(5) Formulation of Quantum Statistics

* Until now, we have considered:

    (A) Classical systems

    (B) Quantum systems of distinguishable particles.

* We will see that treating Q systems of indistinguishable particle requires new _formalism_ and brings _new physics_.

* This new formalism will allow us
    - to obtain classical systems as limit of Q systems
    - justify to normalization of phase space $\frac{1}{h^{3N}}$

(5.1) <u>QM ensemble theory</u>: <u>density matrix</u>

$\begin{cases} \mathcal{N} \text{ identical QM systems}; \quad \mathcal{N} \gg 1 \\ \hat{\mathcal{H}} - \text{Hamiltonian operator} \\ \psi(\bar{r}_i, t) - \text{wave function characterize physical state} \\ \psi^k(\bar{r}_i, t) - \text{physical state of the k-th system.} \end{cases}$

The evolution of the wave function is determined by the <u>Schrödinger equation</u>

$$\boxed{\hat{\mathcal{H}} \psi^k(t) = i\hbar \dot{\psi}^k(t)}$$

where $\frac{df}{dt} = \dot{f}$

We can write the w.f. in a basis (complete orthonormal)

$$\psi^k(t) = \sum_n a_n^k(t) \phi_n$$

where the coefficients $a_n^K(t)$ are

$$a_n^K(t) = \int \phi_n^* \psi^K(t) \, dV$$

— the integration is over the coordinate space

— in bra-ket notation $a_n^K(t) = \langle \phi_n | \psi^K(t) \rangle$

Schrö. $\qquad\qquad |\psi^K(t)\rangle = \sum_n a_n^K(t) |\phi_n\rangle$

$$i\hbar \, \dot{a}_n^K(t) = \int \phi_n^* \left(i\hbar \, \dot{\psi}^K(t) \right) dV$$

$$= \int \phi_n^* \hat{H} \psi^K(t) \, dV$$

$$= \int \phi_n^* \hat{H} \left(\sum_m a_m^K(t) \, \phi_m \right) dV$$

$$= \sum_m a_m^K \int \phi_n^* \hat{H} \phi_m \, dV \equiv \sum_m a_m^K \mathcal{H}_{nm}$$

where we define $\qquad \mathcal{H}_{nm} \equiv \int \phi_n^* \hat{H} \phi_m \, dV = \langle \phi_n | \hat{H} | \phi_m \rangle$

To summarize
$$\boxed{i\hbar \, \dot{a}_n^K = \sum_m \mathcal{H}_{nm} \, a_m^K} \qquad \left[\begin{array}{l} \text{or} \\ i\hbar \, \bar{a}^K = \mathcal{H} \, \bar{a}_m^K \end{array} \right]$$

As usual in QM, the coefficients a_n^K represent the probability to be in a state n of system K

$$|a_n^K(t)|^2 = P_n^K \qquad \text{and} \qquad \sum_n |a_n^K|^2 = 1.$$

The density operator

is defined as a matrix ρ with elements

$$\rho_{mn}(t) = \frac{1}{N} \sum_{K=1}^{N} a_m^K(t) \left[a_n^K(t) \right]^*$$

this is the ensemble average of $\qquad a_m(t) \, a_n(t)^*$.

In particular, the diagonal elements are the average probability $|a_n|^2$

[Note that that is a <u>double</u> average : $|a_n^k(t)|^2$ itself is a probability and then we take average]

$\rho_{nn}(t)$ is the probability that a randomly chosen system is at state n.

By definition of ρ $\qquad \sum_n \rho_{nn} = 1$

Let's see how ρ evolves

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

$$= \frac{1}{N} \sum_{k=1}^{N} \left\{ \left[\sum_\ell H_{m\ell} \, a_\ell^k(t) \right] a_n^k(t) \right.$$

$$\left. - a_m^k(t) \left[\sum_\ell H_{n\ell}^* \, a_\ell^k(t)^* \right] \right\} \qquad = \qquad \searrow \quad H_{n\ell}^* = H_{\ell n}$$

$-i\hbar \, \dot{a}_n^{k*} = \sum' H_{nm}^* \, a_m^{k*}$

$$= \sum_\ell \left[H_{m\ell} \, \rho_{\ell n}(t) - H_{\ell n} \, \rho_{m\ell}(t) \right]$$

To summarize

$$i\hbar \, \dot{\rho}_{mn} = \left[\hat{H}\hat{\rho} - \hat{\rho}\hat{H} \right]_{m,n}$$

or in matrix form

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

This is the QM analogue of an equation we already have seen, the Liouville equation.

Reminder :

Liouville's equation is for the density in phase-space
$\rho(q,p,t)$:

$$\dot{\rho} = [\rho, H] + \frac{\partial \rho}{\partial t}$$

$$[\rho, H] = \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right]$$

and compare to

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

* If the system is at equilibrium, the corresponding ensemble must be <u>stationary</u> $\dot{\rho}_{mn} = 0$.

  This means that :

  (i) $\hat{\rho}$ is an explicit function of $\hat{H}$, $\hat{\rho} = \hat{\rho}(\hat{H})$.

  (ii) The hamitonian must not depend explicitly on time, $\dot{\hat{H}} = 0$.

* Now if ϕ_n are the eigenfunctions of the Hamiltonian then $H_{mn} = E_n \delta_{mn}$

  and since $\hat{\rho} = \hat{\rho}(\hat{H})$ $\rho_{mn} = \rho_n \delta_{mn}$

  So in this basis both matrices are <u>diagonal</u>.

* In any other representation, the matrix may not be diagonal, but usually it is symmetric $\rho_{mn} = \rho_{nm}$.

