end{pmatrix}$$

and
$$\hat{\rho}(t) = \begin{pmatrix} \frac{1}{2} & \frac{1}{2}e^{-i(\theta-\omega t)} \\ \frac{1}{2}e^{i(\theta-\omega t)} & \frac{1}{2} \end{pmatrix},$$

where $\omega = \frac{E_2 - E_1}{\hbar}$.

The observable

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

has
$$\langle \sigma_x \rangle = \mathrm{Tr}\{\rho\sigma_x\} = \mathrm{Tr}\left\{\begin{pmatrix} \rho_1 & 0 \\ 0 & \rho_2 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right\}$$
$$= \mathrm{Tr}\left\{\begin{pmatrix} 0 & \rho_1 \\ \rho_2 & 0 \end{pmatrix}\right\} = 0$$
in the mixed state.

But $\langle \sigma_x(t) \rangle = \mathrm{Tr}\{ \rho(t)\, \sigma_x \}$

$$= \mathrm{Tr}\left\{ \begin{pmatrix} \frac{1}{2} & \frac{1}{2} e^{i(\omega t - \theta)} \\ \frac{1}{2} e^{i(\theta - \omega t)} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right\}$$

$$= \mathrm{Tr}\left\{ \begin{pmatrix} \frac{1}{2} e^{i(\omega t - \theta)} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} e^{i(\theta - \omega t)} \end{pmatrix} \right\}$$

$$= \cos(\omega t - \theta)$$ in the pure state

$$\omega = \frac{E_2 - E_1}{\hbar} = \text{Rabi frequency}$$

Ex. ii) <u>Particle in a box</u> $\quad V = L^3$

$$\hat{H} = \frac{\vec{p}^{\,2}}{2m} \qquad \psi_{\vec{k}} = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$

$$\hat{H}\psi_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m} \psi_{\vec{k}}, \qquad E = \frac{\hbar^2 \vec{k}^2}{2m}$$

P.B.C.s: $\psi(x+L,y,z) = \psi(x,y+L,z)$

$= \psi(x,y,z+L) = \psi(x,y,z)$

$$\Rightarrow \quad k_i = \frac{2\pi n_i}{L}, \quad \vec{k} = \frac{2\pi \vec{n}}{L}$$

$$\langle \vec{r} | e^{-\beta \hat{H}} | \vec{r}\,' \rangle = \sum_{\vec{k}} \langle \vec{r} | \vec{k} \rangle e^{-\beta E_{\vec{k}}} \langle \vec{k} | \vec{r}\,' \rangle$$

$$\langle \vec{r} | \vec{k} \rangle = \psi_{\vec{k}}(\vec{r}), \quad \langle \vec{k} | \vec{r}\,' \rangle = \psi^*_{\vec{k}}(\vec{r}\,')$$

$$\langle \vec{r} | e^{-\beta \hat{H}} | \vec{r}\,' \rangle = \frac{1}{V} \sum_{\vec{k}} e^{-\beta \frac{\hbar^2 k^2}{2m} + i\vec{k}\cdot(\vec{r}-\vec{r}\,')}$$

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

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

$$Z_1 = \mathrm{Tr}\{ e^{-\beta \hat{H}} \} = \int d^3r \, \langle \vec{r} | e^{-\beta \hat{H}} | \vec{r} \rangle$$

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

$$\langle \vec{r} \,|\, \hat{\rho} \,|\, \vec{r}\,' \rangle = \frac{1}{V} e^{-\frac{m|\vec{r}-\vec{r}\,'|^2}{2\beta\hbar^2}}$$

$$E = \langle \hat{H} \rangle = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{3}{2\beta} = \frac{3}{2} k_B T$$

iii) <u>Harmonic oscillator</u>

$$\hat{H} = \frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \dots, \infty$$

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{H_n(\xi)}{(2^n n!)^{1/2}} e^{-\frac{1}{2}\xi^2}$$

$$\xi = \sqrt{\frac{m\omega}{\hbar}}\, x$$

$$\langle x \,|\, e^{-\beta\hat{H}} \,|\, x' \rangle = \sum_{n=0}^{\infty} e^{-\beta E_n} \psi_n(x) \psi_n^*(x')$$

$$= \sqrt{\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)}}$$

$$\times \exp\left\{-\frac{m\omega}{4\hbar}\left[(x+x')^2 \tanh\left(\frac{\beta\hbar\omega}{2}\right) + (x-x')^2 \coth\left(\frac{\beta\hbar\omega}{2}\right)\right]\right\}$$

$$\mathrm{Tr}\{e^{-\beta\hat{H}}\} = \int_{-\infty}^{\infty} dx \ \langle x| e^{-\beta\hat{H}} |x\rangle$$

$$= \sum_{n=0}^{\infty} \langle n| e^{-\beta\hat{H}} |n\rangle = \frac{e^{-\beta\frac{\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}$$

$$= \frac{1}{2\sinh\left(\beta\frac{\hbar\omega}{2}\right)}$$

$$\langle x|\hat{\rho}|x\rangle = \rho(x,x) = \left[\frac{m\omega\tanh\left(\beta\frac{\hbar\omega}{2}\right)}{\pi\hbar}\right]^{1/2}$$

$$\times \exp\left\{-\frac{m\omega x^2}{\hbar}\tanh\left(\beta\frac{\hbar\omega}{2}\right)\right\}$$

$$\langle x^2\rangle = \frac{\hbar}{2m\omega\tanh\beta\frac{\hbar\omega}{2}}$$

$$= \begin{cases} \dfrac{\hbar}{2m\omega}, & \dfrac{k_BT}{\hbar\omega}\to 0 \\[2ex] \dfrac{k_BT}{m\omega^2}, & \dfrac{k_BT}{\hbar\omega}\to\infty \end{cases}$$

$$\langle V \rangle = \frac{m\omega^2}{2} \langle x^2 \rangle = \frac{\hbar\omega}{4 \tanh \beta \frac{\hbar\omega}{2}}$$

$$E = - \frac{\partial \ln \mathrm{Tr}\{e^{-\beta \hat{H}}\}}{\partial \beta} = \frac{\partial}{\partial \beta} \ln \sinh \beta \frac{\hbar\omega}{2}$$

$$= \frac{\hbar\omega}{2} \frac{1}{\tanh \beta \frac{\hbar\omega}{2}} = 2 \langle V \rangle$$

Cf. virial theorem.