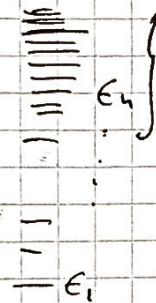


Lecture 1

Detour: Density matrix study. (Lандау & Lifshitz v.1. Stat. Phys)

NO STATIONARY STATES

①  } Microscopically very dense! \Rightarrow b/c of this the body is never in the stationary state

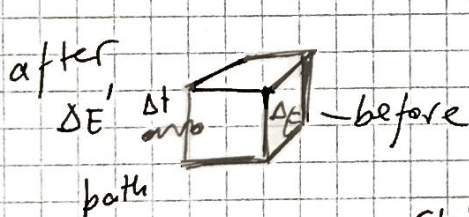
② Moreover, b/c of the coupling to the bath all the ~~the~~ energy will be smeared by the coupling.

$$\Delta E \sim J \gg \Delta E_{n-1} - E_n \quad \text{which is true for any system}$$

\uparrow total energy.

even if the coupling is very small.

③ Another reason



$$|\Delta E' - \Delta E| \sim \frac{\hbar}{\Delta t} \quad \Delta t - \text{the time of interaction}$$

but to stay in the stationary state the system must remain here

$$\Delta E' \ll \underbrace{E_{n-1} - E_n}_{\Delta E} \text{ - which is very small}$$

\Rightarrow to get a macroscopic body into the stationary state $\Delta E' \sim \frac{\hbar}{\Delta t} \rightarrow \Delta t \sim \frac{\hbar}{\Delta E'}$ very small

VERY LARGE TIME!

NOT POSSIBLE TO HAVE A MACR. SYSTEM IN STAT. STATE

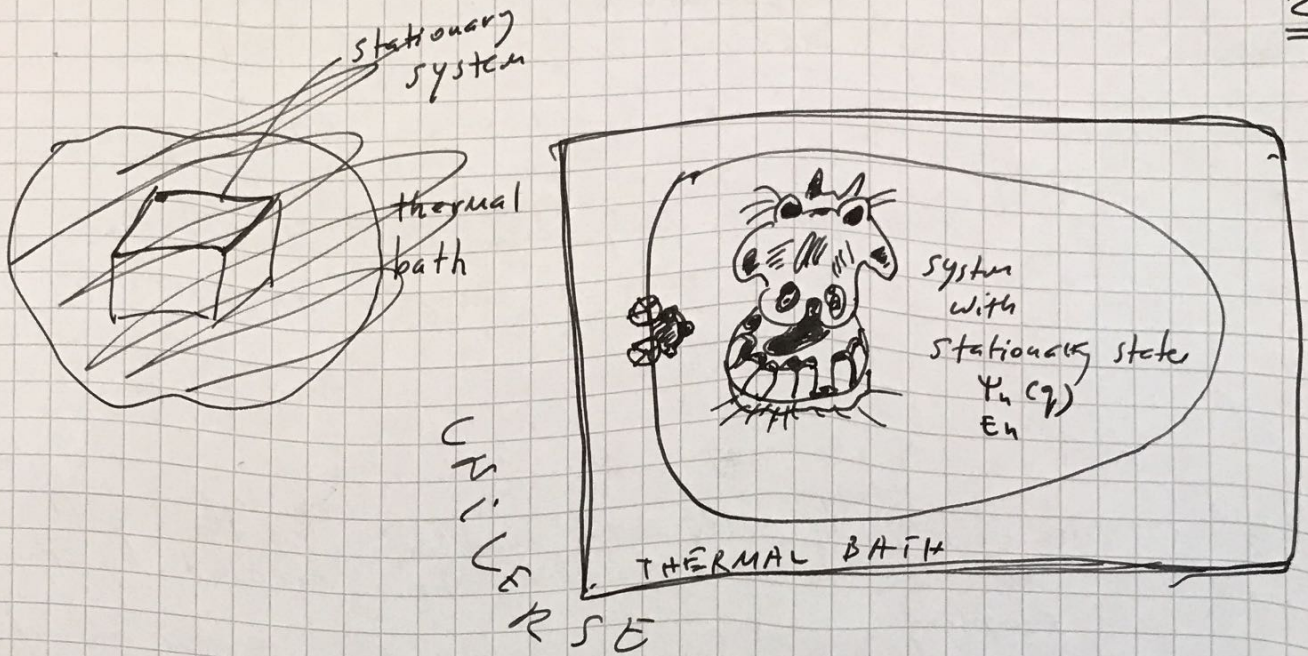
\Rightarrow not possible to describe by the wave function.

