Mecânica Estatística Quântica

Gás Ideal Quântico

→ $\psi(q_1, \cdots, q_i, q_j, \cdots, q_N) = \pm\, \psi(q_1, \cdots, q_j, q_i, \cdots, q_N)$ $\begin{cases} + \rightarrow \text{bósons} \\ - \rightarrow \text{férmions} \end{cases}$

→ $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2, \quad \mathcal{H}_i = \frac{1}{2m}\vec{P}_i^{\,2} + V(\vec{r}_i)$

→ $\mathcal{H}\, \underbrace{\psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2)} = (\varepsilon_{n_1} + \varepsilon_{n_2})\, \psi_{n_1}(\vec{r})\psi_{n_2}(\vec{r})$ } separável

não é função de onda apropriada porque partículas devem ser indistinguíveis

→ Simetrização $\begin{cases} \psi_S = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) + \psi_{n_1}(\vec{r}_2)\psi_{n_2}(\vec{r}_1)\right] \\ \psi_A = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) - \psi_{n_1}(\vec{r}_2)\psi_{n_2}(\vec{r}_1)\right] \end{cases}$

* Princípio de exclusão: $\begin{cases} \psi_S(n_1 = n_2) \propto \psi_{n_1}(\vec{r}_1)\psi_{n_1}(\vec{r}_2) \\ \psi_A(n_1 = n_2) = 0 \;// \end{cases}$

→ $\psi_n(\vec{r})$: orbital / estado da partícula

→ sem potencial: $\left.\begin{matrix} \mathcal{H} = \frac{1}{2m}P^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \\ \mathcal{H}\psi_n = \varepsilon_n \psi_n \end{matrix}\right\}$ $\begin{matrix} \psi_k = Ce^{-ikx} \\ \varepsilon_k = \frac{\hbar^2 k^2}{2m} \end{matrix}$ | Paredes rígidas: $\operatorname{sen} kL = 0 \Rightarrow k = \frac{n\pi}{L},\ n \in \mathbb{Z}$

Contorno periódico: $e^{ikx} = e^{ik(x+L)} \Rightarrow e^{ikL} = 1 \Rightarrow k = \frac{2\pi m}{L},\ m \in \mathbb{Z}$

→ 3 dimensões: $\psi(\vec{r}) = Ce^{i\vec{k}\cdot\vec{r}}, \quad E_k = \frac{\hbar^2 k^2}{2m}$

$\vec{k} = \frac{2\pi}{L_1}m_1\hat{x} + \frac{2\pi}{L_2}m_2\hat{y} + \frac{2\pi}{L_3}m_3\hat{z} \Rightarrow k^2 = (2\pi)^2\left(\frac{m_1^2}{L_1^2} + \frac{m_2^2}{L_2^2} + \frac{m_3^2}{L_3^2}\right)$

→ $\sum_n f(n) = \sum_n f(n)\Delta n, \quad \Delta n = 1$

→ $k = \frac{2\pi}{L}n \Rightarrow \Delta k = \frac{2\pi}{L}\Delta n \Rightarrow \Delta n = \frac{L}{2\pi}\Delta k$

→ Para $\Delta n = 1$: $L \to \infty$ e $\Delta k \to 0$

} $\Delta n \to dn = \frac{L}{2\pi}dk \Rightarrow \sum_n f(n) = \sum_k f(k)\frac{L}{2\pi}dk$

$\boxed{\sum_n f(n) \to \frac{L}{2\pi}\int_{-\infty}^{+\infty} f(k)\,dk}$ → transformamos uma soma em uma integral

→ $\sum_{m_1, m_2, m_3} f(m_1, m_2, m_3)\,\underbrace{\Delta m_1 \Delta m_2 \Delta m_3}_{\Delta m_i = 1} = \sum f(k_1, k_2, k_3)\left(\frac{L_1}{2\pi}\right)\Delta k_1\left(\frac{L_2}{2\pi}\right)\Delta k_2\left(\frac{L_3}{2\pi}\right)\Delta k_3 \rightarrow \frac{V}{(2\pi)^3}\int_{-\infty}^{+\infty} f(k_1, k_2, k_3)\,dk_1\,dk_2\,dk_3$

* Spin:

→ Estado quântico: $j = (\vec{k}, \sigma)$, $\sigma = \pm 1$ } absorvemos o fator $\frac{1}{2}$ na energia