  This comes from the property of <u>detailed balance</u>.

  the forward $m \rightarrow n$ transition rate is like the reverse $n \rightarrow m$.

Finally, we calculate the <u>expectation value</u> of a physical quantity G, represented by the operator $\hat{G}$.

$$\langle G \rangle = \frac{1}{N} \sum_{k=1}^{N} \psi^{k*} G \psi^{k} \, dV = \frac{1}{N} \sum_{k} \langle \psi_{\bullet}^{k} | G | \psi_{\bullet}^{k} \rangle$$

In terms of the basis ϕ_n

$$\langle G \rangle = \sum_{k=1}^{N} \sum_{m,n} a_n^{k*} G_{nm} a_m^{k} \quad \text{where } G_{nm} = \int \phi_n^{*} G \phi_m \, dV$$

$$\left(\text{or} \quad G = \frac{1}{N} \sum \langle \underbrace{\psi^k | \phi_n}_{a_n^{k*}} \rangle \langle \phi_n | G | \phi_m \rangle \underbrace{\langle \phi_m | \psi^{k} \rangle}_{a_m^{k}} \right)$$

Using the definition of the matrix density $\hat{\rho}_{mn} = \frac{1}{N} \sum_{k=1}^{N} a_m^{k} a_n^{k*}$

we find

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

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

* Taking $\hat{G}$ the unity $\hat{G} = \hat{1}$ we have

$$Tr \hat{\rho} = \langle \hat{1} \rangle = 1$$

In general if ψ^k the w.f. are not normalized

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

Note: $\langle G \rangle = Tr(\hat{\rho} \hat{G})$ does not depend on the choice of basis (This is a trace of a matrix)

Statistics of various ensembles

(A) The microcanonical ensemble

This ensemble is characterized by
fixed N, fixed V and fixed E
(practically, we can say that it is in $\left(E - \frac{\Delta}{2}, E + \frac{\Delta}{2}\right)$)
with $\Delta \ll E$

$$\Gamma(N, V, E; \Delta) = \# \text{ of micro-states.}$$

By assumption, all microstates are **equally probable**.
Accordingly, the density matrix must be diagonal:

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

with

$$\rho_n = \begin{cases} 1/\Gamma & \text{for each accessible state} \\ 0 & \text{otherwise} \end{cases}$$

As we have shown all TD is derived from
the entropy

$$S = \ln \Gamma$$

In a real QM calculation we will not need
to introduce a $1/N!$ factor to resolve Gibbs paradox.
for indistinguishable particles.

In a pure state only one state appears in all
systems and $\Gamma = 1$ with $S = \ln \Gamma = 0$,

This means that only one entry in ρ is non-zero

$$\rho = \begin{pmatrix} \ddots & & \\ & 1 & \\ & & \ddots \end{pmatrix} \quad \text{and} \quad \rho^2 = \rho$$

If we write the pure state in a different representation than

$$\rho_{mn} = \frac{1}{M} \sum_{k=1}^{M} a_m^k a_n^{k*} = a_m a_n^*$$

and the square matrix is

$$\rho^2{}_{mn} = \sum_\ell \rho_{m\ell} \rho_{\ell n} = \sum_\ell a_m a_\ell^* a_\ell a_n^*$$

$$= a_m a_n^* \underbrace{\sum_\ell a_\ell^* a_\ell}_{1} = a_m a_n^*$$

In a __mixed state__ $\Gamma > 1$.

To see the properties of $\hat{\rho}$ for a mixed state we need to add another assumption:

__Random a priori phase__ (in addition to equal probabilities) for the probability amplitudes a_n^k.

This implies that the w.f. ψ^k is an __incoherent__ superposition of $\{\phi_n\}$. Thus, in any representation

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

$$= |a|^2 \left\langle e^{i(\Theta_m^k - \Theta_n^k)} \right\rangle = |a|^2 \delta_{mn}$$

We find that ρ continues to be diagonal.

Note that we now used two assumptions ("postulates"):

(1) Equal a priori probability.

(2) Random a priori phase.

Assumption (2) is purely QM: it avoids interference and correlations among systems in the ensemble.

The Canonical Ensemble

Now a macrostate is defined by N, V and T.
E is now a variable quantity chosen _randomly_
from an ensemble according to Boltzmann
distribution $\sim \exp(-\beta E)$.

The density matrix in the energy representation
is therefore

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

$$\rho_n = \frac{e^{-\beta E_n}}{Q_N(\beta)} \quad ; \quad Q_N(\beta) = \sum_n e^{-\beta E_n}$$

with the usual partition function.

We can therefore write

$$\hat{\rho} = \sum_n |\phi_n\rangle \frac{e^{-\beta E_n}}{Q_N(\beta)} \langle\phi_n|$$

$$= \frac{1}{Q_N(\beta)} e^{-\beta \hat{H}} \underbrace{\sum_n |\phi_n\rangle\langle\phi_n|}_{\hat{1}}$$

$$= \frac{e^{-\beta \hat{H}}}{Q_N(\beta)} =$$

$$\boxed{\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\text{Tr}\left(e^{-\beta \hat{H}}\right)}}$$

← use the power expansion

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

Reminder

* The density operator

$$\hat{\rho}_{mn}(t) = \frac{1}{N} \sum_{k=1}^{N} a_m^k(t) \left[a_n^k(t) \right]^*$$

  that is the ensemble average over $a_m a_n^*$

* The Schrödinger equation for $\hat{\rho}$:

