Estatística quântica

Já vimos anteriormente desvios da estatística clássica através do congelamento de níveis que deixam de participar do teorema de equipartição de energia.
A partir de agora vamos estudar o papel da indistinguibilidade das partículas quânticas no desvio da estatística clássica.

Sabemos que o estado físico de N partículas é descrito por $\psi(x_1, x_2 \dots x_N)$ onde $x_i = \vec{x}_i, \sigma_i$

e que $|\psi(x_1 \dots x_i \dots x_j \dots x_N)|^2 = |\psi(x_1 \dots x_j \dots x_i \dots x_N)|^2$

$$\Rightarrow \psi(x_1 \dots x_i \dots x_j \dots x_N) = e^{i\varphi_{ij}} \psi(x_1 \dots x_j \dots x_i \dots x_N)$$

Trocando novamente $i \leftrightarrow j$

$$\psi(x_1 \dots x_i \dots x_j \dots x_N) = e^{2i\varphi_{ij}} \psi(x_1 \dots x_i \dots x_j \dots x_N)$$

$$\Rightarrow e^{2i\varphi_{ij}} = 1 \Rightarrow 2i\varphi_{ij} = 2n\pi \Rightarrow \varphi_{ij} = n\pi$$

onde $n = 0, 1 \Rightarrow e^{i\varphi_{ij}} = \pm 1 \begin{cases} +1 \rightarrow \text{bósons} \\ -1 \rightarrow \text{férmions} \end{cases}$

$$\psi(x_1 \dots x_i \dots x_j \dots x_N, t) = \sum_{E_1 \dots E_N} C(E_1 \dots E_i \dots E_j \dots E_N, t)\, \varphi_{E_1}(x_1) \dots \varphi_{E_i}(x_i) \dots \varphi_{E_j}(x_j)\, \varphi_{E_N}$$

Base: $\{ \varphi_{E_1}(x_1) \dots \varphi_{E_i}(x_i) \dots \varphi_{E_j}(x_j) \dots \varphi_{E_N}(x_N) \}$

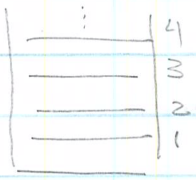
$\to$ auto estados de sistema não interagente.

$$\Rightarrow \psi(x_1 \dots x_j \dots x_i \dots x_N, t) = \pm \sum_{E_1 \dots E_N} C(E_1 \dots E_i \dots E_j \dots E_N, t)\, \varphi_{E_1}(x_1)\, \varphi_{E_i}(x_j) \dots \varphi_{E_j}(x_i) \dots \varphi_{E_N}(x_N)$$

$$= \pm \sum_{E_1 \dots E_N} C(E_1 \dots E_j \dots E_i \dots E_N, t)\, \varphi_{E_1}(x_1) \dots \varphi_{E_j}(x_j) \dots \varphi_{E_i}(x_i) \dots \varphi_{E_N}(x_N)$$

$$\Rightarrow C(E_1 \dots E_i \dots E_j \dots E_N) = \pm C(E_1 \dots E_j \dots E_i \dots E_N)$$

Bósons:



$$C(1123112334 \dots) = C(\underbrace{111\,1}_{n_1}\ \underbrace{2 \dots 2}_{n_2} \dots)$$

$$\Rightarrow \bar{C}(n_1 n_2 \dots n_\infty)$$

Como $\int |\psi|^2 dx_1 \dots dx_N = 1 \Rightarrow \sum_{E_1 \dots E_N} |C(E_1 \dots E_N)|^2 = 1$

$$\Rightarrow \sum_{n_1 \dots n_\infty} |\bar{C}(n_1 \dots n_\infty)|^2 \sum_{\substack{E_1 \dots E_N \\ (n_1 n_2 \dots n_\infty)}} 1 = 1$$

$$\Rightarrow \sum_{n_1 \dots n_\infty} |\bar{C}(n_1 \dots n_\infty)|^2 \frac{N!}{n_1!\, n_2! \dots n_\infty!} = 1$$

$\sum n_i = N$

$$f(n_1 \dots n_\infty) = \sqrt{\frac{N!}{n_1! \dots n_\infty!}}\ \bar{C}(n_1 \dots n_\infty)$$

$$\sum_{n_1 \dots n_\infty} |f|^2 = 1$$

$$\Rightarrow \psi(x_1 \dots x_N) = \sum_{E_1 \dots E_N} C(E_1 \dots E_N)\, \varphi_{E_1}(x_1) \dots \varphi_{E_N}(x_N)$$

$$= \sum_{n_1 \dots n_\infty} f(n_1 \dots n_\infty) \sqrt{\frac{n_1! \dots n_\infty!}{N!}} \sum_{\substack{E_1 \dots E_N \\ (n_1 \dots n_\infty)}} \varphi_{E_1}(x_1) \dots \varphi_{E_N}(x_N)$$