4 números quânticos

$\varepsilon_j = \varepsilon_{\vec{k},\sigma} = \frac{\hbar^2 k^2}{2m} - \mu_B H \sigma$ → faz diferença se há campo magnético, caso contrário, apenas aumenta a degenerescência dos estados

μ_B: magneton de Bohr

→ Bósons: $\{n_j\}$, $n_j = 0, 1, \cdots, \infty$

→ Férmions: $\{n_j\}$, $n_j = 0, 1$

→ Função de partição: $\left.\begin{matrix} Z = \operatorname{Tr} e^{-\beta E} \\ E = \sum \varepsilon_j n_j \end{matrix}\right\}$ $\boxed{Z = \sum_{\{n_j\}} e^{-\beta E(\{n_j\})}}$ → Vínculo: $N = \sum_j n_j$

partículas indistinguíveis → apenas o número de partículas importa

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→ Função grande de partição $\quad \Xi = \mathrm{Tr}\, e^{-\beta E + \boxed{\beta\mu \sum_j n_j}}$ → no GC removemos o vínculo $\sum_j n_j = N$ com a introdução do potencial químico

$E = \sum \varepsilon_j n_j$ → soma sobre números quânticos

↳ se são férmions: $n_j = 0, 1$

✳ Férmions: Restrição sobre o número de partículas

$$\Xi = \mathrm{Tr}\, e^{-\beta \sum_j (\varepsilon_j - \mu) n_j} = \mathrm{Tr} \prod_j e^{-\beta(\varepsilon_j - \mu) n_j} = \prod_j \sum_{n=0}^{1} e^{-\beta(\varepsilon_j - \mu) n} \Rightarrow \boxed{\Xi_{FD} = \prod \left[1 + e^{-\beta(\varepsilon_j - \mu)}\right]}$$

logaritmo separa o produto em soma

$$-\beta\Phi = \ln \Xi_{FD} = \sum_{j(n_1 m, l)} \ln\left[1 + e^{-\beta(\varepsilon_j - \mu)}\right] \Rightarrow \boxed{\Phi_{FD} = -\frac{1}{\beta} \sum_{j(n, m, l)} \ln\left[1 + e^{-\beta(\varepsilon_j - \mu)}\right]}$$

✳ Bósons: Sem restrição sobre o número de partículas

$$\Xi_{BE} = \prod_j \sum_{n=0}^{\infty} e^{-\beta(\varepsilon_j - \mu) n} = \prod_j \sum_{n=0}^{\infty} x_j^n = \prod_j \frac{1}{1 - x_j} \Rightarrow \boxed{\Xi_{BE} = \prod_j \frac{1}{1 - e^{-\beta(\varepsilon_j - \mu)}}}$$

$x_j = e^{-\beta(\varepsilon_j - \mu)}$

$$-\beta\Phi_{BE} = \ln \Xi_{BE} = -\sum_j \ln\left[1 - e^{-\beta(\varepsilon_j - \mu)}\right] \Rightarrow \boxed{\Phi_{BE} = \frac{1}{\beta} \sum_j \ln\left[1 - e^{-\beta(\varepsilon_j - \mu)}\right]}$$

→ Ocupação média de cada estado quântico

$$\langle n_k \rangle = \frac{1}{\Xi} \mathrm{Tr}\, \underbrace{n_k e^{-\beta \sum \varepsilon_j n_j}}_{= -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_k} \Xi} {}^{+ \beta\mu \sum n_j} \Rightarrow \boxed{\langle n_k \rangle = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_k} \ln \Xi}$$

$\langle n_k \rangle_{FD} = \dfrac{1}{e^{\beta(\varepsilon_k - \mu)} + 1} < 1$ → Princípio da exclusão

$\langle n_k \rangle_{BE} = \dfrac{1}{e^{\beta(\varepsilon_k - \mu)} - 1} < \infty$ → Condensação de Bose-Einstein

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→ Função de grande partição: $\boxed{\ln \Xi_{FD, BE} = \pm \sum \ln\left[1 \pm e^{-\beta(\varepsilon_j - \mu)}\right]}$

→ Ocupação média: $\boxed{\langle n_j \rangle_{FD, BE} = \left[e^{\beta(\varepsilon_j - \mu)} \pm 1\right]^{-1}}$

