

# Statistical Entropy and Microscopic ①

## Equilibrium

Objective: apply entropy concept in the microscopic realm

- steps:
- 1.) introduce density matrix  
→ describes probabilistic nature of a QM system (microscopic)
  - 2.) introduce Liouville formalism  
→ describes probabilistic nature of a classical system (microscopic)
  - 3.) introduce entropy of a quantum statistical system  
\* postulate its properties according to information theory  
↓ ↓  
equilibrium density matrix is thus determined
  - 4.) try to derive macroscopic thermodynamics using the equilibrium density matrix

# Quantum Description

②

## Time evolution

in QM the state of a system is given by the eigenvalues of a set of ~~non~~ commuting operators:  $\{\hat{A}_i\}$ :  $[\hat{A}_i, \hat{A}_j] = 0$

$$i = 1, \dots, N$$

state of the system:  $|\Psi(t_0)\rangle =$

$$= |a_1, \dots, a_N\rangle$$

$$\hat{A}_i |a_1, \dots, a_N\rangle = a_i |a_1, \dots, a_N\rangle$$

- the eigenvalues can be used as labels of the state (similar to angular momentum states  $\Rightarrow |lm\rangle$ )

- time evolution of a state is given by the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = H(t) |\Psi(t)\rangle$$

- isolated system:  $H(t) = H$  (independent of time)

- time evolution can also be represented by the time-evolution operator

definition:

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$$|\Psi(t)\rangle = \underline{U(t, t_0)} |\Psi(t_0)\rangle$$

time evolution operator

satisfies  $i\hbar \frac{d}{dt} U(t, t_0) = H(t) U(t, t_0)$

time evolution operator is unitary

$$\langle \Psi(t_0) | \underbrace{U^\dagger(t, t_0) U(t, t_0)}_{\text{identity}} | \Psi(t_0) \rangle$$

$$I = U^\dagger(t, t_0) U(t, t_0)$$

$$\Rightarrow U^\dagger(t, t_0) = U^{-1}(t, t_0)$$

time evolution operator satisfies the group property

$$U(t, t_0) = U(t, t_1) U(t_1, t_0)$$

if  $H$  is time-independent:

$$U(t, t_0) = e^{iH(t-t_0)/\hbar}$$

time-development can be represented in the

"Schrödinger picture"

"Heisenberg picture"

and anywhere in between

consider an operator not explicitly time-  
dependent,  $\hat{A}$  (4)

its expectation value over the time-  
dependent state  $|\Psi(t)\rangle$  is

$$\bar{A}(t) = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle \Rightarrow \text{(Schrödinger picture)}$$

but since  $|\Psi(t)\rangle = U(t, t_0) |\Psi(t_0)\rangle$

we can also take the operator to be  
time-dependent and the state to  
remain fixed

$$\begin{aligned} \bar{A}(t) &= \langle \Psi(t_0) | \underbrace{U^\dagger(t, t_0) \hat{A} U(t, t_0)} | \Psi(t_0) \rangle \\ &= \langle \Psi(t_0) | A_H(t) | \Psi(t_0) \rangle \Rightarrow \text{(Heisenberg picture)} \end{aligned}$$

- time development of an expectation value

$$\begin{aligned} i\hbar \frac{d\bar{A}}{dt} &= i\hbar \left\langle \frac{d\Psi(t)}{dt} | \hat{A} | \Psi(t) \right\rangle \\ &\quad + i\hbar \left\langle \Psi(t) | \hat{A} | \frac{d\Psi(t)}{dt} \right\rangle \\ &= \langle \Psi(t) | [\hat{A}, \hat{H}(t)] | \Psi(t) \rangle \end{aligned}$$

one can define a projection operator as ⑤

$$\hat{D} = |\psi\rangle\langle\psi|$$

$$\text{Tr } \hat{D} \hat{A} = \langle\psi| \hat{A} |\psi\rangle$$

## Density operators and time evolution

- formalism of a single quantum state  $|\psi(t)\rangle$  may not always suffice  $\Rightarrow$  often, we do not have detailed knowledge of a system, and we can only speak of the probabilities with which a system is found in a particular state
- can introduce a quantum mechanical ensemble

let  $|\psi_n\rangle$  span the Hilbert space of a particular system

we can consider an ensemble of identically prepared systems  $\Rightarrow$  i.e. same Hamiltonian and same Hilbert space

define 
$$\hat{D} = \frac{1}{N} \sum_{I=1}^N |\psi_{n_I}\rangle \langle\psi_{n_I}|$$