IF we have a system with incomplete information

\Rightarrow density matrix

if we know density matrix ρ we can calculate any average:

recall $\langle A \rangle = \text{Tr}(\rho A)$



$$|\psi\rangle = \sum_n c_n |\psi_n\rangle$$

$$\langle \psi | A | \psi \rangle = \sum_n \sum_m c_n c_m \langle \psi_n | A | \psi_m \rangle$$

NB. Transition from a complete to "incomplete" description of the system can be described via averaging it over various states $|\psi\rangle$

so we will get

$$c_n^* c_m \equiv w_{nm}$$

$$\langle A \rangle = \sum_{nm} w_{nm} f_{nm}$$

note $w_{nm} \equiv w_{nm}(t)$

is the statistical density matrix in the energy representation.

We can think of w_{nm} = matrix = \hat{w} then

$w_{nm} f_{nm}$ = diagonal matrix $\hat{w} \hat{f}$

$$\langle f \rangle = \sum_n (w \hat{f}) = \text{Tr}(\hat{w} \hat{f})$$

Tr = sum of diagonal elements

NB! in all formulas

$$c_n^* c_m \rightarrow w_{nm}$$

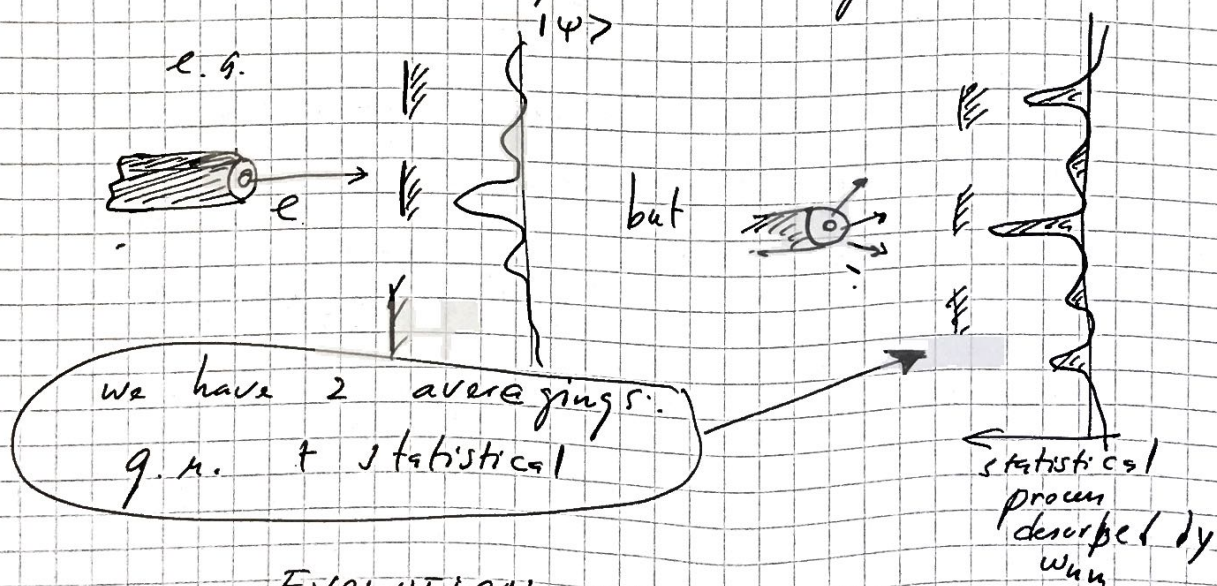
e.g. the probability of the system to be in the state $n \rightarrow w_{nn} > 0$ and $\text{Tr} w_{nm} =$

$$\text{b/c of } \sum_n c_n c_n^* = 1 \longleftrightarrow \sum_n w_{nn} = 1$$

Often mentioned if $|\psi\rangle = \sum c_n |\psi_n\rangle$ - pure state
 if by ~~terms~~ w_{nm} - mixed state

For the statistical description these 2 probabilistic acts

- ① we must use $|\psi\rangle$ b/c. of the incomplete knowledge
- ② The object is macroscopical and ~~parts of it~~ ~~beams~~ and we don't have a complete knowledge.