✳ Limite clássico: sem diferença entre bósons e férmions

$e^{\beta(\varepsilon_j - \mu)} \gg 1 \quad \forall_j \Rightarrow \boxed{e^{-\beta\mu} \gg 1} \quad (j = 0, \varepsilon_0 = 0)$

Fugacidade $\; z = e^{\beta\mu} \Rightarrow \boxed{z \ll 1}$

$$\ln \Xi \to \pm \sum_k \ln\left[1 \pm e^{-\beta(\varepsilon_k - \mu)}\right] = \pm \sum_k \ln\left[1 \pm z e^{-\beta\varepsilon_k}\right]$$

$\ln(1 + x) \approx x$

Expandimos em primeira ordem: $\ln \Xi \to \sum_k z e^{-\beta\varepsilon_k}$ → correções quânticas vêm nas ordens maiores

No contínuo: $\ln \Xi \to \dfrac{V}{(2\pi)^3} \displaystyle\int d^3\vec{k}\, e^{-\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)}$ → em d dimensões: $\dfrac{V_d}{(2\pi)^d} \displaystyle\int d^d k\, f(\varepsilon_k)$

$\therefore \boxed{\ln \Xi \to \dfrac{V e^{\beta\mu}}{\Lambda^3}} \qquad \Lambda = h (2\pi k_B T m)^{-\frac{1}{2}}$

↳ Mesmo resultado de antes, mas não precisamos usar o fator $\frac{1}{N!}$

$$N = \sum_j \langle n_j \rangle = z \frac{\partial}{\partial z} \ln \Xi = \frac{V z}{\Lambda^3} \Rightarrow \boxed{N = \frac{V e^{\beta\mu}}{\Lambda^3}}$$

Separação média entre partículas: $a \sim \left(\dfrac{V}{N}\right)^{\frac{1}{3}} \Rightarrow a^3 \sim \dfrac{V}{N} = \Lambda^3 e^{-\beta\mu}$

$$\boxed{\left(\frac{\Lambda}{a}\right)^3 \sim e^{\beta\mu} \ll 1}$$

se $a \gg \Lambda$, os efeitos quânticos são desprezíveis

→ Grande potencial:

$$\left.\begin{array}{l} -\beta\Phi = \ln \Xi_{FD, BE} \\ \Phi = -pV \end{array}\right\} \quad p = -\frac{\Phi}{V} = \frac{k_B T}{V} \ln \Xi$$

Gás de Férmions

$j = (k_x, k_y, k_z, \sigma) \rightarrow \varepsilon_j$ só depende de k^2 (sem campo externo)

$$U = \sum_j \varepsilon_j \langle n_j \rangle = \sum_j \frac{\varepsilon_j}{e^{\beta(\varepsilon_j - \mu)} + 1} = \sum_{\vec{k}} \sum_{\sigma} \frac{\varepsilon_{\vec{k}}}{e^{\beta(\varepsilon_{\vec{k}} - \mu)} + 1} = \gamma \sum_{\vec{k}} \frac{\varepsilon_{\vec{k}}}{e^{\beta(\varepsilon_{\vec{k}} - \mu)} + 1}$$

$\gamma = 2s + 1$: fator de degenerescência de spin

$$\therefore \boxed{N \rightarrow \frac{V\gamma}{(2\pi)^3} \int d^3k \left[e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} + 1 \right]^{-1}} \qquad \boxed{U \rightarrow \frac{V\gamma}{(2\pi)^3} \int d^3k \left(\frac{\hbar^2 k^2}{2m}\right) \left[e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} + 1 \right]^{-1}}$$

relação de dispersão cinética (não relativística) $\leftarrow \boxed{\varepsilon = \frac{\hbar^2 k^2}{2m}} \rightarrow k = \frac{(2m\varepsilon)^{\frac{1}{2}}}{\hbar}$

→ É usual integrar em ε: $d\varepsilon = \frac{\hbar^2}{m} k\,dk = \frac{\hbar^2}{m} \frac{(2m\varepsilon)^{\frac{1}{2}}}{\hbar} dk$