$N$  - identically prepared systems  $\Rightarrow \hat{D}$  is an average

$$\hat{D} = \frac{1}{N} \sum_i |\Psi_{n_i}\rangle \langle \Psi_{n_i}| = \sum_n P_n |\Psi_n\rangle \langle \Psi_n| \quad (6)$$

$P_n \rightarrow$  fraction of systems in state  $n$

$\hookrightarrow$  can be regarded a probability

$$P_n \geq 0 \quad \sum_n P_n = 1$$

$$\langle A \rangle = \text{Tr} \hat{D} \hat{A} = \sum_n P_n \langle \Psi_n | \hat{A} | \Psi_n \rangle$$

properties of  $\hat{D}$

(\*)  $\hat{D}$  is Hermitian  $\Rightarrow D_{ij}^* = P_{ji}$

Proof: write in some basis

$$|\Psi_n\rangle = \sum_i c_i^{(n)} |\phi_i\rangle$$

$$\hat{D} = \sum_n P_n \sum_{ij} c_i^{(n)} c_j^{*(n)} |\phi_i\rangle \langle \phi_j|$$

matrix elements of  $\hat{D}$  in basis  $|\phi_i\rangle$

$$D_{rs} = \langle \phi_r | \hat{D} | \phi_s \rangle = \sum_n P_n \sum_{ij} c_i^{(n)} c_j^{*(n)} \delta_{ri} \delta_{js}$$

$$= \sum_n P_n c_r^{(n)} c_s^{(n)*}$$

$$D_{rs}^* = \sum_n P_n c_r^{(n)*} c_s^{(n)} = D_{sr}$$

(\*)  $\hat{D}$  has unit trace

~~$$\sum_n P_n \langle \Psi_n | \hat{D} | \Psi_n \rangle = \sum_n P_n$$~~

$$\text{Tr} \hat{D} = \sum_m P_m \langle \Psi_m | \Psi_m \rangle = \sum_m P_m = 1$$

(\*)  $\hat{D}$  is a positive operator

$$\langle \psi | \hat{D} | \psi \rangle = \sum_n p_n |\langle \psi | \psi_n \rangle|^2 \geq 0$$

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for any  $|\psi\rangle$

(\*)  $\hat{D}$  for a pure state satisfies  $\hat{D}' = \hat{D}$   
 $\hat{D}^2 = |\psi\rangle \langle \psi | \psi\rangle \langle \psi | = |\psi\rangle \langle \psi | = \hat{D}$

time evolution

$$\hat{D}(t) = \sum_n p_n |\psi_n(t)\rangle \langle \psi_n(t)|$$

$$\text{its } \frac{d\hat{D}(t)}{dt} = \sum_n p_n H(t) |\psi_n(t)\rangle \langle \psi_n(t)|$$

$$= \sum_n p_n |\psi_n(t)\rangle \langle \psi_n(t)| H(t)$$

$$= \left[ \cancel{\hat{D}(t), H(t)} \right] [H(t), \hat{D}(t)]$$

$$\text{recall that: its } \frac{d\hat{A}(t)}{dt} = \langle \psi(t) | [\hat{A}, H] | \psi(t) \rangle$$

(commutators switch order)

- one can also write expectation values in the  
Schrodinger picture  $[D(t), A]$

or the

Heisenberg picture  $[\hat{D}, A_H(t)]$

(assuming  $\hat{A}$  is not explicitly  
time-dependent)

- a macrostate of a quantum system is described by a density matrix  $\Rightarrow$  there are many microstates consistent with a particular macrostate  $\Rightarrow$  probabilistic description implemented via use of density matrix