~~Ass~~ EVOLUTION IN TIME

Start with pure state $|\psi\rangle = \sum_n c_n(t) |\psi_n\rangle$

$$c_n(t) = e^{-\frac{i E_n t}{\hbar}} c_n$$

$$c_m(t) = e^{-\frac{i E_m t}{\hbar}} c_m$$

$$c_n^* c_m = e^{+\frac{i(E_n - E_m)t}{\hbar}} c_n^* c_m \Rightarrow \frac{d}{dt} (c_n^* c_m) = \left(+\frac{i}{\hbar} (E_n - E_m) \right) c_n^* c_m$$

for density matrix

$$\frac{d}{dt} w_{nm} = \frac{i}{\hbar} (E_n - E_m) w_{nm}$$

$$(E_k - E_m) w_{km} = E_k w_{km} - E_m w_{km} =$$

$$= \sum_e \left[H_{ke} w_{em} - H_{me} w_{ek} \right]$$

H_{mn} = hermitian matrix

\Rightarrow

$$\frac{d}{dt} \hat{w} = \frac{i}{\hbar} (\hat{w} \hat{H} - \hat{H} \hat{w}) = \frac{i}{\hbar} [\hat{w} \hat{H}]$$

if w commutes with $H \Rightarrow$ state is stationary

moreover to make it commuting we need to have w_{km} to be a diagonal matrix

Recall from QM: if matrix commutes then it can be made diagonal along with \hat{H} .

\Rightarrow all w_{km} must be $w_{km} = w_k$
- the distribution function in q.s.

therefore: $\langle f \rangle = \sum_{km} w_{km} f_{km} = \sum_n w_n f_{nn}$

After long tetour:

the basic notion of quantum stat.

$$w_n = A e^{-E_n/T} \Rightarrow$$

$$\sum w_n = 1 \Rightarrow A \sum e^{-E_n/T} = 1 \Rightarrow A = \frac{1}{\sum e^{-E_n/T}} = Z^{-1}$$

$$\Rightarrow Z \text{ is a partition function} = \text{Tr} (e^{-\hat{H}/T})$$

$$w_n = \frac{e^{-E_n/T}}{Z}$$

$$S = - \langle \ln w_n \rangle = - \sum_n w_n \ln w_n = - \sum_n w_n \left(\ln \frac{e^{-E_n/T}}{Z} \right)$$

$$\begin{aligned}
S &= - \sum_n \ln \left(\frac{e^{-E_n/T}}{z} \right) \cdot \frac{e^{-E_n/T}}{z} = \\
&= - \sum_n \left\{ \left(-E_n/T - \ln z \right) \cdot \left(\frac{e^{-E_n/T}}{z} \right) \right\} \\
&= \sum_n \left(\frac{E_n}{T} + \ln z \right) \frac{e^{-E_n/T}}{z} \\
&= \underbrace{\sum_n \frac{E_n}{z} \frac{e^{-E_n/T}}{z}}_{\frac{\langle E \rangle}{T}} + \underbrace{\frac{\ln z}{z} \sum_n e^{-E_n/T}}_{\langle \ln z \rangle} \\
&= \frac{\langle E \rangle}{T} + \langle \ln z \rangle \Rightarrow \text{average energy of the system} \\
\boxed{S = \frac{\langle E \rangle}{T} + \langle \ln z \rangle} &= \text{entropy.}
\end{aligned}$$

also lets introduce: $F = E - TS = -T \ln z$
 $F \equiv$ Helmholtz free energy

$$\boxed{F = E - TS = -T \ln z = -T \ln \left(\sum_n e^{-E_n/T} \right)}$$

NB: ^{LI} Shake hands with an ideal.