$d^3k \rightarrow 4\pi k^2 dk$

$$\left.\begin{array}{l} \boxed{U = \gamma V \int_0^\infty \varepsilon f(\varepsilon) D(\varepsilon) d\varepsilon} \\ \boxed{N = \gamma V \int_0^\infty f(\varepsilon) D(\varepsilon) d\varepsilon} \end{array}\right.$$

→ relações válidas em geral

$f(\varepsilon) = \left[e^{\beta(\varepsilon - \mu)} + 1 \right]^{-1}$ } ocupação média de estados com energia ε

$D(\varepsilon) d\varepsilon = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} d\varepsilon$ } número de estados com energia entre ε e $\varepsilon + d\varepsilon$

↳ densidade de estados → depende da relação de dispersão

→ Definimos $C \equiv \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \Rightarrow D(\varepsilon) = C \boxed{\varepsilon^{\frac{1}{2}}}$

↳ cada relação de dispersão resulta em um expoente diferente

→ Função grande de partição: $\ln \Xi = \gamma V \int_0^\infty D(\varepsilon) d\varepsilon \ln\left[1 + e^{-\beta(\varepsilon - \mu)}\right]$

$= \gamma V C \int_0^\infty \varepsilon^{\frac{1}{2}} d\varepsilon \ln\left[1 + e^{-\beta(\varepsilon - \mu)}\right]$

Sejam $\begin{cases} u = \ln\left[1 + e^{-\beta(\varepsilon-\mu)}\right] \Rightarrow du = -\beta e^{(\varepsilon-\mu)} \left[1 + e^{-\beta(\varepsilon-\mu)}\right]^{-1} d\varepsilon \\ dv = \varepsilon^{\frac{1}{2}} d\varepsilon \Rightarrow v = \frac{2}{3}\varepsilon^{\frac{3}{2}} \end{cases}$

$\varepsilon \rightarrow \infty$: $\varepsilon^{\frac{3}{2}} \rightarrow \infty$, $\ln(\cdots) \rightarrow \ln 1 = 0$

$$\Rightarrow \ln \Xi = \gamma V C \left\{ \frac{2}{3} \varepsilon^{\frac{3}{2}} \ln\left(1 + e^{-\beta(\varepsilon-\mu)}\right) \Big|_0^\infty + \beta \frac{2}{3} \int_0^\infty \varepsilon^{\frac{3}{2}} d\varepsilon f(\varepsilon) \right\}$$

$$= \frac{2}{3} \beta \gamma V \int_0^\infty \varepsilon D(\varepsilon) d\varepsilon f(\varepsilon)$$

$$= \frac{2}{3} \beta U$$

$\ln \Xi = -\beta \Phi = \beta p V = \frac{2}{3} \beta U \Rightarrow \boxed{pV = \frac{2}{3} U}$ → vale tanto para férmions quanto para bósons

↳ em geral: $pV = \frac{\alpha}{d} U$,
com α da relação de dispersão e
d a dimensionalidade do espaço

→ Gás clássico: $U = \frac{3}{2} k_B T N = \frac{3}{2} pV$

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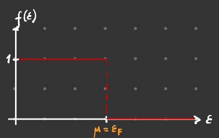
→ $f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$

$T \rightarrow 0$, $\beta \rightarrow \infty$:



Gás de férmions tem energia cinética mesmo a $T \rightarrow 0$

↳ Produz pressão: pressão de degenerescência

↳ Anãs brancas

→ Energia de Fermi: $\boxed{\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}}$

→ $N = \gamma V \int \frac{d^3k}{(2\pi)^3} f(\varepsilon) \stackrel{T=0}{=} \gamma V \int_0^{k_F} \frac{d^3k}{(2\pi)^3} = \gamma V \int_0^{\varepsilon_F} D(\varepsilon) f(\varepsilon)$

d=3 dimensões

→ $D(\varepsilon) = C\varepsilon^{\frac{1}{2}} \Rightarrow N = \gamma V C \int_0^{\varepsilon_F} \varepsilon^{\frac{1}{2}} d\varepsilon = \gamma V C \frac{2}{3} \varepsilon_F^{\frac{3}{2}} = \frac{2}{3} \gamma V \varepsilon_F D(\varepsilon_F)$

$$\therefore \boxed{\varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{\gamma}\right)^{\frac{2}{3}} \left(\frac{N}{V}\right)^{\boxed{\frac{2}{3}}}}$$

