Conditions for thermodynamical equilibrium

Last time we obtained the time evolution of $\hat{\rho}$:

$$i\hbar \dot{\hat{\rho}} = [\hat{H}, \hat{\rho}]$$

Equilibrium:

$$\dot{\hat{\rho}} = 0 \Rightarrow [\hat{H}, \hat{\rho}] = 0$$

$\therefore$ i) $\hat{\rho} = f(\hat{H})$ insures commutation

and ii) $\dot{\hat{H}} = 0$ ($\hat{H}$ does not explicitely depend on t)

Consider $\{|\phi_n\rangle\}$ eigenstates of $\hat{H}$. This basis is called the energy representation.

$H_{mn} = E_n \delta_{mn}$ ($\hat{H}$ is diagonal in the $|\phi_n\rangle$ basis) E_n are the energy levels

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

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

Then in this basis:

$$\hat{\rho} = \sum_{\mu} |\phi_\mu\rangle \rho_\mu \langle\phi_\mu| \quad ⊛$$

D/
$$\rho_{kl} = \langle\phi_k| \sum_{\mu} |\phi_\mu\rangle \rho_\mu \langle\phi_\mu|\phi_l\rangle =$$

$$= \sum_{\mu} \underbrace{\langle\phi_k|\phi_\mu\rangle}_{\delta_{k\mu}} \rho_\mu \underbrace{\langle\phi_\mu|\phi_l\rangle}_{\delta_{\mu l}} =$$

$$= \sum_{\mu} \delta_{k\mu} \delta_{\mu l} \rho_\mu = \rho_k \delta_{kl} \quad \text{diagonal.}$$

ρ_n is the probability that a member of the ensembly randomly chosen is in eigenstate ϕ_n at any time t (since ρ is time independent in equilibrium)
Then since $\hat{\rho} = f(\hat{H}) \Rightarrow \rho_n = f(E_n)$.

Non-energy basis:

In any other basis $\hat{\rho}$ does not have to be diagonal. However, $\rho_{mn} = \rho_{nm}$ (symmetric, or more appropriately hermitic) since the probability of a system going from $m \to n$ has to equal the probability of it going from $n \to m$. (detailed balancing).

Basis $\{\chi_n\}$

$$\rho_{kl} = \langle\chi_k|\hat{\rho}|\chi_l\rangle \overset{⊛}{=} \langle\chi_k| \sum_{\mu} |\phi_\mu\rangle \rho_\mu \langle\phi_\mu|$$
$$|\chi_l\rangle = \sum_{\mu} \langle\chi_k|\phi_\mu\rangle \rho_\mu \langle\phi_\mu|\chi_l\rangle$$

$$|\chi_l\rangle = \sum_n \underbrace{\langle \chi_k|\phi_n\rangle}_{\neq 0} \rho_n \underbrace{\langle \phi_n|\chi_l\rangle}_{\neq 0}$$

$\therefore$ ρ_{kl} is not diagonal.

Expectation values (or average values) of operators (or observables):

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

ψ^k → wave function of each ensemble member.

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

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

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

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

$$= \sum_{m,n}\rho_{nm}G_{nm} = \quad \rightarrow \rho_{nm} = \rho_{mn}$$

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

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

If $\hat{G} = \mathbb{I}$

$\langle \mathbb{I} \rangle = 1 = tr(\hat{\rho}\,\mathbb{I}) = tr\,\hat{\rho} \quad \therefore \; tr\,\hat{\rho} = 1$ (we knew this)

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

$$\langle G \rangle = \frac{Tr(\hat{\rho}\hat{G})}{Tr\,\hat{\rho}}$$ independent of the ~~basis~~

(in this case $P = \frac{\hat{\rho}}{Tr\,\hat{\rho}}$)

Microcanonical Ensemble

$N, V, E \pm \frac{1}{2}\Delta \quad$ with $\quad \Delta \ll E$

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

In energy representation due to the "equal probability" postulate we know that the eigenvalues of ρ are:

$$\rho_n = \begin{cases} \frac{1}{\Gamma} & \text{for states with } E_n \text{ in the interval } E \pm \frac{1}{2}\Delta \\ 0 & \text{otherwise.} \end{cases}$$

and $\hat{\rho}$ is a diagonal matrix. $\rho_{mn} = \rho_n \delta_{mn}$

also $S = k \ln \Gamma$.

