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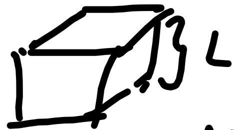
Density matrix:

Free particle in a box: m,



$V = L^3$

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

PBC

$$\phi_E(\bar{r}) = \frac{1}{L^{3/2}} e^{i\bar{k}\cdot\bar{r}} \equiv |E\rangle$$

$$E = \frac{\hbar^2 k^2}{2m} \qquad \bar{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$$

$n_i = 0, \pm 1, \pm 2, \ldots$

Let's work in the canonical formalism assuming that we know β (we also know V and $N=1$).

We want to evaluate $\hat{\rho}$ in the coordinate basis then
$$\hat{\rho} = \frac{\langle r | e^{-\beta \hat{H}} | r' \rangle}{\mathrm{tr}\, e^{-\beta \hat{H}}}$$

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

$$= \sum_E e^{-\beta E} \phi_E(\bar{r}) \phi^*_E(\bar{r}') =$$

$$= \sum_k e^{-\beta \frac{\hbar^2 k^2}{2m}} \frac{1}{L^3} e^{i \bar{k} \cdot \bar{r}} e^{-i \bar{k} \cdot \bar{r}'} =$$

$$= \frac{1}{V}\sum_k e^{-\beta\frac{\hbar^2 k^2}{2m}} e^{i\bar{k}\cdot(\bar{r}-\bar{r}')} \cong$$

$\Delta k \equiv dk$ (very small)

$$\simeq \frac{1}{(2\pi)^3}\int e^{-\beta\frac{\hbar^2k^2}{2m}+i\bar{k}\cdot(\bar{r}-\bar{r}')} d^3k =$$

$$k^2 = k_x^2 + k_y^2 + k_z^2$$

$$\bar{k}\cdot(\bar{r}-\bar{r}') = k_x(x-x') + k_y(y-y') + k_z(z-z')$$

$$e^{-\beta\frac{\hbar^2 k_i^2}{2m} + i k_i (x_i - x_i')} =$$

$$= e^{-\beta\frac{\hbar^2 k_i^2}{2m}}\left(\cos k_i(x_i-x_i') + i \sin k_i(x_i - x_i')\right)$$

at the end of the day we have 3 identical factors of the form

$$\int e^{-\beta\frac{\hbar^2 k_i^2}{2m}} \cos k_i(x_i - x_i')\, dk_i = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2} e^{-\frac{m(x-x')^2}{2\beta\hbar^2}}$$

$$= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} e^{-\frac{m}{2\beta\hbar^2}|\bar{r}-\bar{r}'|^2} = \frac{e^{-\frac{m}{2\beta\hbar^2}|\bar{r}-\bar{r}'|^2}}{\lambda^3}$$

where $\lambda = \dfrac{h}{\sqrt{2\pi m k T}}$ de Broglie wavelength

$$[\lambda] = m$$

Now let's evaluate

$$Tr\ e^{-\beta\hat{H}} = \int \langle r | e^{-\beta\hat{H}} | r \rangle d^3 r$$

$$= \int \frac{1}{\lambda^3} d^3 r = \frac{V}{\lambda^3} \equiv Z_1(\beta)$$

Then

$$\hat{\rho} = \frac{\langle r | e^{-\beta \hat{H}} | r' \rangle}{\mathrm{tr}\, e^{-\beta \hat{H}}} = \frac{1}{V} e^{-\frac{m}{2\beta\hbar^2} |\bar{r} - \bar{r}'|^2}$$

we see that $\rho_{rr'} = \rho_{r'r}$ symmetric matrix.

We see that

$$\rho_{rr} = \frac{1}{V} \quad \forall r$$ (uniform density).

Now let's calculate $\langle H \rangle = U$ (average energy)

$$\langle E\rangle = U = \langle \hat{H}\rangle = \mathrm{Tr}(\hat{H}\hat{\rho}) =$$

$$= -\frac{\hbar^2}{2mV}\int \left\{ \nabla^2 e^{-\frac{m}{2\beta\hbar^2}|\vec{r}-\vec{r}\,'|^2} \right|_{r=r'} d^3r =$$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 \qquad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$= \cancel{-}\frac{\cancel{\hbar^2}}{2\cancel{m}V}\int \sum_{i=1}^{3} \frac{\partial}{\partial x_i}\left[\cancel{-}\frac{\cancel{2}\cancel{m}(x_i - x_i')}{\cancel{2}\beta\cancel{\hbar^2}} e^{-\frac{m}{2\beta\hbar^2}[(x-x')^2+(y-y')^2+(z-z')^2]}\right]_{r=r'} d^3r$$

$$= \frac{1}{2V\beta}\int \sum_{i=1}^{3} \frac{\partial}{\partial x_i}(x_i - x_i')\, e^{-\frac{m}{2\beta\hbar^2}[(x-x')^2+(y-y')^2+(z-z')^2]}\Big|_{r=r'} d^3r =$$

$$= \frac{1}{2V\beta}\int \underbrace{\sum_{i=1}^{3}}_{3}\Big[1 - \underbrace{\frac{2(x_i - x_i')^2 m}{2\beta\hbar^2}}_{0 \text{ for } x=x'}\Big)\underbrace{e^{-\frac{m}{2\beta\hbar^2}\overbrace{|\vec{r}-\vec{r}\,'|^2}^{0}}}_{1}\Big|_{r=r'} d^3r \Rightarrow$$