→ em geral: $\varepsilon_F \propto \left(\frac{N}{V}\right)^{\frac{\alpha}{d}}$

→ $U = \gamma V \int_0^{\varepsilon_F} \varepsilon D(\varepsilon) d\varepsilon = \frac{2}{5} \gamma V D(\varepsilon_F) \varepsilon_F^2$

→ $pV = \frac{2}{3} U \Rightarrow \boxed{p = \frac{\hbar^2}{5m} \left(\frac{6\pi^2}{\gamma}\right)^{\frac{2}{3}} \left(\frac{N}{V}\right)^{\frac{5}{3}}}$

→ Definimos: $T_F \equiv \frac{\varepsilon_F}{k_B} \Rightarrow \boxed{T_F = \frac{\hbar^2}{2mk_B} \left(\frac{6\pi^2}{\gamma}\right)^{\frac{2}{3}} \left(\frac{N}{V}\right)^{\frac{2}{3}}}$

→ $\Lambda^2 = \frac{h^2}{2\pi k_B T m} \Rightarrow \boxed{\frac{T_F}{T} \sim \left(\frac{\Lambda}{a}\right)^2}$ $\begin{cases} \Lambda \ll a: \text{ Limite clássico} \\ \Lambda \sim a: \text{ Efeitos quânticos} \end{cases}$

→ No limite $T \ll T_F$, o número de elétrons excitados será dado por

$$\Delta N = \gamma V \int_{\varepsilon_F}^{\infty} D(\varepsilon)\, d\varepsilon\, f(\varepsilon) \approx \gamma V \int_{\varepsilon_F}^{\varepsilon_F + \Delta\varepsilon} D(\varepsilon)\, d\varepsilon, \quad \Delta\varepsilon \sim k_B T$$

$$\approx \gamma V D(\varepsilon_F)\, \Delta\varepsilon$$

$$\therefore \boxed{\Delta N = \gamma V D(\varepsilon_F) k_B T}$$

→ A variação de energia desses elétrons será

$$\Delta U \approx k_B T \Delta N \Rightarrow \boxed{\Delta U \approx \gamma V D(\varepsilon_F) (k_B T)^2}$$

$$\left.\begin{aligned} c_v &= \frac{1}{N} \left.\frac{\partial U}{\partial T}\right|_{V,N} \\ U &= U_0 + \Delta U \\ N &= \frac{2}{3} \gamma V \varepsilon_F D(\varepsilon_F) \end{aligned}\right\} \quad \boxed{c_v = 3 k_B \frac{T}{T_F}}$$

→ parâmetro perturbativo

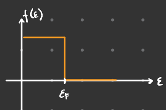
→ argumento de "escala": prefator pode ser diferente

→ Baixas temperaturas: $c_v = \gamma T + \delta T^3$

09/08/2024

Expansão de Sommerfeld

→ $I = \int_0^\infty f(\varepsilon)\, \phi(\varepsilon)\, d\varepsilon \quad \Big| \quad f(\varepsilon) = \left[e^{\beta(\varepsilon - \mu)} + 1\right]^{-1} \quad \Big| \quad \phi(\varepsilon) = A\varepsilon^n, \quad n \geq -\frac{1}{2}$



$$\Rightarrow f'(\varepsilon) = \delta(\varepsilon - \varepsilon_F)$$

→ $u = f(\varepsilon)$, $du = f'(\varepsilon)\, d\varepsilon$

→ $dv = \phi(\varepsilon)\, d\varepsilon$, $v = \int_0^\varepsilon \phi(\varepsilon')\, d\varepsilon' \equiv \psi(\varepsilon)$

$$I = \cancel{f(\varepsilon)\psi(\varepsilon)\Big|_0^\infty}^{\,0} - \int_0^\infty \psi(\varepsilon) f'(\varepsilon)\, d\varepsilon$$

só contribui termo em torno de ε_F

→ $\psi(\varepsilon) = \psi(\mu) + \psi'(\mu)(\varepsilon - \mu) + \cdots = \sum_{k=0}^{\infty} \frac{1}{k!} \psi^k(\mu) (\varepsilon - \mu)^k \Rightarrow I = -\sum_{k=0}^{\infty} \frac{1}{k!} \psi^k(\mu) \int_0^\infty (\varepsilon - \mu)^k f'(\varepsilon)\, d\varepsilon$

