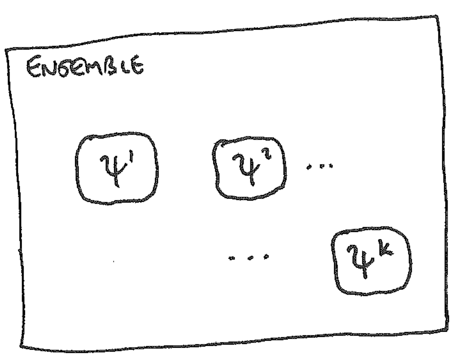
5 Formulation of Quantum Statistics.

We need to consider a formulation of statistical mechanics that is fully consistent with quantum mechanics. Ideally, our approach will not depend on the basis in which we do our calculations. To make this leap, we need to introduce the quantum mechanical equivalent of the probability distribution: the density matrix $\hat{\rho}$

5.1 Density Matrix.

$\mathcal{N}$ identical systems, each in its own quantum state $|\psi^k\rangle$

where $k = 1, 2 \ldots \mathcal{N}$ & $\mathcal{N} \gg 1$.



$|\psi^k\rangle$ is the abstract Dirac notation.

e.g. Harmonic oscillators

$\langle x | \psi^k \rangle = \psi_k(x)$ wavefunction of k-th oscillator

e.g. gas of N atoms

$\langle \vec{x}_1, \vec{x}_2 \ldots \vec{x}_N | \psi^k \rangle \equiv \psi_k(x_1, x_2 \ldots x_N)$ many body wavefn of gas.

$$H|\psi^k\rangle = i\hbar \frac{\partial}{\partial t} |\psi^k\rangle$$

Typically we use a basis, e.g the eigenvalue basis $H|n\rangle = E_n|n\rangle$.

We then write

$$|\psi^k(t)\rangle = \sum_n |n\rangle a_n^k(t)$$

Now typically the basis is orthonormal $\langle m|n\rangle = \delta_{nm}$, so that

$$\boxed{\langle m|\psi^k(t)\rangle = \sum_n \langle m|n\rangle a_n^k(t) = a_n^k(t)}$$

$$\boxed{\langle m|\psi^k\rangle \equiv a_m^k(t)}$$

e.g Harmonic oscillators $|n\rangle$, $E_n = \hbar\omega(n+\frac{1}{2})$.

You may be more familiar with the idea of a wavefunction

$$\varphi_n(x) = \langle x|n\rangle \quad \text{one particle}$$

$$\varphi_n(\vec{x}_1, \vec{x}_2 .. \vec{x}_N) = \langle \vec{x}_1, \vec{x}_2 .. \vec{x}_N|n\rangle \quad \text{many particles.}$$

So

$$|\psi^k(t)\rangle = \sum_n |n\rangle\langle n|\psi^k(t)\rangle$$

Since this holds for all states $|\psi^k(t)\rangle$, it follows that

$$\boxed{1 = \sum_n |n\rangle\langle n|}$$ Completeness.

Now also

$$\langle\psi^k(t)|\psi^k(t)\rangle = 1$$ Normalization

so that

$$\sum_n \overbrace{\langle\psi^k(t)|n\rangle}^{[a_n^k(t)]^*}\overbrace{\langle n|\psi^k(t)\rangle}^{a_n^k(t)} = \sum |a_n^k(t)|^2 = 1$$

$|a_n^k|^2 =$ probability to be in state $|n\rangle$.

Time evolution of $a_n^k(t) = \langle n | \psi^k(t) \rangle$?

$$\boxed{H|\psi^k\rangle = i\hbar \frac{\partial}{\partial t} |\psi^k\rangle}$$

$$i\hbar \frac{\partial}{\partial t} a_n^k(t) = i\hbar \frac{\partial}{\partial t} \langle n | \psi^k(t) \rangle$$

$$= i\hbar \langle n | \frac{\partial}{\partial t} | \psi^k(t) \rangle$$

$$= \langle n | H | \psi^k(t) \rangle$$

$$= \sum_m \overbrace{\langle n | H | m \rangle}^{H_{nm}} \overbrace{\langle m | \psi^k(t) \rangle}^{a_m^k(t)}$$

