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Last time: $V = L^3$

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

$\rho_{rr} = \frac{1}{V}$ uniform density.

Also:

$$E = \langle \hat{H} \rangle = \mathrm{Tr}(\hat{H}\hat{\rho}) = -\frac{\hbar^2}{2mV} \int \left. \left\{ \nabla_r^2\, e^{-\frac{m}{2\beta\hbar^2}|\bar{r}-\bar{r}'|^2} \right\} \right|_{r=r'} d^3r$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_r^2$$

$$|\bar{r} - \bar{r}'|^2 = [(x-x')^2 + (y-y')^2 + (z-z')^2]$$

$$\nabla_r^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Performing the calculations (you can do it also in spherical coordinates) you will find out

$$\bar{E} = \langle H \rangle = \frac{3kT}{2}$$

Indistinguishable particles (quantum mechanics):

N non interacting free particles (identical)

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

$\hat{H}_i \rightarrow$ single particle H.

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

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

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 a $\{n_i\}$ distribution of the N particles with energy ε_i in a stationary state.

Then we need that

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

$\therefore$

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

Boltzmannian wave function.

(indistinguishability is NOT considered)

$m \equiv q_m$

But if we permute the coordinates of the N particles what happens?

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

$$\begin{array}{ccc} q_1 & q_2 & q_3 \\ \bullet & \bullet & \bullet \\ 1 & 2 & 3 \end{array} \xrightarrow{P} \begin{array}{ccc} q_3 & q_2 & q_1 \\ \bullet & \bullet & \bullet \\ 1 & 2 & 3 \end{array}$$

Then

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

Each of this generate $\dfrac{N!}{n_1!\, n_2! \dots}$ microstates.

But since the physics did not change all of these permutations should be identified with one single microstate.

We need in quantum mechanics that

$W_q\{n_i\} = 1$ then we need to combine all the permutations to obtain the wave function of the microstate.

Combine the $N!$ permutations satisfying that

$|P\psi|^2 = |\psi|^2$ to conserve the probability.

$\therefore \quad P\psi = \psi \quad \forall \; P$ (symmetric combination)

or $P\psi = \begin{cases} -\psi & \forall \text{ odd permutations} \\ \psi & \forall \text{ even permutations} \end{cases}$ (antisymmetric combination).

Ir

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

$3! = 6$ possible equivalent functions

Also $P\psi = e^{i\phi}\psi$ possible but gives raise to particles called anyons that we will not study.

$\therefore$ $$\psi_S(\bar{q}) = C \sum_P P\psi_{Boltzm}(\bar{q})$$ $N!$ terms in each sum.

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

$\delta_P \to +1$ for even P (312) ← 123

$\to -1$ for odd permutations. (213)

$$\psi_A(\bar{q}) = C' \begin{vmatrix} u_i(1) & u_i(2) & \cdots & u_i(N) \\ u_j(1) & u_j(2) & \cdots & u_j(N) \\ \vdots & & \ddots & \vdots \\ u_e(1) & u_e(2) & \cdots & u_e(N) \end{vmatrix}$$

$u_i(1), u_j(2), \ldots, u_e(N)$ are the N Boltzmann functions.

In our example.

$$\psi_S(\xi) = C \sum_{P_i=0}^{5} P_i \left(u_1(\xi_1) u_2(\xi_2) u_3(\xi_3) \right)$$

$$\psi_A(\xi) = C' \begin{vmatrix} u_1(\xi_1) & u_1(\xi_2) & u_1(\xi_3) \\ u_2(\xi_1) & u_2(\xi_2) & u_2(\xi_3) \\ u_3(\xi_1) & u_3(\xi_2) & u_3(\xi_3) \end{vmatrix} = P_0(\ ) + P_4(\ ) +$$

$$+ P_5(\ ) - P_2(\ ) - P_1(\ ) - P_3(\xi)$$

You see that if $\xi_1 = \xi_2$ $\psi_A(\xi) = 0$

If 2 particles have the same quantum numbers (coordinates in this case) $\psi_A(\xi) = 0$ - This is Pauli's exclusion principle.

Particles with antisymmetric wave functions are called fermions. They obey Fermi-Dirac statistics and for them:

$$W_{F.D.}\{n_i\} = \begin{cases} 1 & \text{if } \sum_i n_i^2 = N \\ 0 & \text{if } \sum_i n_i^2 > N \end{cases}$$

this means that $\{n_i\} = 0$ or 1 for all i.

true if at least one i has $n_i \geq 2$.

Particles with symmetric wave functions are called bosons. They satisfy Bose-Einstein statistics and for them

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

Let's obtain $\hat{\rho}$ and Z_N for an ideal gas formed by N free undistinguishable particles.