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

  $\rightarrow$ if $\hat{\rho} = \hat{\rho}(\hat{H})$ and has no explicit time dependence

$$\dot{\hat{\rho}} = 0$$

* The expectation value = the average of G

$$\langle G \rangle = Tr(\hat{\rho}\hat{G}) \quad \text{or} \quad \langle G \rangle = \frac{Tr(\hat{\rho}\hat{G})}{Tr(\hat{\rho})}$$

  if $\hat{\rho}$ not normalized

* if $\hat{\rho} = \hat{\rho}(\hat{H})$ we can write it as a diagonal matrix if we take the energy basis $\{\phi_n\}$

  Then $H_{mn} = E_n \delta_{mn}$ and $\rho_{mn} = \rho_n \delta_{mn}$

* Microcanonical Ensemble:

Diagonal $\qquad \rho_n = \begin{cases} \frac{1}{\Gamma} & \text{for states with E} \\ 0 & \text{otherwise} \end{cases}$

* Canonical Ensemble:

Diagonal $\qquad \rho_n = \dfrac{e^{-\beta E_n}}{Q_N(\beta)} \quad \text{or} \quad \hat{\rho} = \dfrac{e^{-\beta \hat{H}}}{Tr(e^{-\beta \hat{H}})}$

The expectation value of an operator G is

$$\langle G \rangle_N = Tr(\hat{\rho} \hat{G}) = \frac{1}{Q_N(\beta)} Tr(e^{-\beta \hat{H}} G)$$

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

The Grand Canonical Ensemble

In this ensemble $\hat{\rho}$ operates on a space where <u>the number of particles can be any integer ≥ 0.</u> $\hat{\rho}$ must therefore commute with $\hat{H}$ and with the <u>number operator</u> $\hat{n}$ whose eigenvalues are $0, 1, 2 \dots$ The precise form of the density operator is

$$\hat{\rho} = \frac{1}{Q(\mu, V, T)} e^{-\beta(\hat{H} - \mu\hat{n})}$$

with the usual grand partition function

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

The ensemble average of G is

$$\langle G \rangle = \frac{1}{Q(\mu, V, T)} Tr\left(\hat{G} e^{-\beta \hat{H}} e^{\beta \mu \hat{n}}\right)$$

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

$$z = e^{\beta \mu}$$

$$\langle G \rangle_N = \frac{1}{Q_N} Tr(e^{-\beta \hat{H}} \hat{G})$$

/ (5.3) EXAMPLES

(A) Electron in a magnetic field

The electron has intrinsic spin $\frac{1}{2}\hbar\hat{\sigma}$ $\left(\begin{array}{l}\hat{\sigma}\ \text{Pauli}\\ \text{spin operator}\end{array}\right)$

The electron has $J=\frac{1}{2}$ so it has $2J+1=2$ states,

up or down $\uparrow\downarrow$.

The magnetic field is in the z direction,
so the configurational Hamiltonian is

$$\hat{H} = -\mu_B(\hat{\sigma}\cdot B) = -\mu_B B\,\hat{\sigma}_z = -\mu_B B\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

where $\mu_B = \dfrac{e\hbar}{2mc}$ is the Bohr magneton.

and Pauli matrices are

$$\hat{\sigma}_x = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \;;\; \hat{\sigma}_y = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \;;\; \hat{\sigma}_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

The density matrix in the canonical ensemble is

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{Tr(e^{-\beta\hat{H}})} = \frac{1}{e^{\beta\mu_B B}+e^{-\beta\mu_B B}}\begin{pmatrix}e^{\beta\mu_B B} & 0\\ 0 & e^{-\beta\mu_B B}\end{pmatrix}$$

To calculate $e^{-\beta\hat{H}}$ we can write it as

$$e^{-\beta\hat{H}} = \sum_{K=0}^{\infty}\frac{1}{K!}(\beta\hat{A})^K = \sum_{K=0}^{\infty}\frac{1}{K!}(\beta\mu_B B)^K(\hat{\sigma}_z)^K$$
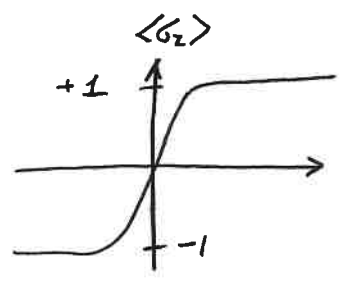
$$(1\ 0)\left(e^{-\beta\hat{H}}\right)\begin{pmatrix}1\\ 0\end{pmatrix} = \sum_{k=0}^{\infty}\frac{1}{K!}(\beta\mu_B B)^K\left[(\hat{\sigma}_z)_{11}\right]^K = e^{\beta\mu_B B}$$

$$\underbrace{\phantom{(\hat{\sigma}_z)_{11}}}_{1}$$

and so on and so furth

If we want the expectation value of $\hat{\sigma}_z$

$$\langle \hat{\sigma}_z \rangle = \frac{Tr(\hat{\sigma} e^{-\beta \hat{H}})}{Tr(e^{-\beta \hat{H}})} = \frac{1}{Tr(e^{-\beta \hat{H}})} Tr \begin{pmatrix} e^{\beta \mu_B B} & 0 \\ 0 & -e^{-\beta \mu_B B} \end{pmatrix}$$

$$\langle \hat{\sigma}_z \rangle = \frac{e^{\beta \mu_B B} - e^{-\beta \mu_B B}}{e^{\beta \mu_B B} + e^{-\beta \mu_B B}} = tgh(\beta \mu_B B)$$

A particle in a box

A free particle of mass m in a box L^3

The Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

with periodic ~~boundary~~ conditions

$$\phi(x,y,z) = \phi(x+L,y,z) = \phi(x,y+L,z) = \phi(x,y,z+L)$$

The general solutions are

$$\phi_E(\vec{r}) = \frac{1}{L^{3/2}} e^{i\vec{k}\cdot\vec{r}}$$

with energy

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

The wave-length that satisfy the B.C. are

$$\vec{K} \equiv (K_x, K_y, K_z) = \frac{2\pi}{L}(n_x, n_y, n_z) \quad \text{with the}$$

integer quantum numbers (n_x, n_y, n_z)

We can write $\vec{K} = \frac{2\pi}{L} \vec{n}$ where $\vec{n}$ is a vector $0, \pm 1, \pm 2 \ldots$

Let us now calculate the density matrix $\hat{\rho}$.