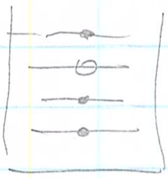
$$\phi_{n_1 n_2 \dots n_\infty}(x_1 \dots x_N) \equiv \sqrt{\frac{n_1! \dots n_\infty!}{N!}} \sum_{\substack{E_1 \dots E_N \\ (n_1 \dots n_\infty)}} \varphi_{E_1}(x_1) \dots \varphi_{E_N}(x_N)$$

Ex: $\phi_{2,1,0\dots 0}(x_1 x_2 x_3) = \frac{1}{\sqrt{3}} \{ \varphi_1(x_1)\varphi_1(x_2)\varphi_2(x_3) + \varphi_1(x_1)\varphi_2(x_2)\varphi_1(x_3) + \varphi_2(x_1)\varphi_1(x_2)\varphi_1(x_3) \}$

$\phi_{n_1 n_2 \dots n_\infty}(x_1 \dots x_N) \equiv \langle x_1 x_2 \dots x_N | n_1 n_2 \dots n_\infty \rangle$.

$|n_1 n_2 \dots n_\infty\rangle$ base no espaço de Fock.

Férmions:



$C(\dots E_i \dots E_j \dots) = - C(\dots E_j \dots E_i \dots)$

se $E_i = E_j \quad C = 0 \quad \Rightarrow \quad n_i = 0, 1$.

$\sum_{E_1 \dots E_N} |C(+\dots E_i \dots E_j \dots)|^2 = 1$

$\Rightarrow \quad \bar{C}(n_1 n_2 \dots n_\infty) \sum_{\substack{E_1 E_2 \dots \\ \{n_1 n_2 \dots\}}} 1 = \bar{C}(n_1 \dots n_\infty) N!$

$\bar{C}(n_1 \dots n_\infty) = C(E_1 < E_2 \dots) \; ; \; f(n_1 \dots n_\infty) = \sqrt{N!}\, \bar{C}(n_1 \dots n_\infty)$

$$\phi_{n_1 \dots n_\infty}(x_1 \dots x_N) = \frac{1}{\sqrt{N!}} \sum_{\substack{E_1 \dots E_N \\ (n_1 \dots n_\infty)}} \epsilon^{E_1 \dots E_N} \varphi_{E_1}(x_1) \dots \varphi_{E_N}(x_N)$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{E_1}(x_1) & \dots & \varphi_{E_1}(x_N) \\ \vdots & & \\ \varphi_{E_N}(x_1) & \dots & \varphi_{E_N}(x_N) \end{vmatrix} \Rightarrow \text{determinante de Slater}$$

$|n_1 \dots n_\infty\rangle \Rightarrow$ base no espaço de Fock.

Teorema do spin e estatística:

Bósons: spin inteiro: $0, 1, \dots$

Férmions: spin semi-inteiro $\frac{1}{2}, \frac{3}{2}, \dots$

$|\psi\rangle = \sum_{n_1 \dots n_\infty} f(n_1 \dots n_\infty, t) |n_1 \dots n_\infty\rangle \rightarrow$ geral!

Configurações de energia $r = \{n_1, n_2 \ldots n_\infty\} = \{n_\ell\}$

e $\{\epsilon_\ell\} = \{\epsilon_0, \epsilon_1 \ldots \epsilon_\infty\}$

$\Rightarrow E_r = E(\{n_\ell\})$

$$\mathrm{Tr} = \sum_r = \sum_{\{n_\ell\}}$$

Função de partição: $Z_N = \sum_r e^{-\beta E_r}$ (canônico)

$$= \sum_{\substack{\{n_\ell\} \\ \sum n_\ell = N}} e^{-\beta E\{n_\ell\}} = \sum_{\substack{\{n_\ell\} \\ \sum n_\ell = N}} \prod_{l=0}^{\infty} e^{-\beta n_\ell \epsilon_\ell}$$