- Notice that the particles are indistinguishable so we should not expect Gibbs paradox.
- If $\Gamma = 1 \Rightarrow S = 0$ (as expected from third law) $T = 0$ $\Gamma = 1$ (or small #). Then only $\rho_{11} \neq 0$ in $\hat{\rho}$ - $\rho_{11} = 1$

We see then that $\rho^2 = \rho$.

- Consider a different basis (not the energy basis)

Now $\psi^k = \sum_r c_r^k |\chi_r\rangle$

$$\rho_{mn} = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} c_m^k c_n^{k*} = c_m c_n^* \underbrace{\sum_{k=1} \frac{1}{\mathcal{N}}}_{1} \equiv c_m c_n^* \quad (1)$$

because all members of the ensemble are in the same unique state.

$$\therefore \rho^2 = \rho^2_{mn} = \sum_l \rho_{ml} \rho_{ln} \overset{(1)}{=}$$

$$= \sum_l c_m c_l^* c_l c_n^* = c_m \underbrace{\sum_l |c_l|^2}_{1} c_n^* =$$

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

$$\therefore \rho^2 = \rho$$

If $\Gamma > 1$ (so we have a mixed state).

In any basis a microcanonical ensemble

has to have a diagonal density matrix - this is ensured by requesting that there is no interactions among the different ensemble members.

In any representation:

$$\rho_{mn} = \rho_n \delta_{mn} \qquad \text{(microcanonical)}$$

with $\rho_n = \frac{1}{\Gamma}$ for accessible states.

D/ $\psi^k = \sum_n c_n^k \chi_n$ (any basis).

$c_n^k \to c\, e^{i\theta_n^k}$ with $c^2 = \frac{1}{\Gamma}$

$$\rho_{mn} = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} c_n^k c_m^{k*} = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} |c|^2 e^{i(\theta_n^k - \theta_m^k)} =$$

$$= |c|^2 \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} e^{i(\theta_n^k - \theta_m^k)} = c \underbrace{\langle e^{i(\theta_n^k - \theta_m^k)} \rangle}_{\delta_{m,n}}$$

$$= c\, \delta_{m,n} \quad \text{with } c = 1/\Gamma$$

random a priori phases postulate.

We need to a priori postulates now:

- equal probability of accessible states
- random phases.

—— × ——

$\hat{\rho}$ in the canonical ensemble

... canonical and (N, V, T)

$P_r \propto e^{-\beta \epsilon_r}$ in the canonical and (N, V, T) define the ensemble.

In energy representation $\hat{\rho} \equiv \rho_n \delta_{nm} = \rho_{nm}$

$n = 0, 1, 2, ---$

$\therefore$

(2) $\rho_n = C \, e^{-\beta \epsilon_n}$ and $C = \dfrac{1}{\sum_n e^{-\beta \epsilon_n}} = \dfrac{1}{Z_N(\beta)}$

Then

$$\hat{\rho} = \sum_n |\phi_n\rangle \rho_n \langle \phi_n| \overset{(2)}{=} \sum_n |\phi_n\rangle \frac{e^{-\beta \epsilon_n}}{Z_N(\beta)} \langle \phi_n| =$$

$$= \frac{1}{Z_N(\beta)} \sum_n e^{-\beta \epsilon_n} |\phi_n\rangle \langle \phi_n| \overset{(3)}{=}$$