We will use coordinate representation, i.e. w.f. of $\bar{r}$.

$$\langle \bar{r} | e^{-\beta \hat{H}} | \bar{r}' \rangle = \sum_{E,E'} \langle \bar{r} | E \rangle \underbrace{\langle E | e^{-\beta \hat{H}} | E' \rangle}_{e^{-\beta E} \delta_{EE'}} \langle E' | \bar{r}' \rangle$$

$$= \sum_E \underbrace{\langle \bar{r} | E \rangle}_{\phi_E(\bar{r})} e^{-\beta E} \underbrace{\langle E | \bar{r}' \rangle}_{\phi_E^*(r')} = \sum_E e^{-\beta E} \phi_E(\bar{r}) \phi_E^*(\bar{r}')$$

We can now substitute the eigenfunctions $\phi_E(\bar{r}) = \dfrac{1}{L^{3/2}} e^{i\bar{k}\cdot\bar{r}}$

$$\langle \bar{r} | e^{-\beta \hat{H}} | \bar{r}' \rangle = \sum_K e^{-\beta E(k)} \phi_K(\bar{r}) \phi_K(\bar{r}')^* \quad \leftarrow \left| \begin{array}{l} \text{Since } E = \dfrac{\hbar k^2}{2m} \text{ we} \\ \text{can sum over } K \end{array} \right.$$

$$= \frac{1}{L^3} \sum_K \exp\left[-\frac{\beta \hbar^2}{2m} K^2 + i\bar{K}\cdot(\bar{r}-\bar{r}') \right]$$

Replace sum by integral $\left. \sum_k \to \left(\frac{L}{2\pi}\right)^3 \int d^3k \right\rangle \longrightarrow$
$$= \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \exp\left[-\frac{\beta \hbar^2}{2m} K^2 + i\bar{K}(\bar{r}-\bar{r}') \right] d^3k$$

The integral is the inverse Fourier transform.

$$\mathcal{F}^{-1}[e^{-\alpha k^2}] = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-\alpha k^2} e^{-ikr} dk = \frac{1}{2\pi^{1/2} \alpha^{1/2}} e^{-\frac{r^2}{4\alpha}}$$

We can write it as a product

$$\langle \bar{r} | e^{-\beta \hat{H}} | \bar{r}' \rangle = \left[\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-\alpha k_x^2} e^{ik_x(x'-x)} dx \right]\left[\begin{array}{c} \text{same for} \\ y \end{array} \right]\left[\begin{array}{c} \text{same} \\ z \end{array} \right]$$

with $\alpha = \dfrac{\beta \hbar^2}{2m}$

$$= \left(\frac{1}{2\pi^{1/2} \alpha^{1/2}} \right)^3 e^{-\frac{1}{4\alpha} |\bar{r}-r'|^2}$$

Finally,

$$\langle \vec{F} | e^{-\beta \hat{H}} | \vec{F}' \rangle = \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3/2} \exp \left(-\frac{m}{2\beta \hbar^2} |\vec{F} - \vec{F}'|^2 \right)$$

The partition function is

$$Tr\left(e^{-\beta \hat{H}} \right) = \int d^3r \, \langle \vec{F} | e^{-\beta \hat{H}} | \vec{F} \rangle = \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3/2} \int d^3r$$

$$= \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3/2} V$$

This is the well-known partition function of single particle $Q_1(\beta)$.

We can now write the density matrix

$$\boxed{ \langle \vec{F} | \hat{\rho} | \vec{F}' \rangle = \frac{\langle \vec{F} | e^{-\beta \hat{H}} | \vec{F}' \rangle}{Tr(e^{-\beta \hat{H}})} = \frac{1}{V} \exp \left[-\frac{m}{2\beta \hbar^2} |\vec{r} - \vec{r}'|^2 \right] }$$

— As expected, the density matrix is <u>symmetric</u>

$$\langle \vec{F} | \hat{\rho} | \vec{F}' \rangle = \langle F' | \hat{\rho} | \vec{F} \rangle.$$
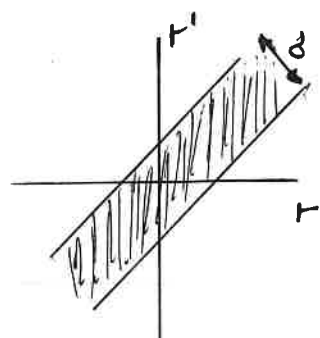
— Moreover, the diagonal elements are $\langle \vec{F} | \hat{\rho} | \vec{F} \rangle = \frac{1}{V}$.

All positions in the box are <u>equally probable</u>.

— The non-diagonal elements represent the probability
for $\vec{F} \rightleftarrows \vec{F}'$ transitions.

— The spatial extent of the wave packet is

$$\frac{1}{2\delta^2} = \frac{m}{2\beta \hbar^2} \longrightarrow \boxed{ \delta = \left(\frac{\beta}{m} \right)^{1/2} \hbar = \frac{\hbar}{(mT)^{1/2}} }$$

This QM vanishes at high-temperature and
we get δ-function of a point particle.