$$= \sum_m H_{nm} a_m^k(t)$$

$$\boxed{i\hbar \dot{a}_n^k(t) = \sum_m H_{nm} a_m^k(t)}$$

$$\left(-i\hbar (\dot{a}_n^k)^* = \sum a_m^{k*} H_{nm}^* = \sum a_m^{k*} H_{mn}. \right)$$

$$H_{nm}^* = H_{mn}$$

Time evolution of density matrix

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

$$= \frac{1}{N}\sum_{k=1}^{N}\left[\left(\sum_e H_{me}\, a_e^k\right) a_n^{k\,*} - a_m^k \underbrace{\left(H_{ne}\, a_e^k\right)^*}_{a_e^{k\,*} H_{en}}\right]$$

$$= \sum_e \left(H_{me}\rho_{en} - \rho_{me}H_{en}\right)$$

$$= [H, \rho]_{mn}$$

$$\boxed{i\hbar\,\dot{\rho} = [\hat{H}, \hat{\rho}]} \qquad \dot{\rho} = \frac{1}{i\hbar}[\hat{H}, \hat{\rho}]$$

c.f classically

$$\dot{\rho} = [H, \rho]_{PB}$$

* Note how $[H, \rho]_{PB} \longrightarrow \frac{1}{i\hbar}[\hat{H}, \hat{\rho}]$.

Expectation values

$$\langle G \rangle = \sum \frac{1}{N}\langle \psi^k | \hat{G} | \psi^k \rangle$$

$\sum |n\rangle\langle n| = 1$

$\sum |m\rangle\langle m| = 1$

$$= \sum_{k=1}^{N} \frac{1}{N} \sum_{n,m} \langle \psi^k | n \rangle \langle n | G | m \rangle \langle m | \psi^k \rangle$$

$$= \sum_{n,m} \langle n | G | m \rangle \overbrace{\sum_k \langle m | \psi^k \rangle \frac{1}{N} \langle \psi^k | n \rangle}^{\rho_{mn}.}$$

Density matrix $\hat{\rho}$

$$\rho_{mn}(t) = \frac{1}{\mathcal{N}} \sum a_m^k(t) \left(a_n^k(t)\right)^*$$

$$= \sum_k \langle m | \psi^k(t) \rangle \frac{1}{\mathcal{N}} \langle \psi^k(t) | n \rangle$$

$$= \sum_k \langle m | \psi^k(t) \rangle p_k \langle \psi^k(t) | n \rangle$$

$$\boxed{\rho_{mn} = \langle m | \hat{\rho} | n \rangle}$$ Co-ordinate basis

$$\boxed{\hat{\rho} = \sum_k |\psi^k\rangle p_k \langle \psi^k|}$$ Co-ordinate independent

$$\sum \rho_{mm} = \frac{1}{\mathcal{N}} \sum_k \overbrace{\sum_m |a_m^k(t)|^2}^{1} = \underline{1}$$

$$\mathrm{Tr}\,\hat{\rho} = 1$$

$$\langle G \rangle = \sum_{m,n} G_{mn} \rho_{nm}$$

$$= \mathrm{Tr}[\hat{G} \hat{\rho}]$$

Taking $\hat{G} = 1$ $\quad \mathrm{Tr}\,\hat{\rho} = 1$ same as $\sum_k \sum_n \langle n | \psi^k \rangle \frac{1}{N} \langle \psi^k | n \rangle$

$$= \sum_k \frac{1}{N} = 1 .$$

5.2 STATISTICS OF ENSEMBLES

A Microcanonical.

We introduced at the begining, the concept of "equal à Priori probability", whereby each accessible quantum microstate is equally probable. Written in terms of our density matrix

$$\rho_{mn} = p_n \, \delta_{nm}$$

where the probability

$$p_n = \begin{cases} \dfrac{1}{\Gamma} & \text{accessible states} \quad \left(E \in \left(E_0 - \Delta/2, E_0 + \Delta/2\right)\right) \\ 0 & \text{otherwise} \end{cases}$$

- Note $S = k_B \ln \Gamma$, if there is a single ground-state $|\Psi_0\rangle$, then the third law of Thermodynamics is automatically satisfied.
- If we use quantum states, we will take care of indistinguishability.

- $\Gamma = 1$ is a "pure state" $\hat{\rho} = |\psi\rangle\langle\psi|$.