Then

$$\langle \epsilon \rangle = \frac{3\cancel{N}}{2\cancel{N}\beta} = \frac{3}{2}kT$$

N indistinguishable free particles: (non-interacting)

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

non-interacting

single particle

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

energy representation

Notice that

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

with

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

and

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

We need to specify the distribution $\{n_i\}$ of particles with energy ε_i in the stationary state.

$$\sum_i n_i = N \quad \text{and} \quad \sum_i n_i \varepsilon_i = E$$

$$\therefore \quad \psi_E(q) = \underbrace{\prod_{m=1}^{n_1} u_1(m)}_{} \prod_{m=n_1+1}^{n_1+n_2} u_2(m) \cdots\cdots \qquad (1)$$

takes into account the n_i particles with energy ε_i

Boltzmannian function

But what happens if we permute the coordinates of the N particles? $(1, 2, \ldots N) \longrightarrow (P1, P2, \ldots, PN)$?

we will get

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

There are $\dfrac{N!}{n_1!\, n_2! \dots}$ permutations, but

if the particles are identical all these permuted states represent a single microstate.
We see that this is an overcounting that occurs in classical mechanics. Gibbs corrected for $N!$ but he ignored the $n_i!$
Correct for ideal gas where $n_i = 0$ or 1 at most.

In quantum mechanics we should get that

$W_q\{n_i\} = 1$ all permutations correspond to the same microstate.

To do this we will consider linear combinations of all the permutations and we will fix the Boltzmannian function.

The combinations should satisfy that

$|P\psi|^2 = |\psi|^2 \Rightarrow P\psi = e^{-i\phi}\psi$

if $\phi = 0 \Rightarrow$ bosons

$\phi = \pi \Rightarrow$ fermions

$\phi \neq 0, \pi \Rightarrow$ anyons (only in 2D)

If we concentrate in $\phi = 0$ or π we get that

$$P\psi = \begin{cases} -\psi & \forall \text{ odd permutation} \\ \psi & \forall \text{ even permutation} \end{cases} \Bigg\}$$ antisymmetric ψ function.

$$P\psi = \psi \quad \forall P$$ symmetric ψ function.

Example with $N = 3$:

$P_0 \, \psi_E(q) = u_1(q_1)\, u_2(q_2)\, u_3(q_3)$ even

$P_1 \, \psi_E(q) = u_1(q_2)\, u_2(q_1)\, u_3(q_3)$ odd

$P_2 \, \psi_E(q) = u_1(q_3)\, u_2(q_2)\, u_3(q_1)$ odd

$P_3 \, \psi_E(q) = u_1(q_1)\, u_2(q_3)\, u_3(q_2)$ odd

$P_4\, \psi_E(q) = u_1(q_2)\, u_2(q_3)\, u_3(q_1)$ even

$P_5\, \psi_E(q) = u_1(q_3)\, u_2(q_1)\, u_3(q_2)$ even

$$\psi_S(q) = C \sum_P P\, \psi_{Boltz}(q)$$

$$\psi_A(q) = C' \sum_P \delta_P\, P\, \psi_{Boltz}(q)$$

δ_P: 1 for even P, −1 for odd P

$123 \to (2,3,1)$ even

$123 \to (1,3,2)$ odd

For non-interacting system $\psi_A(q)$ is obtained using a Slater determinant given by:

$$\psi_A(q) = C' \begin{vmatrix} u_1(1) & u_1(2) & \cdots & u_1(N) \\ u_2(1) & u_2(2) & \cdots & u_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ u_N(1) & u_N(2) & \cdots & u_N(N) \end{vmatrix}$$

Example: $(N=3)$

$$\psi_S(q) = C \sum_{P_\alpha=0}^{5} P_\alpha \left(u_1(q_1)\, u_2(q_2)\, u_3(q_3)\right)$$

$$\psi_A(q) = C' \begin{vmatrix} u_1(q_1) & u_1(q_2) & u_1(q_3) \\ u_2(q_1) & u_2(q_2) & u_2(q_3) \\ u_3(q_1) & u_3(q_2) & u_3(q_3) \end{vmatrix} = \overbrace{u_1(q_1)\, u_2(q_2)\, u_3(q_3)}^{P_0}$$

$$+ \underbrace{u_1(q_2)\, u_2(q_3)\, u_3(q_1)}_{P_4} + \underbrace{u_1(q_3)\, u_2(q_1)\, u_3(q_2)}_{P_5} -$$

$$-\underbrace{u_1(\xi_3)\,u_2(\xi_2)}_{P_2}u_3(\xi_1) - u_1(\xi_2)\underbrace{u_2(\xi_1)u_3(\xi_3)}_{P_1} -$$

$$-u_1(\xi_1)\underbrace{u_2(\xi_3)u_3(\xi_2)}_{P_3}$$

For ψ_A two particles cannot have the same coordinates because the term would not change sign under an odd permutation unless the term is 0. This is Pauli's exclusion principle for fermions. It is due to the antisymmetry of the wave function.

$$\therefore \quad W_{F.D}\{n_i\} = \begin{cases} 1 & \text{if } \sum_i n_i = N \\ 0 & \text{if } \sum_i n_i > N \end{cases}$$

true for $n_i = 0$ or 1

true for any $n_i > 1$.

and $W_{B.E}\{n_i\} = 1 \qquad n_i = 0, 1, 2, \ldots\ldots$

Notice for bosons ψ is symmetric and for fermions ψ is antisymmetric even if there are interactions.

However, you cannot use Slater determinant for interacting system.