Finally, we calculate the expectation value
of the Hamiltonian

$$\langle H \rangle = \text{Tr}\left(\hat{H}\hat{\rho}\right) = \frac{\text{Tr}\left(\hat{H}e^{-\beta\hat{H}}\right)}{\text{Tr}\left(e^{-\beta\hat{H}}\right)}.$$

$$= -\frac{\partial}{\partial\beta} \ln \text{Tr}\left(e^{-\beta\hat{H}}\right) = -\frac{\partial}{\partial\beta} \ln\left[\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} V\right]$$

$$= -\frac{\partial}{\partial\beta}\left[-\frac{3}{2}\ln\beta\right] = \frac{3}{2}\cdot\frac{1}{\beta} = \frac{3}{2}T$$

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In the book by Pathria this is calculated in
real space representation. Here we will use
energy representation

$$\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + \frac{1}{2}m\omega^2 q^2$$

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2, 3 \ldots$$

$\phi_n(q)$ are Hermite polynomials

$$\phi_n(q) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{H_n(\xi)}{(2^n n!)^{1/2}} e^{-\frac{1}{2}\xi^2} \qquad \xi = \left(\frac{m\omega}{\hbar}\right)^{1/2} q$$

However we use the simple energy representation
in which

$$\text{Tr}\left(e^{-\beta\hat{H}}\right) = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega}$$

$$= e^{-\frac{1}{2}\beta\hbar\omega} \cdot \frac{1}{1-e^{-\beta\hbar\omega}} = 1/2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)$$

$$\langle H \rangle = -\frac{\partial}{\partial \beta} \ln Tr (e^{-\beta \hat{H}}) = -\frac{\partial}{\partial \beta} \ln \frac{1}{2 \sinh(\frac{1}{2}\beta \hbar \omega)}$$

$$= \frac{\partial}{\partial \beta} \ln \left[2 \sinh(\frac{1}{2}\beta \hbar \omega) \right] =$$

$$= \frac{\cosh(\frac{1}{2}\beta \hbar \omega)}{\sinh(\frac{1}{2}\beta \hbar \omega)} \cdot \frac{1}{2}\hbar \omega = \coth(\frac{1}{2}\beta \hbar \omega) \frac{1}{2}\hbar \omega$$

The limits :

(i) low T ; $\beta \to \infty$
$\qquad \langle H \rangle = \frac{1}{2}\hbar \omega \leftarrow \coth x \simeq 1$

(ii) high T ; $\beta \to \infty$
$\qquad \langle H \rangle = \frac{\frac{1}{2}\hbar \omega}{\frac{1}{2}\beta \hbar \omega} = \frac{1}{\beta} = T$

the classical limit $\qquad\qquad \nwarrow$

$\coth x \simeq \frac{1}{x}$

(5.4) Systems composed of indistinguishable particles

Take N <u>identical</u> particles.

For simplicity assume that they are non-interacting.
The Hamiltonian is a sum of single-particle Hamiltonians

$$\hat{H}(p,q) = \sum_{i=1}^{N} \hat{H}_i(q_i, p_i)$$

The $\hat{H}_i$ are the same for all particles.

The Schrödinger equation is (time-independent)

$$\hat{H}\,\psi_E(\bar{q}) = E\,\psi_E(\bar{q})$$

A straightforward solution would be:

$$\psi_E(\bar{q}) = \prod_{i=1}^{N} u_{\varepsilon_i}(q_i)$$

where each $u_{\varepsilon_i}(q_i)$ is eigenfunction of $\hat{H}_i$

$$\hat{H}_i\, u_{\varepsilon_i}(q_i) = \varepsilon_i\, u_{\varepsilon_i}(q_i)$$

and
$$E = \sum_{i=1}^{N} \varepsilon_i$$

* From all this we see that a stationary state
may be described in terms of constituent particles.

In general, we can identify the state by
specifing $\{n_i\}$ = # of particles in eigenstate ε_i.

As usual, $\qquad \sum_i n_i = N$

$$\sum_i n_i \varepsilon_i = E$$

Accordingly, the wave-function is

$$\psi_E(\bar{q}) = \prod_{m=1}^{n_1} u_1(q_m) \prod_{m=n_1+1}^{n_1+n_2} u_2(q_m) \ldots$$

Assume, that we apply a permutation of coordinates

$$(1, 2, \ldots N) \longrightarrow (P1, P2 \ldots PN)$$

The resulting wave-function is $P\psi_E(\bar{q})$

$$P\psi_E(\bar{q}) = \prod_{m=1}^{n_1} u_1(q_{Pm}) \prod_{m=n_1+1}^{n_1+n_2} u_2(q_{Pm}) \ldots$$

In classical physics particles are <u>distinguishable</u> so permutations of identical particles create new states.

This leads to $\left[\dfrac{N!}{n_1! \, n_2! \ldots} \quad \text{states for the partition} \quad \{n_i\} \right]$

Previously we applied Gibbs recipe:
Divide by $N!$ and get $\qquad W_C\{n_i\} = \dfrac{1}{n_1! \, n_2! \ldots}$

But in QM this is not enough because even if two particles are in different energy levels it is still physically the same state.

* The whole concept of indexing particles is wrong.

* Only the numbers $\{n_i\}$ matter.

* So all permutations which keep $\{n_i\}$ give the same state.

In other words $\quad W_q \{n_i\} = 1$

At the same time, the wave function we previously wrote

$$\psi_E(\bar{q}) = \prod_{m=1}^{n_1} u_1(q_m) \prod_{m=n_1+1}^{n_1+n_2} u_2(q_m)$$

is inappropriate, because when we interchange coordinates between u_i and u_j with $i \neq j$, we get a different form of wave function.

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* We therefore need to construct a form of $\psi_{\bar{E}}(\bar{q})$ that is __insensitive__ to such changes.

— A simple recipe is to take a combination of all $N!$ w.f.

