10/4

- Homework #7 due on 10/11 and included in midterm.
- Midterm on 10/13 (Thursday) – (Home part due on 10/18

Last time: Density matrix.

$$\hat{H} \qquad \hat{H}\psi_k(t) = i\hbar\dot{\psi}_k(t)$$

$$\psi_k(t) = \sum_n a_n(t)\phi_n$$

$$\rho_{mn}(t) = \frac{1}{N}\sum_{k=1}^{N} a_m^k(t)\, a_n^{k*}(t) = \langle a_m(t) a_n^*(t)\rangle$$

Then

$$\rho_{nn} = \rho_n = \langle |a_n|^2 \rangle$$

$$\sum_m \rho_m = \sum_m |a_m|^2 = 1 = \mathrm{tr}\,\hat{\rho}$$

Liouville's theorem:

$$i\hbar \dot{\hat{\rho}} = [\hat{H}, \hat{\rho}]. \quad (1)$$

In equilibrium $\dot{\rho} = 0$ (same as classically). (2)

Because of (1) and (2) in equilibrium $[\hat{H}, \hat{\rho}] = 0$. (3)

To ensure ③ it is needed that

i) $\hat{\rho} = f(\hat{H})$ to insure commutation.

ii) $\dot{\hat{H}} = 0$ so that $\dot{\hat{\rho}} = 0$ also.

If ϕ_n are eigenstates of $\hat{H}$ it means that in this basis:

$$H_{mn} = E_n \delta_{mn}$$ (H is diagonal in the ϕ_n bases).

Then in this basis $\hat{\rho}$ is also diagonal because $\hat{\rho} = f(\hat{H})$.

$$\rho_{mn} = \rho_n \delta_{mn}.$$

This $\{\phi_n\}$ is called the energy representation and in this basis:

$$\hat{\rho} = \sum_n |\phi_n\rangle \rho_n \langle \phi_n| \qquad *$$

Using ⊛ for the operator we can find its matrix element in the energy representation:

$$\rho_{kl} = \langle \phi_k | \sum_n | \phi_n \rangle \rho_n \langle \phi_n | \phi_l \rangle =$$

$$= \sum_n \langle \underbrace{\phi_k | \phi_n}_{\delta_{kn}} \rangle \rho_n \langle \underbrace{\phi_n | \phi_l}_{\delta_{nl}} \rangle =$$

$$= \rho_k \, \delta_{kl}$$ it is diagonal.

Remember that ρ_n is the probability that a member of the ensemble is in eigenstate ϕ_n at time t.

Clearly ρ_n will be a function of E_n.

Notice that in an arbitrary basis the density matrix may not be diagonal but $\rho_{mn} = \rho_{nm}$ it will be symmetric because it is equally likely that a system will go from state n to m as vice versa.

This is called <u>detailed balance</u>.

Consider a different basis $\{\chi_k\}$

$$\rho_{kl} = \langle \chi_k | \sum_m |\phi_m\rangle \rho_m \langle \phi_m | \chi_l \rangle =$$

$$= \sum_m \langle \chi_k | \phi_m \rangle \rho_m \langle \phi_m | \chi_l \rangle$$

in general not diagonal.

How to calculate average values of any observable using $\hat{\rho}$:

$$\langle G \rangle = \langle \hat{G} \rangle = \frac{1}{N} \sum_{k=1}^{N} \int \psi^{k*} \hat{G} \psi^{k} \, d\tau =$$

$$= \frac{1}{N} \sum_{k=1}^{N} \int \sum_{n} a_n^{k*} \phi_n^{*} \hat{G} \sum_{m} a_m^{k} \phi_m \, d\tau =$$

$$= \frac{1}{N} \sum_{k=1}^{N} \sum_{m,n} a_n^{k*} a_m^{k} \underbrace{\int \phi_n^{*} \hat{G} \phi_m \, d\tau}_{G_{nm}} =$$

$$= \frac{1}{N} \sum_{k=1}^{N} \left[\sum_{m,n} a_n^{k*} a_m^{k} G_{nm} \right]$$

$$= \sum_{m,n} \overbrace{\frac{1}{N} \sum_{k=1}^{N} a_n^{k*} a_m^{k}}^{\rho_{nm}} G_{nm}$$

$\rho_{nm} = \rho_{mn}$

then

$$\langle G \rangle = \sum_{m,n} \rho_{mn} G_{nm} = \sum_{m} (\hat{\rho}\hat{G})_{mm} =$$

$$= tr(\hat{\rho}\hat{G})$$

Notice that if $G = \mathbb{I} \Rightarrow tr\,\hat{\rho} = 1$

so $tr\,\hat{\rho} = 1$ in any basis as expected.