  In this case $\hat{\rho}^2 = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = |\psi\rangle\langle\psi| = \hat{\rho}$.

- $\Gamma > 1$ "a mixed state".

How could we have anticipated $\rho_{mn} = p_n \delta_{nm}$? The general expression is

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

If we assume equal à Priori probabilities. To obtain a diagonal density matrix, we need to supplement the postulate of equal à Priori probabilities with the postulate of Random à Priori Phases

$$\rho_{mn} = |a|^2 \left\langle e^{i(\theta_m^k - \theta_n^k)} \right\rangle = |a|^2 \delta_{nm}$$

So we need two postulates rather than one!

B CANONICAL ENSEMBLE

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

$$\rho_n = C e^{-\beta E_n}$$

where $$C = \frac{1}{\sum e^{-\beta E_n}} = \frac{1}{Q_N(\beta)}$$

$$\hat{\rho} = \sum |n\rangle \frac{1}{Q_N(\beta)} e^{-\beta E_n} \langle n|$$

$$= \sum_n e^{-\beta \hat{H}} \frac{|n\rangle\langle n|}{Q_N(\beta)} = \frac{e^{-\beta \hat{H}}}{Q_N(\beta)}$$

$$\boxed{\hat{\rho} = Q^{-1} e^{-\beta \hat{H}}}$$

$$\boxed{Q = \sum e^{-\beta E_n} = \mathrm{Tr}\, e^{-\beta \hat{H}}}$$

$$\boxed{\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta H}}}$$

Expectation values

$$\langle G \rangle = \mathrm{Tr}\, \rho \hat{G} = \frac{\mathrm{Tr}\, \hat{G} e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}$$

C. GRAND CANONICAL

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

where
$$p_n = \frac{e^{-\beta(E_n - \mu N_n)}}{Z}$$

and
$$Z = \sum_{\substack{n \in \text{Fock} \\ \text{Space}}} e^{-\beta(E_n - \mu N_n)}$$

$$\hat{\rho} = \sum |n\rangle \frac{e^{-\beta(E_n - \mu N_n)}}{Z} \langle n|$$

$$= \frac{e^{-\beta(\hat{H} - \mu\hat{N})}}{Z} \overbrace{\sum |n\rangle\langle n|}^{1}$$

$$Z = \sum_n \langle n| e^{-\beta(\hat{H} - \mu\hat{N})} |n\rangle$$

$$Z = \mathrm{Tr}\left[e^{-\beta(\hat{H} - \mu\hat{N})}\right]$$

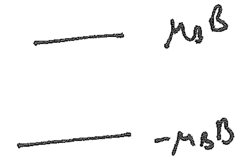
$$\boxed{\rho = \frac{e^{-\beta(\hat{H} - \mu\hat{N})}}{Z}}$$

$$F = -k_B T \ln Z$$

$$\boxed{F = -k_B T \ln \mathrm{Tr}\left[e^{-\beta(\hat{H} - \mu\hat{N})}\right]}$$

5.3 EXAMPLES OF APPLICATION OF DENSITY MATRIX.

A Electron in a field



$$\hat{H} = -\mu_B \left(\vec{\sigma}\cdot\vec{B}\right) = -\mu_B \sigma_z B_z$$

where

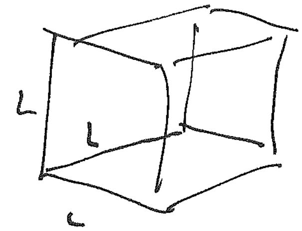
$$\vec{\sigma} = \left(\sigma_x, \sigma_y, \sigma_z\right) = \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & \\ & -1 \end{pmatrix} \right)$$

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

$$\langle \sigma_z \rangle = \mathrm{Tr}\, \rho\, \sigma_z = \frac{e^{\beta\mu_B B} - e^{-\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} = \tanh \beta\mu_B B$$