Grau-canônico:

$$Z_G = \sum_{N=0}^{\infty} z^N Z_N(T,V) = \sum_{N=0}^{\infty} \sum_{\substack{\{n_\ell\} \\ \sum n_\ell = N}} \prod_{l=0}^{\infty} z^{n_\ell} e^{-\beta n_\ell \epsilon_\ell} \quad ; \quad z = e^{\beta\mu}.$$

$$\sum_{N=0}^{\infty} \sum_{\substack{\{n_\ell\} \\ \sum n_\ell = N}} = \sum_N \sum_{\{n_\ell\}} \delta_{N, \sum_\ell n_\ell} = \sum_{\{n_\ell\}}$$

$$\Rightarrow Z_G = \sum_{\{n_\ell\}} \prod_\ell \left(z e^{-\beta \epsilon_\ell}\right)^{n_\ell} = \prod_\ell \sum_{n_\ell} \left(z e^{-\beta\epsilon_\ell}\right)^{n_\ell}$$

Estatística de Fermi-Dirac: $n_\ell = 0$ ou 1

$$\Rightarrow Z_G = \prod_\ell \left(1 + z e^{-\beta\epsilon_\ell}\right)$$

Estatística de Bose-Einstein n_ℓ é qualquer.

$$\Rightarrow Z_G = \prod_\ell \frac{1}{1 - z e^{-\beta\epsilon_\ell}} \quad \text{se} \quad z e^{-\beta\epsilon_\ell} < 1$$

mas $z e^{-\beta\epsilon_\ell} = e^{(\mu - \epsilon_\ell)\beta} < 1 \Rightarrow \mu < \epsilon_\ell \quad \forall \ell \Rightarrow \mu < \epsilon_0$

Assim $Z_G = \prod_l \left(1 \pm z e^{-\beta\epsilon_\ell}\right)^{\pm 1}$; $\begin{cases} + \rightarrow \text{férmions} \\ - \rightarrow \text{bósons.} \end{cases}$

Mas $\Omega = -kT \ln Z_G$, e $\left.\frac{\partial \Omega}{\partial \mu}\right|_{T,V} = -N$

$$\Omega = -kT \ln Z_G = -kT \sum_l \ln\left(1 \pm z e^{-\beta \epsilon_l}\right)^{\pm 1}$$

$$\Rightarrow \quad N = kT \sum_l \frac{\partial}{\partial \mu} \ln\left(1 \pm z e^{-\beta \epsilon_l}\right)^{\pm 1}$$

$$= \pm kT \sum_l \frac{\partial z}{\partial \mu} \frac{\partial}{\partial z} \ln\left(1 \pm z e^{-\beta \epsilon_l}\right)$$

$$\frac{\partial z}{\partial \mu} = \beta e^{\mu \beta} \quad \Rightarrow \quad N = \pm \sum_l e^{\beta \mu} \frac{(\pm) e^{-\beta \epsilon_l}}{1 \pm z e^{-\beta \epsilon_l}}$$

$$N = \sum_l \frac{e^{\beta(\mu - \epsilon_l)}}{1 \pm e^{\beta(\mu - \epsilon_l)}} = \sum_l \frac{1}{e^{\beta(\epsilon_l - \mu)} \pm 1} = \sum_l n_l$$

$n_l \to$ n.º de ocupação médio

$$\begin{cases} (+) \text{ e } \forall \mu \text{ p/ férmions} \\ (-) \text{ e } \mu \leq \epsilon_0 \text{ p/ bósons.} \end{cases}$$

Limite clássico: Maxwell-Boltzmann.

Neste caso $\langle n_l \rangle_{FD} = \langle n_l \rangle_{BE} \Rightarrow z \ll 1$

e $\langle n_l \rangle_{MB} = e^{-\beta(\epsilon_l - \mu)}$

$$Z_G = e^{\ln \prod_l \left(1 \pm z e^{-\beta \epsilon_l}\right)^{\pm 1}} = e^{\pm \sum_l \ln\left(1 \pm z e^{-\beta \epsilon_l}\right)}$$

$$= e^{\sum_l z e^{-\beta \epsilon_l}} = e^{z \sum_l e^{-\beta \epsilon_l}} \quad \Rightarrow \quad N = -\frac{\partial \Omega}{\partial \mu} = kT \frac{\partial}{\partial \mu} \ln \Omega$$

$$= kT \frac{\partial z}{\partial \mu} \frac{\partial}{\partial z}\left(z \sum_l e^{-\beta \epsilon_l}\right) = \sum_l e^{-\beta(\epsilon_l - \mu)}$$