The combination must have the following property:

$$|P\psi|^2 = |\psi|^2 \qquad \text{conservation of probability.}$$

There are two possibilities:

(A) $\qquad P\psi = \psi \quad$ for all P

(B) $\qquad P\psi = \begin{cases} +\psi & : P \text{ is an even permutation} \\ -\psi & : P \text{ is an odd permutation} \end{cases}$

These are called __symmetric__ ψ_S and __anti-symmetric__ ψ_A wave functions.

Their mathematical structure is given by

$$\psi_S(\bar{q}) \propto \sum_P P \psi_B(\bar{q})$$

$$\psi_A(\bar{q}) \propto \sum_P \delta_P P \psi_B(\bar{q})$$

where $\psi_B = \prod_{m=1}^{n_1} u_1(q_m) \prod_{m=n_1+1}^{n_1+n_2} u_2(q_m) \cdots$ is the product form

and δ_P is the _parity_ of the permutation $\left[\begin{array}{l} = \text{\# of} \\ \text{pair exchanges} \end{array} \right]$

$\delta_P = +1$ for even and $\delta_P = -1$ for odd.

We can write the anti-symmetric form using the _determinant_, which is the anti-symmetric invariant

$$\psi_A(\bar{q}) = \begin{vmatrix} u_i(q_1) & u_i(q_2) & \cdots & u_i(q_N) \\ u_j(q_1) & u_j(q_2) & \cdots & u_j(q_N) \\ \vdots & & & \\ u_\ell(q_1) & u_\ell(q_2) & \cdots & u_\ell(q_N) \end{vmatrix}$$

(Slater's determinant)

In the determinant we can get the signs through the expansion.

For example:

$$\begin{vmatrix} u_1(q_1) & u_1(q_2) \\ u_2(q_1) & u_2(q_2) \end{vmatrix} = u_1(q_1) u_2(q_2) - u_1(q_2) u_2(q_1)$$

In general, $\det | u_i(q_\alpha) | = \sum_P \delta_P P \psi_B(\bar{q})$

(A) When we exchange the arguments of a pair of particles, we exchange the columns of the determinant and it changes sign

$$\begin{vmatrix} u_i(q_1) \ldots u_i(q_\alpha) \ldots u_i(q_\beta) \ldots u_i(q_N) \\ u_j(q_1) \ldots u_j(q_\alpha) \ldots u_j(q_\beta) \ldots u_j(q_N) \\ \vdots \\ u_\ell(q_1) \ldots u_\ell(q_\alpha) \ldots u_\ell(q_\beta) \ldots u_\ell(q_N) \end{vmatrix}$$

(B) If two particles are in the same single particle state we have two rows that are equal to each other (because the same u_j appears at two rows) and the determinant vanishes.

$\Rightarrow$ A system of indistinguishable particles with <u>anti-symmetric</u> wave-functions has all particles in <u>different</u> single particle states

This is <u>Pauli's Exclusion Principle</u>

* The inverse is also true: Particles obeying an exclusion principle are described by an anti-symmetric wave function.

* The particles obey <u>Fermi-Dirac statistics</u>

$$W_{FD}\{n_i\} = \begin{cases} 1 & \text{if } \sum_i n_i^2 = N \\ 0 & \text{if } \sum_i n_i^2 > N \end{cases} \quad \boxed{\text{Fermions}}$$

Particles that are described by <u>symmetric</u> wave function have no similar restriction and can have any non-negative $\{n_i\}$

These statistics are called <u>Bose-Einstein</u>.

For such <u>BOSONS</u> all such states are equally probable

$$W_{BE}\{n_i\} = 1 \quad \text{for} \quad n_i = 0, 1, 2 \ldots$$

Statistics is linked to <u>spin</u>:

Particles with integral spin (in units of $\hbar$) are <u>bosons</u> — with half-integral spin are <u>fermions</u>.

<u>Bosons</u>: photons, phonons, gravitons, α particles

<u>Fermions</u>: electrons, protons, neutrons

Our conclusions remain valid also for <u>interacting</u> particles, but still the wave function obeys:
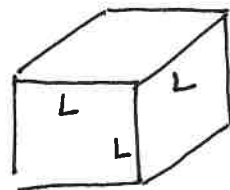
$$P\psi_S = \psi_S$$

$$P\psi_A = \begin{cases} \psi_A & \text{even } P \\ -\psi_A & \text{odd } P \end{cases}$$

The Density matrix and Partition function for free particles

N indisinguishable non-interacting particles.

V volume of the system $= L^3$

In the canonical ensemble

$$\langle r_1 \dots r_N | \hat{\rho} | r_1' \dots r_N' \rangle = \frac{1}{Q_N(\beta)} \langle r_1 \dots r_N | e^{-\beta \hat{H}} | r_1' \dots r_N' \rangle$$

with the partition function:

$$Q_N(\beta) = Tr\left(e^{-\beta \hat{H}}\right) = \int \langle r_1 \dots r_N | e^{-\beta \hat{H}} | r_1 \dots r_N \rangle \, d^{3N} r$$

Shorthand notation $\quad r_i \to i \; ; \; r_i' \to i'$

$$\langle 1 \dots N | \psi_E \rangle = \psi_E(1, \dots N) \quad \text{are eigenfunctions with energies } E.$$

We can then expand:

$$\langle 1 \dots N | e^{-\beta \hat{H}} | 1' \dots N' \rangle = \sum_{E, E'} \langle 1 \dots N | \psi_E \rangle \langle \psi_E | e^{-\beta \hat{H}} | \psi_{E'} \rangle \langle \psi_{E'} | 1' \dots N' \rangle$$

$$= \sum_{E, E'} \langle 1 \dots N | \psi_E \rangle \, e^{-\beta E} \delta_{EE'} \langle \psi_{E'} | 1' \dots N' \rangle$$

$$= \sum_{E} e^{-\beta E} \psi_E(1 \dots N) \, \psi_E^*(1' \dots N')$$

Since particles are non-interacting, we can express the eigenfunctions in terms of single particles and their eigenfunctions $u_i(m)$