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- Two more things from QM

1.) density of states - refers to number of states with a given energy  $E$   
 (more precisely  $\Rightarrow$  in interval  $E, E + \Delta E$ )

let's calculate this for a free-particle system

- start with particle in a box of side  $L$

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) = E \Psi(\mathbf{r}, t)$$

eigenstates are  $\Psi(\mathbf{r}, t) = \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{\sqrt{L^3}}$

assuming periodic boundary conditions in

all three directions  $\Psi(x+L, y, z) = \Psi(x, y, z)$

in this case

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2) \Psi(\mathbf{r}, t)$$

$n_x, n_y, n_z$  - integers

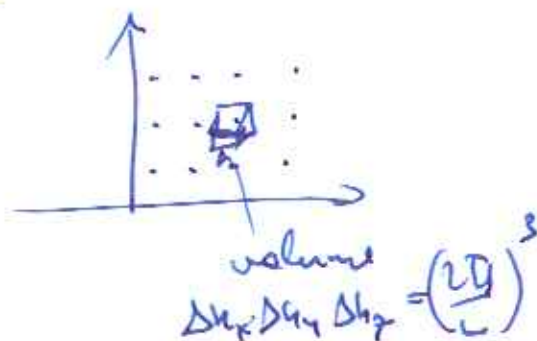


in the 3D space spanned by  $(k_x, k_y, k_z)$  (9)

the volume associated with one ~~to~~ state is  $\left(\frac{2\pi}{L}\right)^3$  ~~this~~ this follows from the

fact that  $(k_x, k_y, k_z) \cong \frac{2\pi}{L} (n_x, n_y, n_z)$

with  $n_x, n_y, n_z$  - integers  $\Rightarrow$



a sum over states in the limit  $L \rightarrow \infty$  ( $\frac{2\pi}{L} \rightarrow 0$ )

$$\lim_{L \rightarrow \infty} \sum_{n_x, n_y, n_z} f(n_x, n_y, n_z) \rightarrow \frac{V}{(2\pi)^3} \int d^3k f(\vec{k})$$
$$= \int d^3k f(\vec{k}) \rho(\vec{k})$$

$$\rho(\vec{k}) = \frac{V}{(2\pi)^3}$$

- to calculate the density of states  $\rho(E)$  consider a volume which includes all states below a certain energy  $E$

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m} k_E^2$$

clearly  $\Rightarrow$  this volume is a sphere with radius  $k_E$

call this volume  $\Omega(E)$

$$\Omega(E) = \frac{V}{(2\pi)^3} \int_0^{k_E} k^2 dk = \frac{V}{(2\pi)^3} \frac{4\pi}{3} k_E^3$$

$$\Omega(E) = \frac{V}{(2\pi)^3} \frac{4\pi}{3} \left( \frac{\sqrt{2mE}}{\hbar} \right)^3$$

$$= \frac{V}{\hbar^3} \frac{4\pi}{3} (2m)^{3/2} E^{3/2}$$

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the density of states is given by the surface of this volume

$$\rho(E) = \frac{d\Omega(E)}{dE} = \frac{3}{2} \frac{V}{\hbar^3} \frac{4\pi}{3} (2m)^{3/2} E^{1/2}$$

$$\rho(E) = \frac{2\pi V}{\hbar^3} (2m)^{3/2} E^{1/2}$$

PVE relation of mono-atomic gases

one particle in a box:

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{2m} \left( \frac{2\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2)$$

$$\langle E_{n_x, n_y, n_z} \rangle = \frac{\hbar^2}{2m} \left( \frac{2\pi}{L} \right)^2 \left[ \langle n_x^2 \rangle + \langle n_y^2 \rangle + \langle n_z^2 \rangle \right]$$

main point  $\Rightarrow$  average energy will

depend on  $L$  as  $E(L) = \frac{\alpha}{L^2}$

or on  $V$  as  $E(V) = \frac{\alpha}{V^{2/3}}$

$$P(V) = - \frac{\partial E(V)}{\partial V} = \frac{2}{3V} E(V)$$

$$\Rightarrow \boxed{PV = \frac{2}{3} E}$$