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

(needed when $\hat{H}$ is a basis in which it is not diagonal)

$$\underbrace{e^{-\beta \hat{H}} |\phi_n\rangle}_{\text{energy basis}} = \sum_{j=0}^{\infty} (-1)^j \frac{(\beta \hat{H})^j}{j!} |\phi_n\rangle = \sum_{j=0}^{\infty} (-1)^j \frac{(\beta \epsilon_n)^j}{j!} |\phi_n\rangle$$

$$= e^{-\beta \epsilon_n} |\phi_n\rangle \quad (3)$$

$$= \frac{e^{-\beta \hat{H}}}{Z_N(\beta)} \underbrace{\sum_n |\phi_n\rangle \langle \phi_n|}_{1} = \frac{e^{-\beta \hat{H}}}{Z_N(\beta)} \overset{(4)}{=} \frac{e^{-\beta \hat{H}}}{\operatorname{tr} e^{-\beta \hat{H}}}$$

$$Z_N(\beta) = \sum_n e^{-\beta \epsilon_n} \equiv \operatorname{tr} e^{-\beta \hat{H}} \quad (4)$$

$\therefore \quad \hat{\rho} = \dfrac{e^{-\beta \hat{H}}}{Tr\, e^{-\beta \hat{H}}}$ this is basis independent.

Notice that $\hat{\rho}$ is diagonal in energy basis but not in other basis.

Now:

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

$Tr\, AB = Tr\, BA$

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

$$= \sum_m \sum_n B_{mn} A_{nm} =$$

$$= \sum_m (BA)_{mm} = Tr\, BA$$

———— × ————

$\hat{\rho}$ in the Grand canonical ensemble

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

in energy representation $\rho_{mn} = \rho_n \delta_{mn}$

$$\therefore \quad \hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{n})}}{\mathcal{Z}(\mu, V, T)} \qquad \mathcal{Z}(\mu, V, T) = \sum_{r,s} e^{-\beta(E_r - \mu N_s)}$$

$$D/ \quad e^{-\beta\mu\hat{n}} \underbrace{\sum_{s,r} |\phi_{s,r}\rangle\langle\phi_{s,r}|}_{1} = \sum_{s,r} \sum_j \frac{(-1)^j (\beta\mu\hat{n})^j}{j!} |\phi_{s,r}\rangle$$

$$\langle \phi_{sr}| = \sum_{s,r} \sum_{j} \frac{(-1)^j (\beta\mu N_r)^j}{j!} |\phi_{s,r}\rangle\langle \phi_{sr}| =$$

$$= e^{-\beta\mu N_r} = z^{N_r} \qquad z = e^{-\beta\mu}$$

$$\therefore \quad \langle G \rangle = \frac{Tr\left(\hat{G}\, e^{-\beta\hat{H}}\, e^{\beta\mu\hat{N}}\right)}{\mathcal{Z}(\mu, V, T)} = \frac{\sum_{N=0}^{\infty} z^N \langle G \rangle_N Z_N(\beta)}{\sum_{N=0}^{\infty} z^N Z_N(\beta)}$$

— x —

Example: consider a system of electrons under spin 1/2.

$$\hat{S} = \frac{\hbar}{2}\hat{\sigma} \qquad \text{(spin operator)} \qquad \hat{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$$

Pauli matrices.

$$\hat{H} = -\mu_B\,(\hat{\sigma}\cdot\bar{B}) \equiv -\mu_B B\,\hat{\sigma}_z \qquad \text{if } \hat{z} \parallel \bar{B} \qquad \mu_B = \frac{e\hbar}{2mc}$$

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

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

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

$$\boxed{\langle \sigma_z \rangle} = Tr(\hat{\rho}\,\hat{\sigma}_z) = Tr\left(\frac{\begin{matrix} e^{\beta\mu_B B} & 0 \\ 0 & -e^{-\beta\mu_B B} \end{matrix}}{2\cosh(\beta\mu_B B)}\right) =$$

similar to

$2\cosh \beta\mu_B B$

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

similar to the magnetization that we found before.