B. Particle in a box

$$H = \frac{p^2}{2m} \equiv \frac{-\hbar^2}{2m} \vec{\nabla}^2$$



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

$$\psi_E = \frac{1}{\sqrt{L^3}}\, e^{i\vec{k}\cdot\vec{r}} \qquad E = \frac{\hbar^2 k^2}{2m} \qquad \vec{k} = \frac{2\pi}{L}\left(l, m, n\right) = \frac{2\pi}{L}\hat{n}$$

$$\sum_{\vec{p}} = \sum_{l,m,n} = \left(\frac{L}{2\pi\hbar}\right)^3 \int d^3p. \qquad \Delta p = \frac{2\pi\hbar}{L} = \frac{h}{L}$$

Density matrix in momentum space

$$\Omega_1 = \sum_n e^{-\beta\epsilon(k_n)} \approx L^3 \int \frac{d^3p}{h^3}\, e^{-\beta(p^2/2m)}$$

$$= L^3 \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\Omega_1}$$

$$\langle p|\hat{\rho}|p'\rangle = \delta_{pp'} \frac{e^{-\beta p^2/2m}}{\Omega_1} \qquad \delta_{\hat{p}\hat{p}'} = \delta_{\hat{n},\hat{n}'}$$

$$\langle \vec{x}|\hat{\rho}|\vec{x}'\rangle = \frac{1}{\Lambda}\sum_{p,p'} \langle \vec{x}|p\rangle\langle \vec{p}|\hat{\rho}|p'\rangle\langle p'|x'\rangle$$

$$= \frac{1}{\Lambda}\sum_{\vec{p}} \frac{\langle x|p\rangle\langle p|x'\rangle\, e^{-\beta p^2/2m}}{\Omega_1} \qquad \vec{p} = \hbar k$$

$$= \frac{L^3}{\Lambda}\int \frac{d^3p}{h^3}\, \frac{e^{i\vec{p}(\vec{x}-x')/\hbar}}{L^3}\, e^{-\beta(p^2/2m)}$$

$$= \frac{1}{\Lambda}\left(\int \frac{dp_x}{h} \exp\left(-\frac{\beta p_x^2}{2m} + \frac{i p_x(x-x')}{\hbar}\right)\right)\left(\int\frac{dp_y}{h}\cdots\right)\left[\int \frac{dp_z}{h}\cdots\right]$$

$$-\frac{\beta}{2m}\left(p_x - i\frac{(x-x')m}{\hbar\beta}\right)^2 - \frac{\beta}{2m}\frac{(x-x')^2 m^2}{\hbar^2\beta^2}$$

$$= \frac{1}{\Omega_1}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \exp\left[-\frac{m k_B T\,(\vec{x}-\vec{x}')^2}{2\hbar^2}\right]$$

$$= \frac{1}{L^3} \exp\left[-\frac{m k_B T\,(\vec{x}-\vec{x}')^2}{2\hbar^2}\right]$$

$$= \frac{1}{V} \exp\left[-\frac{(x-x')^2}{2\tilde{\lambda}_T^2}\right] \qquad \tilde{\lambda}_T^2 = \left(\frac{\hbar^2}{m k_B T.}\right)$$

$$= \frac{h^2}{(2\pi)^2 m k_B T} = \frac{\lambda_T^2}{2\pi}$$

To calculate

$$\langle H\rangle = Tr\,(H\hat{\rho}) = \sum \langle p|\,H\rho\,|p\rangle$$

$$= \frac{\sum_p \left(\frac{p^2}{2m}\right) \exp\left[-\frac{\beta p^2}{2m}\right]}{\sum \exp\left[-\frac{\beta p^2}{2m}\right]}$$

$$= -\frac{\partial}{\partial\beta} \ln \sum_p \exp\left[-\frac{\beta p^2}{2m}\right]$$

$$= -\frac{\partial}{\partial\beta} \ln\left(\frac{2\pi k_B T m}{h^2}\right)^{3/2} = \frac{3}{2} k_B T.$$

HARMONIC OSCILLATOR

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2$$

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

$$\rho_{n,n'} = \langle n | \hat{\rho} | n' \rangle = \frac{e^{-\beta E_n}}{\Omega} \delta_{nn'}$$

$$\Omega = \sum e^{-\beta\hbar\omega(n+\frac{1}{2})} = \frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}$$

$$\langle x | e^{-\beta H} | x' \rangle = \sum \varphi_n(x)\, \varphi_n(x')\, e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