→ $I_k = -\int_0^\infty (\varepsilon - \mu)^k f'(\varepsilon)\, d\varepsilon$

$$\rightarrow f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}, \quad f'(\varepsilon) = \frac{-\beta e^{\beta(\varepsilon - \mu)}}{\left[e^{\beta(\varepsilon-\mu)} + 1\right]^2} \quad \left\}\begin{aligned} x &\equiv \beta(\varepsilon - \mu) \\ dx &= \beta\, d\varepsilon \end{aligned}\right.$$

$$\rightarrow I_k = \frac{1}{\beta^k} \int_{-\infty}^{\infty} \frac{x^k e^x e^{-x}}{(e^x + 1)^2 (e^{-\frac{x}{2}})^2} = \frac{1}{\beta^k} \int_{-\infty}^{\infty} \frac{x^k}{\left[e^{\frac{x}{2}} + e^{-\frac{x}{2}}\right]^2}\, dx$$

↳ $I_k = 0$ se k ímpar

↳ $I_0 = 1 \; \Big| \; I_2 = \frac{\pi^2}{3\beta^2}$

$$\therefore \boxed{I = \int_0^\mu \phi(\varepsilon)\, d\varepsilon + \frac{1}{2!} \left.\frac{d\phi}{d\varepsilon}\right|_{\varepsilon = \mu} \frac{\pi^2}{3\beta^2}}$$

→ apenas até 2ª ordem

→ $U = \gamma V \int_0^\infty f(\varepsilon)\, \varepsilon D(\varepsilon)\, d\varepsilon$, $D(\varepsilon) = C\varepsilon^{\frac{1}{2}}$

$= \gamma V C \int_0^\infty f(\varepsilon)\, \varepsilon^{\frac{3}{2}}\, d\varepsilon$ → $\phi(\varepsilon) = \varepsilon^{\frac{3}{2}}$

$$\therefore \boxed{U = \gamma V C \left[\frac{2}{5} \mu^{\frac{5}{2}} + \frac{\pi^2}{6} (k_B T)^2 \frac{3}{2} \mu^{\frac{1}{2}}\right]}$$

→ Energia em termos do número de partículas: $N = \gamma V C \int_0^\infty f(\varepsilon)\, C\varepsilon^{\frac{1}{2}}\, d\varepsilon$

$$N = \gamma V C \left\{\frac{2}{3} \mu^{\frac{3}{2}} + \frac{\pi^2}{12} (k_B T)^2 \mu^{-\frac{1}{2}}\right\}$$

→ Mas, pela definição de ε_F, $N \equiv \frac{2}{3} \gamma V C \varepsilon_F^{\frac{3}{2}} \Rightarrow \boxed{\varepsilon_F^{\frac{3}{2}} = \mu^{\frac{3}{2}} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu}\right)^2\right]}$ → para $T = 0$: $\varepsilon_F = \mu$

→ Queremos $\mu(T)$, mas a equação anterior é difícil de inverter. Escrevemos de forma perturbativa:

$$\mu(T) = \varepsilon_F\left[1 + A\left(\frac{T}{T_F}\right) + B\left(\frac{T}{T_F}\right)^2\right]$$ → aproximações anteriores vão até 2ª ordem

→ O único termo que contribui em $\left(\frac{k_B T}{\mu}\right)^2$ é o de ordem zero

→ Para o restante, fazemos a expansão: $\mu^{\frac{3}{2}} = \varepsilon_F^{\frac{3}{2}}\left[1 + A\left(\frac{T}{T_F}\right) + B\left(\frac{T}{T_F}\right)^2\right]^{\frac{3}{2}}$, $(1+x)^{\frac{3}{2}} = 1 + \frac{3}{2}x + a x^2$

→ Comparamos os coeficientes e determinamos A e B: $A = 0$, $B = -\frac{\pi^2}{12}$

$$\therefore \boxed{\mu = \varepsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right]}$$

$$\boxed{U = \frac{3}{5}N\varepsilon_F\left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right]}$$

→ Calor específico: $\boxed{c_v = \frac{1}{N}\frac{\partial U}{\partial T}\Big|_V = \frac{\pi^2}{2}k_B\frac{T}{T_F}}$ → muito próximo do resultado empírico obtido anteriormente