If ψ^k is not normalized then $tr\,\hat{\rho} \neq 1$ and

$$\langle G \rangle = \frac{Tr(\hat{\rho}\hat{G})}{Tr(\hat{\rho})}.$$

Let's calculate $\hat{\rho}$ in the different ensembles:

1) Microcanonical:

$$N, V, E \pm \frac{1}{2}\Delta \qquad \Delta << E$$

$\Gamma(N, V, E; \Delta)$ # of accessible states.

- Due to equal a priori probability postulate we know that

$$\rho_n = \begin{cases} \frac{1}{\Gamma} & \text{for accessible states} \\ 0 & \text{otherwise} \end{cases}$$

and $\rho_{mn} = \rho_n \delta_{m,n}$ in energy basis.

then $S = k \ln \Gamma$

Pure case: if $\Gamma = 1 \Rightarrow S = 0$.

(Nernst theorem is satisfied in this case; ground state at $T=0$).

The density matrix is given by:

$\rho_{11} = 1$ $\rho_{nn} = 0$ $\forall n \neq 0$.

$$\hat{\rho} = \begin{pmatrix} 1 & & 0 \\ & 0 \ddots & \\ 0 & & 0 \end{pmatrix}$$

Notice that $\rho^2 = \rho$.

Assume that we now use a different basis.

$$\psi_k = \sum_r c_r^k |\chi_r\rangle$$

$\underbrace{|\chi_r\rangle}$ new basis.

(instead of $\psi_k = \sum_n a_n^k |\phi_n\rangle$)

Then

$$\rho_{mn} = \frac{1}{N} \sum_{k=1}^{N} \underbrace{c_m^k c_n^{k*}}_{\text{they are } k \text{ independent}} =$$

they are k independent because all the members of the ensemble are in the ground state.

$$= \frac{N}{N} c_m c_n^* =$$

$$= c_m c_n^* \qquad (1)$$

Now let's calculate ρ^2:

$$\rho^2 = \rho^2_{mn} = \sum_e \rho_{me}\rho_{en} =$$

$$= \sum_e c_m c_e^* c_e c_n^* = c_m c_n^* \underbrace{\sum_e c_e^* c_e}_{1} =$$

$$= c_m c_n^* = \rho_{mn}$$

We see that $\hat{\rho}^2 = \hat{\rho}$ in all representations.

What happens if $\Gamma > 1$ $(T > 0)$?

(mixed case).

Now we need an additional postulate:

"Random a priori phases"

it ensures that there are no correlations among the different members of the ensemble.

$$\psi_k = \sum_m a_n \phi_n$$

is an incoherent superposition of the $\{\phi_n\}$. For any basis.

$$a_m^k = a\, e^{-i\theta_m^k}$$

$$a_n^{k*} = a^* e^{-i\theta_n^k}$$

$$\rho_{mn} = \frac{1}{N}\sum_{k=1}^{N} a_m^k a_n^{k*} = \frac{1}{N}\sum_{k=1}^{N} |a|^2 e^{i(\theta_m^k - \theta_n^k)}$$

$$= c \left\langle e^{i(\theta_m^k - \theta_n^k)} \right\rangle = c\, \delta_{m,n}$$

$$\langle e^{i(\theta_m^t - \theta_n^t)} \rangle = \begin{cases} 0 & \text{if } m \neq n \\ 1 & \text{if } m = n \end{cases}$$

due to the postulate.

So in the microcanonical ensemble

$\rho_{mn} = c\,\delta_{mn}$ in any basis

with $c = \begin{cases} \frac{1}{\Gamma} & \text{for the accessible states} \\ 0 & \text{otherwise} \end{cases}$

ii) Canonical ensemble: N, V, T

$$P_r \propto e^{-\beta \epsilon_r}$$

In energy representation

$$\rho_{mn} = \rho_n \delta_{mn}$$

and $\rho_n = C e^{-\beta \epsilon_n}$ because it is proportional to the probability of the system being in state n.