Detailed evaluation (tubo)

$$\langle x | e^{-\beta H} | x' \rangle = \sqrt{\frac{m\omega}{2\pi\hbar \cosh \beta\hbar\omega}} \exp\left[-\frac{m\omega}{4\hbar} \left\{ (x+x')^2 \tanh\frac{\beta\hbar\omega}{2} + (x-x')^2 \coth\frac{\beta\hbar\omega}{2} \right\} \right]$$

$$\langle x | \rho | x \rangle = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}$$

$$\sigma^2 = \frac{\hbar}{2m\omega \tanh\left(\frac{\beta\hbar\omega}{2}\right)} = \frac{\hbar}{m\omega}\left(\underbrace{\frac{1}{2}}_{\text{zero point}} + \overbrace{\frac{1}{e^{\beta\hbar\omega}-1}}^{\text{THERMAL}} \right) \longrightarrow \frac{k_B T}{m\omega^2}$$

$k_B T \gg \hbar\omega$.

INDISTINGUISHABLE PARTICLES

$$H = \sum_{i=1}^{N} H_0(q_i, p_i) + \text{interaction}$$

$$\hat{H} = \sum \left[-\frac{\hbar^2 \nabla_i^2}{2m} + V(x_i) \right] + \sum_{i<j} U(x_i - x_j)$$

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

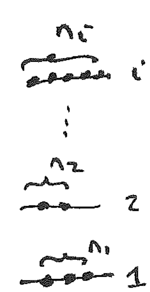
Without interactions, can decompose $\psi(q_i)$ in one particle wavefunctions.

$$\psi_E(q) = \prod_{i=1}^{N} u_{\epsilon_i}(q_i) \qquad \hat{H}_i u_i = E_i u_i$$

Let

$$E = \sum \epsilon_i$$

In general if we have n_i particles in state i, then



$$\sum n_i = N \qquad \sum n_i \epsilon_i = E.$$

and

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

"Boltzmanian" wavefunction.

Now if we permute the particles

$$(1, 2 \ldots N) \longrightarrow (P_1, P_2 \ldots P_N)$$

then the wavefunction changes

$$P\Psi_E(q) = \prod_{m=1}^{n_1} u_1(P_m) \prod_{m=n_1+1}^{n_1+n_2} u_2(P_m) \cdots \prod_{m=\sum_{i<r} n_i+1}^{\sum_{i=1}^{r} n_i} u_r(P_m) \cdots$$

but the energies are <u>unchanged</u>. $[P, H] = 0$

$$W_q[\{n_r\}] = \frac{N!}{n_1! \ldots n_r!}$$ supposedly distinct microstates.

Quantum mechanically we must regard these permuted states as indistinguishable.

$$W_q[\{n_r\}] = 1$$

i.e $$Z = \sum_{\{n_r\}} e^{-\beta[E_i - \mu N_i]} \times \overset{\overset{1}{\shortparallel}}{W_q}[\{n_r\}]$$

Now since $[P, H] = 0$ we can simultaneously diagonalize

H wit respect to all permutations of particle.

$$P = \prod_{\text{pairwise permutations}} P_{i_1 i_2}$$

$$P_{i_1 i_2}\Psi = \pm \Psi \qquad \text{since} \quad P_{i_1 i_2}^2 \Psi = \Psi$$

Since particle i_2 is no different from particle j, we expect to have the same permutation eigenvalue for all particles of the same type

Bosons

$$P\Psi = \Psi \qquad P_{i,j}\Psi = \Psi$$

Fermions

$$P\Psi = \begin{cases} +\Psi & \text{even \# permutat} \\ -\Psi & \text{odd \# permutation} \end{cases}$$

$$P_{ij}\Psi = -\Psi \qquad \text{pairwise permutation.}$$

Bosons

$$\psi_s(q) = \# \sum_P P\, \psi_{Boltz}(q) = \begin{vmatrix} u_1(1) & & u_1(N) \\ \vdots & & \\ u_N(1) & & u_N(N) \end{vmatrix}_+$$

Fermions

$$\psi_A(q) = \# \sum_P (-1)^p P\, \psi_B(q)$$

$p = \#$ pairwise permutations in P.

$$\psi_A(q) = \# \begin{vmatrix} u_i(1) & u_i(2) & \cdots & u_i(N) \\ \vdots & & & \vdots \\ u_e(1) & \cdots & & u_e(N) \end{vmatrix} \leftarrow \text{determinant.}$$