$$\Rightarrow \langle n_\ell \rangle_{MB} = e^{-\beta(\epsilon_\ell - \mu)}$$

Voltemos à Z_G: $\quad Z_G = e^{z \sum_\ell e^{-\beta \epsilon_\ell}}$

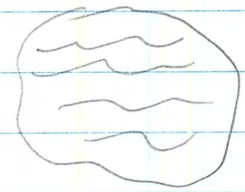
$$= \sum_{N=0}^{\infty} \frac{z^N}{N!} \left(\sum_\ell e^{-\beta \epsilon_\ell} \right)^N \qquad N = \sum_\ell n_\ell$$

$$\Rightarrow Z_N = \frac{\left(\sum_\ell e^{-\beta \epsilon_\ell} \right)^N}{N!} = \sum_{\{n_\ell\}} \frac{1}{n_0! n_1! \ldots n_\infty!} e^{-\beta \epsilon_0 n_0} \ldots e^{-\beta \epsilon_\infty n_\infty}$$

$\Rightarrow$ justificativa do $N!$ presente no caso clássico.

<u>Potencial químico e relatividade</u>

N.º de fótons é variável porque equilíbrio do gás a Temperatura T depende de emissão e absorção



$F(T, V, N)$ é mínimo p/ T = const V = const, mas... N ñ é constante

$$\Rightarrow dF = -S \underbrace{dT}_{0} - p \underbrace{dV}_{0} + \mu \, dN = 0$$

$$\Rightarrow \mu = \left. \frac{\partial F}{\partial N} \right|_{T,V} = 0 \; !$$

Se há lei de conservação: $e^{(+)} + e^{(-)} \rightarrow 2\gamma$

$N^{(-)} - N^{(+)} = N_0 \rightarrow$ fixo

$$F(T, V, N_0; N^{(-)}) = F(T, V; N^{(-)}, N^{(+)} = -N_0 + N^{(-)})$$

$$\Rightarrow \left. \frac{\partial F}{\partial N^{(-)}} \right|_{N_0} = \left. \frac{\partial F}{\partial N^{(-)}} \right|_{N^{(+)}} + \left. \frac{\partial F}{\partial N^{(+)}} \right|_{N^{(-)}} \frac{\partial N^{(+)}}{\partial N^{(-)}} = \mu^{(-)} + \mu^{(+)} = 0$$

$\Rightarrow \mu^{(+)} = -\mu^{(-)}$ ou $e^{(+)} + e^{(-)} \rightarrow 2\gamma$

$$\sum \nu_i \mu_i = 0 \Rightarrow \nu^{(+)} \mu^{(+)} + \nu^{(-)} \mu^{(-)} + \cancel{\nu^{(\gamma)} \mu^{\gamma}}^{\,0}$$

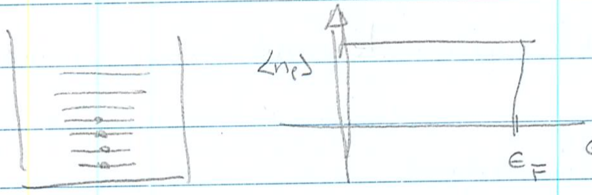
Energia relativística: $\epsilon_p = \sqrt{p^2c^2+m^2c^4}$

$$\langle n_p \rangle = \frac{1}{e^{\beta(\epsilon_p-\mu)}-1} \quad \text{e} \quad \mu < \epsilon_0 = mc^2 \, !$$

Gás ideal de Férmions:

. A $T=0$ E é mínima.

$\Rightarrow$



$$n_p = \begin{cases} 1 & \text{se} \quad \epsilon_p < \epsilon_F \\ 0 & \text{se} \quad \epsilon_p > \epsilon_F \end{cases} \Rightarrow n_p = \Theta(\epsilon_F - \epsilon_p)$$

De fato, $\lim_{\beta \to \infty} \frac{1}{e^{\beta(\epsilon_p-\mu)}+1} = \Theta(\mu - \epsilon_p)$

$\Rightarrow \mu(T=0) = \epsilon_F$

Mas $\mu(T=0) = \frac{\partial E}{\partial N} = E(N) - E(N-1) = \epsilon_F$

Se o gás tem massa m e spin s (semi-inteiro) $\{\vec{p}, s_z\}$ $\quad g = (2s+1)$

$$\sum_1 = \sum_{\vec{p}, s_z} = g \frac{V}{h^3} \int d^3p \quad \text{pois} \quad \sum_{\vec{k}} \to \frac{V}{(2\pi)^3} \int d^3k$$

$$N = g \frac{V}{h^3} \int_{p \leq p_F} d^3p = g \frac{V}{h^3} \int_0^{p_F} 4\pi p^2 \, dp = g \frac{V}{h^3} \frac{4\pi}{3} p_F^3$$