C has to make $\mathrm{tr}\,\hat{\rho} = 1 \Rightarrow$

$$C = \frac{1}{\sum_m e^{-\beta \epsilon_n}} = \frac{1}{Z_N(\beta)}$$

normalization of P_r (and $\hat{\rho}$)

$$\rho_n = \frac{e^{-\beta \epsilon_n}}{Z_N(\beta)}$$

$$\hat{\rho} = \sum_m |\phi_n\rangle \rho_n \langle \phi_n| =$$

$$= \sum_n |\phi_n\rangle \frac{e^{-\beta \epsilon_n}}{Z_N(\beta)} \langle \phi_n| =$$

$$= \frac{e^{-\beta \hat{H}}}{Z_N(\beta)} \underbrace{\sum_m |\phi_m\rangle\langle\phi_m|}_{1} = \frac{e^{-\beta\hat{H}}}{T_r\, e^{-\beta\hat{H}}}$$

In energy representation $\hat{H}$ is diagonal so

$$\left(e^{-\beta\hat{H}}\right)_{nn} = e^{-\beta \epsilon_n}$$

$$\therefore \quad Z_N = \sum_m e^{-\beta\epsilon_n} = \sum_n \left(e^{-\beta\hat{H}}\right)_{nn} =$$

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

Remember that

$$e^{-\beta\hat{H}} \equiv \sum_{j=0}^{\infty} (-1)^j \frac{(\beta\hat{H})^j}{j!}$$

you need to use this if $\hat{H}$ is not diagonal

Then:

$$\langle G \rangle_N = Tr(\hat{\rho}\hat{G}) = \frac{Tr(\hat{G}e^{-\beta\hat{H}})}{Tr\, e^{-\beta\hat{H}}}$$

we found this before

since $\hat{\rho} = \dfrac{e^{-\beta\hat{H}}}{Tr\, e^{-\beta\hat{H}}}$ → matrix → scalar

$$Tr(\hat{\rho}\hat{G}) = Tr(\hat{G}\hat{\rho})$$

$$Tr(AB) = \sum_n (AB)_{nn} = \sum_n \sum_m A_{nm} B_{mn} =$$

$$= \sum_{n,m} B_{mn} A_{nm} = Tr\, BA.$$

iii) Grand-Canonical ensemble:

$$P_{r,s} = \frac{e^{-\beta(E_s - \mu N_s)}}{\mathcal{Z}(\mu, V, T)}$$

$\rho_{mn} = \rho_n \delta_{m,n}$ in energy representation.

$$\Rightarrow \hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{n})}}{\mathcal{Z}(\mu, V, T)}$$

$$\mathcal{Z}(\mu, V, T) = \sum_{r,s} e^{-\beta(E_r - \mu N_s)} = \mathrm{Tr}\, e^{-\beta \hat{H} - \mu \hat{n}}$$

$$\langle G \rangle = \frac{\mathrm{Tr}\left(\hat{G}\, e^{-\beta \hat{H}}\, e^{\beta \mu \hat{n}}\right)}{\mathcal{Z}(\mu, V, T)} =$$

$$= \frac{\sum_{N=0}^{\infty} z^N \langle G \rangle_N Z_N(\beta)}{\sum_{N=0}^{\infty} z^N Z_N(\beta)}$$

$$\hat{G}\, e^{-\beta \hat{H}} = \langle G \rangle_N Z_N(\beta)$$

Example: e^- $\quad s = \frac{\hbar}{2}\hat{\sigma}$ $\quad \mu_B = \frac{e\hbar}{2mc}$

For a spin in a magnetic field $\bar{B}$.

$$\hat{H} = -\mu_B(\underbrace{\hat{\sigma}}_{\text{Pauli }(\sigma_x,\sigma_y,\sigma_z)} \cdot \bar{B}) = -\mu_B B \hat{\sigma}_z = \begin{pmatrix} -\mu_B B & 0 \\ 0 & +\mu_B B \end{pmatrix}$$

if $\bar{B} = B_z$

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{Tr\, e^{-\beta\hat{H}}} = \frac{\begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix}}{2\cosh(\beta\mu_B B)}.$$

Let's calculate $\langle \sigma_z \rangle$: $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$\mathrm{Tr}(\hat{\rho}\,\hat{\sigma}_z) = \mathrm{Tr}\,\frac{\begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & -e^{-\beta\mu_B B} \end{pmatrix}}{2\cosh(\beta\mu_B B)} =$$

$$= \frac{2\sinh(\beta\mu_B B)}{2\cosh(\beta\mu_B B)} = \tanh \beta\mu_B B$$

Same as already calculated.