$\psi_A = 0$ if two rows are the same

$\therefore$ no two particles in same state

$\equiv$ PAULI EXCLUSION PRINCIPLE

So

$$W_{FD}[\{n_i\}] = \begin{cases} 1 & \sum n_i^2 = N \\ 0 & \text{otherwise} \end{cases}$$

$$W_{BE}[\{n_i\}] = 1 \quad \text{all states.}$$

$$W_{FD}[\{n_i\}] = \begin{cases} 1 & \sum n_i = N \\ 0 & \text{otherwise} \end{cases}$$

$$W_B[\{n_i\}] = 1 \qquad n_i = 0, 1, 2 \ldots$$

<u>Density Matrix</u>

$$\langle x_1 \ldots x_N | \hat{\rho} | x_1' \ldots x_N' \rangle = \frac{1}{Q_N(\beta)} \langle x_1 \ldots x_N | e^{-\beta H} | x_1' \ldots x_N' \rangle$$

$$x_1 \equiv 1 \quad x_2 \equiv 2 \quad \ldots \quad x_N \equiv N$$

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

$$= \sum_E \Psi_E(1, \ldots N) \Psi_E^*(1' \ldots N') e^{-\beta E}.$$

$$\left. \begin{aligned} E &= \sum_{j=1}^{N} \frac{\hbar^2}{2m} k_j^2 \\ u_k(x) &= \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot \vec{x}} \end{aligned} \right\} \qquad \vec{k} = \frac{2\pi}{L} (n_x, n_y, n_z) = \frac{2\pi}{L} \vec{n}$$

e.g. Two particles in a box

$$\psi_{(q)} = \frac{1}{\sqrt{2!}} \frac{1}{V} \begin{vmatrix} e^{i\vec{k}_1 \cdot \vec{x}_1} & e^{ik_1 x_2} \\ e^{i\vec{k}_2 \cdot x_1} & e^{i\vec{k}_2 \cdot \vec{x}_2} \end{vmatrix}_{\pm}$$

$$= \frac{1}{\sqrt{2!}} \frac{1}{V} \left(e^{i\vec{k}_1 \vec{x}_1 + \vec{k}_2 x_2} \pm e^{i\vec{k}_1 \vec{x}_2 + \vec{k}_2 \vec{x}_1} \right)$$

<u>Density matrix</u>

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}$$ CANONICAL ENSEMBLE

$|\{n_i\}\rangle$ occupation # basis

$$\langle \{n_i\} | \hat{\rho} | \{n_i\} \rangle = \frac{1}{\Omega_N} e^{-\beta \sum \epsilon_j n_j}$$

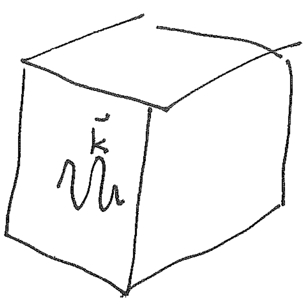
What about real space?

$$\langle x_1 \ldots x_N | \hat{\rho} | x_1' \ldots x_N' \rangle = \frac{1}{Q_N(\beta)} \langle x_1 \ldots x_N | e^{-\beta H} | x_1' \ldots x_N' \rangle$$

$x_1 \equiv 1, \; x_2 \equiv 2, \; \ldots \; x_N \equiv N$

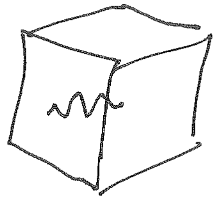
$$\langle 1, 2 \ldots N | e^{-\beta H} | 1, 2 \ldots N \rangle = \sum_E e^{-\beta E} \langle 1, \ldots N | \psi_E \rangle \langle \psi_E | 1' \ldots N' \rangle$$

Free particles in a box



$$\left.\begin{aligned} E &= \sum_{j=1}^{N} \frac{\hbar^2 k_j^2}{2m} \\ u_k(x) &= \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot \vec{x}} \end{aligned}\right\} \quad \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$$

e.g <u>one particle</u> !



