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Equation of motion for the density matrix:

$$i\hbar\dot{\rho}_{mn}(t) = i\hbar \frac{1}{N}\sum_{k=1}^{N}\left\{\dot{a}^k_m(t)\, a^{*k}_n(t) + a^k_m(t)\, \dot{a}^{k*}_n(t)\right\} =$$

$$= \frac{1}{N}\sum_{k=1}^{N}\left\{\sum_j H_{mj}\, a^k_j(t)\, a^{*k}_n(t) + a^k_m(t)\,(-)\sum_j H^*_{nj}\, a^{k*}_j(t)\right\} =$$

$$= \sum_j H_{mj}\left[\frac{1}{N}\sum_{k=1}^{N} a^k_j(t)\, a^{*k}_n(t)\right] - \sum_j H^*_{nj}\frac{1}{N}\sum_k a^k_m(t)\, a^{k*}_j(t) =$$

$$= \sum_j \left[H_{mj}\,\rho_{jn} - H_{jn}\,\rho_{mj}\right] = \sum_j \left[H_{mj}\rho_{jn} - \rho_{mj} H_{jn}\right] =$$

$$\rho_{mn} = \frac{1}{N}\sum_{k=1}^{N} a^k_m(t)\, a^{k*}_n(t) \qquad = (\hat{H}\hat{\rho} - \hat{\rho}\hat{H})_{m,n}$$

$$i\hbar\,\dot{a}^k_n(t) = \sum_m H_{nm}\, a^k_m(t) \qquad H^*_{nm} = H_{mn}$$

$$-i\hbar\,\dot{a}^{*k}_n(t) = \sum_m H^*_{nm}\, a^{*k}_m(t)$$

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

Notice that this is the quantum mechanical equivalent of Liouville's theorem.

Liouville said: $\dfrac{d\rho}{dt} = \dfrac{\partial\rho}{\partial t} + [\rho, H] = 0$

Now Poisson's bracket is replaced by the commutator.

<u>In equilibrium</u> $\dot{\hat{\rho}} = 0 \quad \therefore \quad [\hat{H}, \hat{\rho}] = 0.$

Quantum mechanically for equilibrium we need that:

i) $\hat{\rho} = f(\hat{H})$ to make sure that $[\hat{\rho}, \hat{H}] = 0$

and

ii) $\dot{\hat{H}} = 0$ to make sure that $\dot{\hat{\rho}} = 0$

Properties of $\hat{\rho}$:

Energy representation

Consider $\{\phi_n\}$ that are eigenstates of $\hat{H}$.

$\therefore$

$H_{mn} = E_n \delta_{mn}$ H is diagonal in the energy basis.

Since $\hat{\rho} = \hat{\rho}(\hat{H}) \Rightarrow$

$\rho_{mn} = \rho_n \delta_{mn}$ in this basis (also diagonal)

In the energy representation

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

Let's obtain ρ_{kl} in the energy basis:

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

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

Notice that ρ_n is the probability that a member of the ensemble is in state ϕ_n at any time t. In equilibrium ρ_n are time independent. ρ_n will be a function of E_n.

Notice that in a generic basis $\rho_{mn} \neq 0$ but $\rho_{mn} = \rho_{nm}$, i.e. $\hat{\rho}$ is a symmetric matrix because the probability of a member of the ensemble going from m to n has to be equal to that of going from n to m to keep equilibrium.

Consider a basis $\{\chi_n\}$ different from $\{\phi_n\}$

Now

$$\rho_{ke} = \langle \chi_k | \hat{\rho} | \chi_e \rangle = \langle \chi_k | \sum_M | \phi_n \rangle \rho_n \langle \phi_n | \chi_e \rangle$$

$$= \sum_M \underbrace{\langle \chi_k | \phi_n \rangle}_{} \rho_n \underbrace{\langle \phi_n | \chi_e \rangle}_{}$$

not zero in general.

Average value of an operator:

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

ensemble average

ψ^{k} → ground state wave function for k member of the ensemble.

$\psi^{k} = \sum_n a_n^k \phi_n$

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

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

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

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

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

$\therefore \quad \langle \hat{G} \rangle = tr(\hat{\rho}\hat{G})$

In particular if $\hat{G} = \underline{\mathbb{I}}$

$1 = tr(\hat{\rho})$ this is true in any basis

If ψ^k are orthogonal but not orthonormal.

$\therefore \; tr\,\hat{\rho} \neq 1$ but

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

Microcanonical ensemble:

$$N, \; V, \quad E \pm \tfrac{1}{2}\Delta \qquad \Delta \ll E.$$

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

In the energy representation $\rho_{mn} = \rho_n \delta_{mn}$

Due to the equal a priori probabilities we know that

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

and $S = k \ln \Gamma$.

- Since now the particles are undistinguishable no Gibbs paradox will occur.

- If $\Gamma = 1 \Rightarrow S = 0$ (Nernst's theorem).

  In this case $\rho_{11} = 1$ and $\rho_{nn} = 0 \ \forall \ n \neq 1$.

  Also $\rho^2 = \rho$.

What happens if in this situation we want to calculate ρ in a different basis?

Now

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

ground state of ensemble member k

$|x_r\rangle$ is a basis different from $|\phi_n\rangle$.

(before we had

$$\psi_k = \sum_m a_m^k |\phi_n\rangle$$

$$\rho_{mn} = \frac{1}{N} \sum_{k=1}^{N} c_m^k c_n^{k*} = c_m c_n^* \frac{N}{N} = c_m c_n^*$$

Then

$$\rho^2 = \rho_{mn}^2 = \sum_l \rho_{ml} \rho_{ln} = \sum_l c_m c_l^* c_l c_n^* =$$

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

For $T=0$ in a non-degenerate ground state it is true that $\rho^2=\rho$ regardless of the basis.

What happens if $\Gamma > 1$?

Now we have a mixed case.

In any representation

$\rho_{mn} = \rho_n \delta_{mn}$ and $\rho_n = 1/\Gamma$ for the Γ accessible states.

In order to ensure this we will need an additional postulate.

Random a priori phases postulate:

$$\psi^k = \sum_n a_n^k \phi_n$$

state of ensemble member k.

it is an incoherent superposition of the $\{\phi_n\}$ (true in any basis)

$\therefore$ in any base:

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

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

This ensures that ρ_{mn} is diagonal in any basis in the microcanonical ensemble.

$c = |a|^2 = \frac{1}{\Gamma}$ for all accessible states or 0 otherwise.

The phases are incoherent meaning that there are no correlations between the ensemble members.

$\therefore$ now 2 postulates are needed to insure the correct physics in the microcanonical ensemble.