Define some thermodynamic variables.
We already got entropy S and F . The next step:

Helmholtz free energy depends on $T, u = \frac{U}{N}$ or
if N is constant then on V : $F(T, V)$

Recall thermodynamic potentials:

$$\Phi(P, T) = \underbrace{E - TS + PV}_F = F + PV \Leftrightarrow \text{Gibbs free energy}$$

$$W(P, T) = E + PV \quad - \text{enthalpy (energy for a new phase formation)}$$

Energy $E(U, S)$ - is also a potential

general rule

A general rule: many-body particle system
at equilibrium tends to minimize F or Φ .

or e.g.

$$d\Phi = -dT \cancel{S} + V dP = 0 \Rightarrow$$

$$S = -\left(\frac{d\Phi}{dT}\right)_{\text{const } P} \quad \text{and} \quad \left(\frac{d\Phi}{dP}\right)_{\text{const } T} = V$$

similarly

$$dF = -S dT - P dV = 0 \Rightarrow$$

$$S = -\left(\frac{dF}{dT}\right)_{\text{const } V} \quad P = -\left(\frac{dF}{dV}\right)_{\text{const } T}$$

Other useful relations:

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$$\text{specific heat: } C_V = \left(\frac{dE}{dT} \right)_V = T \left(\frac{dS}{dT} \right)_V$$

$$C_P = T \left(\frac{dS}{dT} \right)_P = \left(\frac{\partial W}{\partial T} \right)_P$$

Skipping all math, we can quote the relations for elastic coefficients, e.g. specific heat, linear thermal expansion α and volume thermal expansion β .

$$\beta = \frac{1}{V} \frac{\partial V}{\partial T}$$

$$\text{compressibility } \kappa = -\frac{1}{V} \frac{\partial V}{\partial P}$$

$$C_P - C_V = -T \frac{\left(\frac{\partial V}{\partial T} \right)_P^2}{\left(\frac{\partial V}{\partial P} \right)_T} = VT \frac{\beta^2}{\kappa}$$

One can expand these relationships to the system with a variable number of particles. e.g. $n = \frac{N}{V}$

$$F = N f_1 \left(\frac{V}{V}, T \right)$$

$$\Phi = N f_2(P, T)$$

$$E = N f_3 \left(\frac{S}{N}, \frac{V}{N} \right)$$

$$d\Phi = -SdT + \cancel{V}dP + \frac{dE}{dN} dN = \mu dN = \left(\frac{\partial E}{\partial N} \right)_{S,V} dN$$

$$dF = -SdT - PdV + \mu dN$$

$$dE = TdS - PdV + \mu dN$$

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V} = \left(\frac{\partial F}{\partial N} \right)_{T,N} = \left(\frac{\partial \Phi}{\partial N} \right)_{P,T}$$

$$\Phi = N f_2(P, T) \Rightarrow \frac{\partial \Phi}{\partial N} = f_2(P, T) \Rightarrow \mu = f_2 \Rightarrow$$

$$\boxed{\mu = \frac{\partial \Phi}{\partial N}}$$

NB1. If the number of L^1 particles is not conserved, e.g. Phonons, then the value of N is determined from min of $\frac{\partial F}{\partial N} = 0$
 $\frac{\partial F}{\partial N} |_{\text{const } P, \bar{V}} = \mu = 0!$

NB μ and N are conjugate variables
 e.g. S and T , P and V , μ and N
 \Rightarrow we can introduce new potentials based on μ not on N

$\Omega(V, T, \mu)$:

$z = \sum_n e^{-E_n/T}$, $F = -T \ln z = E - TS$
 $z = e^{-F/T}$
 $w_n = \frac{e^{-E_n/T}}{z}$

$w_n = e^{(F - E_n)/T}$
 $w_{n,N} = e^{(\Omega + \mu N - E_{n,n})/T}$

where $\Omega(V, T, \mu) = F - \mu N$

$\Rightarrow d\Omega = -SdT - PdV - Nd\mu$

the total # of particles connected to Chem potential:

$N = \left(\frac{\partial \Omega}{\partial \mu} \right)_{T, V}$

* exercise: prove $\Omega = -PV$