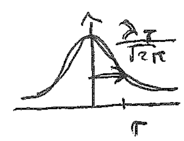
$$\langle \vec{x} | e^{-\beta u} | \vec{x}' \rangle = \sum_{\vec{k}} \langle x | \vec{k} \rangle \langle \vec{k} | x' \rangle \, e^{-\beta \epsilon_{\vec{k}}}$$

$$= \int \frac{d^3k}{(2\pi)^3} \, e^{i(\vec{k})\cdot(\vec{x}-\vec{x}')} \, e^{-\frac{\beta \hbar^2}{2m} k^2}$$

$$= \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \exp\left[-\frac{1}{2} \frac{(x-x')^2 m}{\beta \hbar^2} \right]$$

Recall $\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$ $\qquad \lambda_T^2 = \frac{\hbar^2 2\pi}{m k_B T} = \frac{2\pi \beta \hbar^2}{m}$

$$\langle x | e^{-\beta \hat{u}} | x' \rangle = \frac{1}{\lambda_T^3} \exp\left[-\frac{\pi}{\lambda_T^2} (x-x')^2 \right] = f_{xx'}$$



$$Z = \int \frac{d^3x}{\lambda_T^3} = \frac{V}{\lambda_T^3} \quad ✓$$

Correlation length $= \frac{\lambda_T}{\sqrt{2\pi}}$

$$\boxed{\langle x | \rho | x' \rangle = \frac{1}{V} e^{-\frac{\pi}{\lambda_T^2}(x-x')^2}}$$

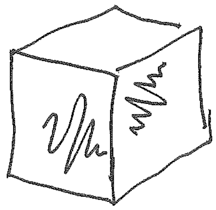
Confirm: $\left\langle \frac{p^2}{2m} \right\rangle = \frac{3 k_B T}{2}$ $\qquad \frac{p^2}{2m} = \left(\frac{\hbar^2}{2m} - \nabla^2 \right)$ $\cdot$ $\boxed{\int d^3x \, d^3x' \langle x | \frac{p^2}{2m} | x' \rangle \rho_{x'x}}$

$$\left\langle \frac{p^2}{2m} \right\rangle = \int d^3x'\, d^3x \quad \delta^3(x-x') \; -\frac{\hbar^2}{2m} \nabla_{x'}^2 \; \frac{1}{V} \; e^{-\frac{\pi}{\lambda_T^2}(x-x')^2}$$

$$= \frac{1}{V} \int d^3x\, d^3x' \;\; \delta^3(x-x') \; \frac{\hbar^2}{2m} \left(3\, \frac{2\pi}{\lambda_T^2} - \left(\frac{2\pi}{\lambda_T^2}\right)^2 (x-x')^2 \right) e^{-\frac{\pi}{\lambda_T^2}(x-x')^2}$$

$$= 3 \int \frac{d^3x}{V} \;\; \frac{\hbar^2}{2m} \left(\frac{2\pi}{\lambda_T^2}\right) \quad = \quad \frac{3}{2} k_B T \;\checkmark$$

Two particles



$$\langle 1,2|e^{-\beta H}|1',2'\rangle = \frac{1}{2!}\int \frac{d^3k_1}{(2\pi)^3}\frac{d^3k_2}{(2\pi)^3}\, e^{-\beta(\epsilon_1+\epsilon_2)}$$

$$\times \underbrace{\begin{vmatrix} e^{+ik_1x_1} & e^{+ik_1x_2} \\ e^{+ik_2x_1} & e^{+ik_2x_2} \end{vmatrix}^{*} \begin{vmatrix} e^{ik_1x_1'} & e^{ik_1x_2'} \\ e^{ik_1x_1'} & e^{ik_2x_2'} \end{vmatrix}^{*}}$$

$$\text{Integrand} = \sum_{P,P'} (-1)^{P+P'}\, e^{ik_1(x_{P_1}-x_{P_1'}')}\, e^{ik_2(x_{P_2}-x_{P_2'}')}\, e^{-\beta(\epsilon_1+\epsilon_2)}$$

$$= \sum_{P,P'} (-1)^{P+P'}\, e^{ik_{P_1'}(x_{P_1}-x_1')}\, e^{ik_{P_2'}(x_{P_2}-x_2')}\, e^{-\beta(\epsilon_1+\epsilon_2)}$$