Canonical : N, V, β

In coordinate space:

$$\langle \bar{r}_1, \bar{r}_2, \dots, \bar{r}_N | \hat{\rho} | r_1', \dots, r_N' \rangle = \frac{1}{Z_N(\beta)} \langle \bar{r}_1, \dots, \bar{r}_N | e^{-\beta \hat{H}} | r_1', \dots, r_N' \rangle$$

where

$$Z_N(\beta) = \mathrm{Tr}\, e^{-\beta \hat{H}} = \int \langle \bar{r}_1, \dots, \bar{r}_N | e^{-\beta H} | \bar{r}_1, \dots, \bar{r}_N \rangle \, d^{3N} r$$

Now let's $r_i \equiv i$ and $r_i' \equiv i'$

ψ_E : eigenfunction in energy representation.

and

$$\langle \bar{r}_1, \ldots \bar{r}_N | E \rangle = \psi_E(\bar{r})$$

$$\sum_E |E\rangle\langle E| = \mathbb{I}$$

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

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

But $$E = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2}{2m}(k_1^2 + k_2^2 + \ldots + k_N^2)$$

$$PBC \Rightarrow u_k(\bar{r}) = V^{-1/2} e^{i\bar{k}\cdot\bar{r}}$$

$$\bar{k} = \frac{2\pi}{V^{1/3}} \bar{n}$$

$$\bar{n} = (n_x, n_y, n_z)$$

$$n_\alpha = 0, \pm 1, \pm 2, \ldots$$

Now

$$\psi_k(1,\ldots,N) = \frac{1}{\sqrt{N!}} \sum_P \delta_P \, P\left[u_{k_1}(1) \cdots u_{k_N}(N)\right\} = |1,\ldots,N\rangle$$

$\delta_P \to 1$ for bosons

$\delta_P \to \pm 1$ for fermions

ψ_k: I can use k instead of E.

$$k^2 = k_1^2 + k_2^2 + \ldots + k_N^2$$

Notice that

$$P\{u_{k_i}(i)\} \equiv u_{P k_i}(i) = u_{k_i}(P_i)$$

they can be obtained by permuting q_i or k_i.

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

$$P_1 = u_1(q_2)\, u_2(q_1)\, u_3(q_3) \qquad q_1 \Leftrightarrow q_2$$

$$\overset{\shortparallel}{P}_{k_1} = u_2(q_1)\, u_1(q_2)\, u_3(q_3) \qquad k_1 \Longleftrightarrow k_2$$

$\therefore$

$$\psi_K(1,\ldots,N) = \frac{1}{\sqrt{N!}} \sum_P \delta_P \{u_{k_1}(P1)\ldots u_{k_N}(PN)\} \equiv$$

$$\equiv \frac{1}{\sqrt{N!}} \sum_P \delta_P \{u_{Pk_1}(1)\ldots u_{Pk_N}(N)\}$$

$\therefore$

$$\langle 1,\ldots,N|e^{-\beta\hat{H}}|1',\ldots,N'\rangle = \frac{1}{N!}\sum_K e^{-\beta\frac{\hbar^2K^2}{2m}}$$

$$\left[\sum_P \delta_P\{u_{k_1}(P1)\ldots u_{k_N}(PN)\}\right]\left[\sum_{\bar{P}} \delta_{\bar{P}}\{u^*_{\bar{P}k_1}(1')\ldots u^*_{\bar{P}k_N}(N')\}\right]$$

P and $\bar{P}$ are any of the $N!$ possible permutations.
K^2 and $\langle\psi\psi^*\rangle$ are independent of the permutations
since $P^2=1$, and K is unchanged under permutations.

Then $\sum_{K} \equiv \frac{1}{N!} \sum_{k_i}$ (independently).

Also since all the N-fold summations over $\bar{k}_i$ all the permutations $\bar{P}$ will contribute equally to the sum. Then we can consider only the term with $(\tilde{P}k_1 = k_1, \ldots \tilde{P}k_N = k_N)$ with $\delta_{\tilde{p}} = 1$ and include $N!$ to take into account the other $\tilde{P}$'s.

Then:

$$\langle 1, \ldots N | e^{-\beta H} | 1', \ldots N' \rangle = \frac{1}{N!} \sum_{k_1 \ldots k_N} e^{-\frac{\beta \hbar^2}{2m}(k_1^2 + \ldots + k_N^2)}$$

$$\left[\sum_{P} \delta_P \{ u_{k_1}(P1) u^*_{k_1}(1') \} \ldots \{ u_{k_N}(PN) u^*_{k_N}(N') \} \right]$$