The single particle energies are written in terms of the momentum:

$$E = \frac{\hbar^2}{2m} K^2 = \frac{\hbar^2}{2m} (\bar{K}_1^2 + \bar{K}_2^2 + \dots + \bar{K}_N^2) = \sum_i' \varepsilon_i$$

With periodic boundary conditions

$$u_{\bar{K}}(\bar{r}) = \frac{1}{V^{1/2}} e^{i\bar{K}\cdot\bar{r}} \quad \text{with} \quad \bar{K} = \frac{2\pi}{L} \bar{n}$$

The factor $\frac{1}{V^{1/2}}$ ensures normalization $\int |u_{\bar{K}}(\bar{r})|^2 d\bar{r} = 1$

$\bar{n}$ is a vector of integers $\quad 0, \pm 1, \pm 2 \dots$

The total wave function is then sum of permutation

$$\boxed{\psi_K(1 \dots N) = (N!)^{-1/2} \sum_P \delta_P \, P\left[u_{K_1}(1) \dots u_{K_N}(N)\right]}$$

where $\delta_P = +1$ if the particles are __bosons__

and $\delta_P = \text{sgn}(P) = \pm 1$ for __fermions__.

and the total momentum amplitude $K^2 = K_1^2 + \dots + K_N^2$

When we permute, we can either change the particles or change the momenta $K_1, \dots K_N$
These will give the same permutations

$$\psi_K(1 \dots N) = (N!)^{-1/2} \sum_P \delta_P \left[u_{K_1}(P1) \dots u_{K_N}(PN)\right]$$

$$= (N!)^{-1/2} \sum_P \delta_P \left[u_{PK_1}(1) \dots u_{PK_N}(N)\right]$$

We can now substitute into the density operator

$$\langle 1 \dots N | e^{-\beta \hat{H}} | 1' \dots N' \rangle = \sum_E e^{-\beta E} \psi_E(1 \dots N) \psi_E^*(1' \dots N')$$

$$= \frac{1}{N!} \sum_K e^{-\frac{\beta \hbar^2}{2m} K^2} \left\{ \sum_P \delta_P \left[u_{K_1}(P1) \dots u_{K_N}(PN) \right] \right.$$

$$\left. \times \sum_{\widetilde{P}} \delta_{\widetilde{P}} \left[u^*_{\widetilde{P}K_1}(1') \dots u^*_{\widetilde{P}K_N}(N') \right] \right\}$$

two $(N!)^{-1/2}$ factors

sum over k instead of E

Three comments

(i) The quantity $\{\psi \psi^*\}$ is invariant to permutation of K_i.

(ii) The summation is therefore equivalent to summing the K_i <u>independently</u> and then dividing by $\frac{1}{N!}$

This is equivalent to trying all permutations
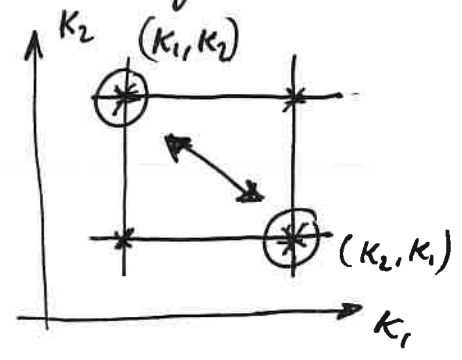
(iii) Similarly, the N-fold summation over the K_i all the permutations $\widetilde{P}$ will contribute the same.

Therefore we can take only one of them, say $\widetilde{P}K_1 = K_1, \dots P K_n = K_n$, and multiply by $(N!)$

The end result is

$$\langle 1 \dots N | e^{-\beta \hat{H}} | 1' \dots N' \rangle = \frac{1}{N!} \sum_{K_1 \dots K_N} e^{-\frac{\beta \hbar^2}{2m}(K_1^2 + \dots K_N^2)}$$

$$\times \left[\sum_P \delta_P \left[u_{K_1}(P1) u^*_{K_1}(1') \right] \dots \left[u_{K_N}(PN) u^*_{K_N}(N') \right] \right]$$

We can now replace all the discrete summation over k_i by integrations

$$\sum_{k_i} \longrightarrow \int \frac{L}{2\pi} \, dk_i$$

$$\langle 1 \ldots N | \, e^{-\beta \hat{H}} \, | 1' \ldots N' \rangle =$$

$$= \frac{1}{N!} \cdot \frac{1}{(2\pi)^{3N}} \sum_{P} \delta_P \left[\iint \left[e^{-\frac{\beta \hbar^2}{2m} k_1^2 + ik_1 (P1 - 1')} \right] dk_1 \right] \times$$

the L^{3N} cancels with the $\frac{1}{V^{1/2}}$ factors in the $\mu_i(m)$

$$\cdots \times \left[\iint \left[e^{-\frac{\beta \hbar^2}{2m} k_N^2 + ik_N (PN - N')} dk_N \right] \right.$$

Integration is Fourier transform over Gaussian

$$= \frac{1}{(N!)} \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3N/2} \sum_{P} \delta_P \left[f(P1 - 1') \cdots f(PN - N') \right]$$

where $f(x) = e^{-\frac{m}{2\beta \hbar^2} x^2}$ is the F.T. of Gaussian.