$$\tilde{P} \doteq P, P'$$

$$= 2!\sum (\pm 1)^{\tilde{P}'}\, e^{ik_1(x_{\tilde{P}_1}-x_1')}\, e^{ik_2(\tilde{x}_{P_2}-x_2')}$$

$$\langle 1,2|e^{-\beta H}|1',2'\rangle = \sum (-1)^P f(P1-1')\, f(P2-2')$$

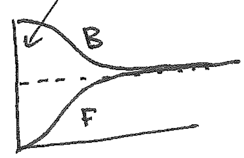
$$= f(1-1')f(2-2') \pm f(2-1')f(1-2')$$

$$\langle x_1, x_2 | \hat{\rho} | x_1' x_2' \rangle$$

$$= \frac{1}{(\lambda_T^3)^2 \Omega_2} \left[e^{-\frac{\pi}{\lambda_T^2}\left[(1-1')^2+(2-2')^2\right]} - e^{-\pi/\lambda_T^2\left[(1-2')^2+(2-1')^2\right]} \right]$$

$$\langle x_1, x_2 | \hat{\rho} | x_1, x_2 \rangle = \frac{1}{(\lambda_T^3)^2 \Omega_2} \left[1 \pm e^{-2\pi/\lambda_T^2 (x_1 - x_2)^2} \right]$$

correlation hole/bump.



$\rho(x_1 - x_2)$

Bosons like to congregate!

Fermions avoid!

$$\Omega_2 = \int \frac{d^3x_1\, d^3x_2}{(\lambda_T)^6} \left(1 \pm e^{-2\pi/\lambda_T^2 (x_1 - x_2)^2} \right)$$

$$= \frac{V^2}{\lambda_T^6} \pm \frac{8V}{\lambda_T^3} = \frac{V^2}{\lambda_T^6}\left(1 \pm 8\frac{\lambda_T^3}{V}\right)$$

$$\boxed{\langle x_1, x_2 | \hat{\rho} | x_1, x_2 \rangle = \frac{1}{V^2\left(1 \pm 8\left(\frac{\lambda_T^3}{V}\right)\right)} \left[1 \pm e^{-2\pi/\lambda_T^2 (x_1 - x_2)^2} \right]}$$

$$V_{eff}(r_1 - r_2) = -k_B T \ln\left[1 \pm e^{-\frac{2\pi}{\lambda_T^2}(r_1 - r_2)^2} \right]$$

Uhlenbeck + Gropper 1932.

Generalization to N fermions / bosons.

$$\langle 1,2..N|\rho|1,2..N'\rangle = \frac{1}{N!}\sum_{\{k\}}\sum_{P,P'} \delta^P \delta^{P'} \prod u_1(P_1)\cdots u_N(P_N) \times \prod u_1^*(P_1')\cdots u_N^*(P_N') \; e^{-\sum \epsilon_j}$$

$$= \frac{1}{N!}\sum_k \sum_{P,P'} \delta^{P+P'} \prod u_{P_1'}(P_1) u^*_{P_1'}(1) \cdots u_{P_N'}(P_N) u^*_{P_N'}(N) \; e^{-\sum \epsilon_j}$$

$$= \sum_{k,\tilde{P}} \delta^{\tilde{P}} \prod u_j(\tilde{P}_j) u_j^*(j) e^{-\sum \epsilon_j}$$

$$= \sum_{\tilde{P}} (\pm 1)^{\tilde{P}} \prod_j f(\tilde{P}_j - j)$$

$$\langle 1,..N|\hat{\rho}|1...N'\rangle = \frac{1}{\Omega_N}\sum_P (\pm 1)^P \prod f(\tilde{P}_j - j)$$

$$f(i-j) = \frac{1}{\lambda^3} e^{-\frac{\pi}{\lambda_T^3}(\vec{x}_i - \vec{x}_j)^2} \qquad \tilde{f}_{ij} = e^{-\frac{\pi}{\lambda_T}(x_i - x_j)^2}$$

$$\langle 1,...N|\hat{\rho}|1...N\rangle = \frac{1}{VN}\left(1 \pm \sum_{i-j} \tilde{f}_{ij}\tilde{f}_{ji} + \sum_{i<j<k} \tilde{f}_{ij}\tilde{f}_{jk}\tilde{f}_{ki} + \ldots\right)$$