Use the definition of the thermal de Broglie wave length

$$\lambda = \frac{\hbar}{(2\pi m T)^{1/2}} = \hbar \left(\frac{2\pi \beta}{m} \right)^{1/2} \quad \text{and finally get.}$$

$$\boxed{\langle 1 \ldots N | \, e^{-\beta \hat{H}} \, | 1' \ldots N' \rangle = \frac{1}{N! \lambda^{3N}} \sum_{P} \delta_P \left[f(Pr_1 - r_1) \cdots f(Pr_N - r_N) \right]}$$

with

$$f(r) = e^{-\pi r^2 / \lambda^2}$$

To calculate the partition function we have to integrate the density matrix:

$$Q_N(\beta) = Tr(e^{-\beta\hat{H}}) = \int dr_1 \dots dr_N \langle 1 \dots N | e^{-\beta\hat{H}} | 1 \dots N^* \rangle$$

Before we do that, note that:

(i) The leading term in the summation is when $Pr_i = r_i$ and then we get 1

(ii) The second term will include one pair exchange,

$$f(r_j - r_i) f(r_j - r_i)$$

(iii) The next term will include triplets

So we have

$$\sum_P = 1 \pm \underset{i<j}{\sum} f_{ij} f_{ji} + \underset{i<j<k}{\sum} f_{ij} f_{jk} f_{ki} + \dots$$

bosons ↗ (arrow pointing to $1 \pm$ region)

termions ↙

where the shorthand is $f_{ij} = f(r_i - r_j)$

Note that the scale of the Gaussian in f is λ, so if the typical distances between the particles are larger, $f \ll 1$.

In other words when $n\lambda^3 = \dfrac{n h^3}{(2\pi m T)^{3/2}} \ll 1$

the system can be approximated by the first term

This yields $Q_N(\beta) = Tr(e^{-\beta\hat{H}}) =$

Classical Ideal Gas $\longrightarrow$ $= \dfrac{1}{N! \lambda^{3N}} \int d^{3N}r \cdot 1 = \dfrac{V^N}{N! \lambda^{3N}}$

* This shows that we get the the ideal gas partition function from precise QM. Indeed, the Gibbs recipe is correct and originates from the symmetrization of wave functions.

* It also shows that the correspondence between the phase-space integration of classical mechanics over phase space and the summation over the density operator when we divide by cells of volume $\omega_0 = h^{3N}$

The normalized density operator is

$$\langle 1...N | \hat{\rho} | 1'...N' \rangle = \frac{1}{Q_N} \langle 1...N | e^{-\beta \hat{H}} | 1'...N' \rangle$$

In the classical limit

$$\langle 1...N | \hat{\rho} | 1'...N' \rangle = \frac{1}{N! \lambda^{3N}} \Big/ \frac{V^N}{N! \lambda^{3N}} = \frac{1}{V^N} \prod_i \delta(r_i - r_i')$$

which is a product of N single particle $\frac{1}{V}$ factors since

$$\langle r | \hat{\rho}_1 | r' \rangle = \frac{1}{V} \delta(r - r')$$

From this we see that in the classical limit there are no correlations between the particles:

However, when the system is genuinely QM and it is degenerate $n\lambda^3 \gtrsim 1$ there could be correlations even if the particles are not interacting through the Hamiltonian.

These purely QM interactions come from the symmetrization of the wave functions.

Of course, these interactions are significant when the inter-particle distance is comparable to λ, $n^{-1/3} \lesssim \lambda$.

We can see this by considering two particles $N=2$.

The summation is now simple

$$\langle r_1 r_2 | e^{-\beta \hat{H}} | r_1, r_2 \rangle = \frac{1}{2! \lambda^6} \left[1 \pm e^{-2\pi \frac{r_{12}^2}{\lambda^2}} \right]$$

So the partition function is

$$Q_2(\beta) = \frac{1}{2\lambda^6} \int \left(1 \pm e^{-2\pi \frac{r_{12}^2}{\lambda^2}} \right) dr_1 \, dr_2$$

$$= \frac{1}{2} \frac{V}{\lambda^6} \left[V \pm \int_0^\infty e^{-2\pi \frac{r^2}{\lambda^2}} 4\pi r^2 dr \right] \quad \longleftarrow \quad \begin{cases} \text{change coordinates} \\ \text{to } \binom{r_1}{r_2} \to \binom{r_1 - r_2 = r}{r_1} \end{cases}$$

$$= \frac{1}{2} \left(\frac{V}{\lambda^3} \right)^2 \left[1 \pm \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{V} \right) \right] \approx \frac{1}{2} \left(\frac{V}{\lambda^3} \right)^2$$

The density operator is therefore (diagonal terms)

$$\langle r_1, r_2 | \hat{\rho} | r_1, r_2 \rangle = \frac{1}{V^2} \left[1 \pm e^{-2\pi \frac{r_{12}^2}{\lambda^2}} \right]$$

We see that the probability differs considerably from the classical value $\frac{1}{V^2}$

$$P(r_1, r_2) = \langle r_1 r_2 | \hat{\rho} | r_1 r_2 \rangle = \frac{1}{V^2} \left[1 \pm \exp\left(\frac{2\pi r_{12}^2}{\pm \lambda^2} \right) \right]$$

- For bosons $\quad P(r_1 = r_2) = \frac{2}{V^2} \quad$ twice as classical particles

- For fermions $\quad P(r_1 = r_2) = 0 \quad$ Pauli's exclusion

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Sometimes it is useful to describe this QM effect by a classical potential $v_s(r)$.

The relation between correlation functions and potentials give

$$e^{-\beta v_s(r)} = g(r)$$

$\rightarrow \quad v_s(r) = -\frac{1}{\beta} \ln \left[1 \pm \exp\left(\frac{-2\pi r^2}{\lambda^2} \right) \right]$