Paramagnetismo de Pauli

12/08/24

→ Campo externo H

→ $\varepsilon_{\vec{k},\sigma} = \frac{\hbar^2 k^2}{2m} - \mu_B H \sigma$ → $\sigma = \pm 1 \leftrightarrow g_s m_s$

magneton de Bohr

→ $\Xi = \mathrm{Tr}\, e^{-\beta\mathcal{H} + \beta\mu N}$

→ $\mathcal{H} = \sum_k \left(\varepsilon_{k\uparrow} n_{k\uparrow} + \varepsilon_{k\downarrow} n_{k\downarrow}\right)$

$$\Xi = \mathrm{Tr}\prod_{\vec{k}} e^{-\beta(\varepsilon_{\vec{k}\uparrow} - \mu)n_{\vec{k}\uparrow}}\, e^{-\beta(\varepsilon_{\vec{k}\downarrow} - \mu)n_{\vec{k}\downarrow}}$$

0 ou 1

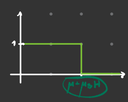
$$= \prod_k \left[1 + e^{-\beta(\varepsilon_{k\uparrow} - \mu)}\right]\left[1 + e^{-\beta(\varepsilon_{k\downarrow} - \mu)}\right]$$

→ $\ln\Xi = \sum_{\vec{k}}\sum_{\sigma=\pm1}\ln\left(1 + z e^{-\beta\frac{\hbar^2 k^2}{2m} + \beta\mu_B H\sigma}\right) = \ln\Xi_+ + \ln\Xi_-$

→ Escrevendo na forma integral: $\ln\Xi_\pm = VC\int_0^\infty \varepsilon^{\frac{1}{2}}\ln\left(1 + z e^{-\beta\varepsilon \pm \beta\mu_B H}\right)d\varepsilon$

→ $\langle N\rangle = z\frac{\partial}{\partial z}\ln\Xi = \langle N_+\rangle + \langle N_-\rangle$ | $\langle N_\pm\rangle = z\frac{\partial}{\partial z}\ln\Xi_\pm = VC\int_0^\infty \frac{\varepsilon^{\frac{1}{2}}}{z^{-1}e^{\beta\varepsilon \mp \beta\mu_B H} + 1}d\varepsilon$

"$\varepsilon_F \to \mu + \mu_B H$"



* $T \to 0$, $\beta \to \infty$

→ $\langle N_+\rangle = VC\int_0^{\mu+\mu_B H}\varepsilon^{\frac{1}{2}}d\varepsilon = \frac{2}{3}VC(\mu + \mu_B H)^{\frac{3}{2}}$

$\langle N_-\rangle = VC\int_0^{\mu-\mu_B H}\varepsilon^{\frac{1}{2}}d\varepsilon = \frac{2}{3}VC(\mu - \mu_B H)^{\frac{3}{2}}$

$$\langle N\rangle = \frac{2}{3}VC\left[(\mu + \mu_B H)^{\frac{3}{2}} + (\mu - \mu_B H)^{\frac{3}{2}}\right]$$

→ $M = (N_+ - N_-)\mu_B = \frac{2}{3}VC\mu_B\left[(\mu + \mu_B H)^{\frac{3}{2}} - (\mu - \mu_B H)^{\frac{3}{2}}\right] = \frac{2}{3}VC\mu_B\mu^{\frac{3}{2}}\left[\left(1 + \frac{\mu_B H}{\mu}\right)^{\frac{3}{2}}\left(1 - \frac{\mu_B H}{\mu}\right)^{\frac{3}{2}}\right]$

→ Aplicando o mesmo procedimento em $\langle N\rangle$: $\boxed{N = \frac{4}{3}VC\varepsilon_F^{\frac{3}{2}} = \frac{4}{3}VC\mu^{\frac{3}{2}} + O\left[\left(\frac{\mu_B H}{\mu}\right)^2\right]}$

$$\boxed{M = \frac{3}{2}N\frac{\mu_B^2 H}{\varepsilon_F}}$$

* $0 < T \ll T_F$

→ $f(x) = \left[e^{\beta(x-\mu)} + 1\right]^{-1}$ ⇒ $M = \mu_B VC\int_0^\infty d\varepsilon\,\varepsilon^{\frac{1}{2}}\left[\underbrace{f(\varepsilon - \mu_B H) - f(\varepsilon + \mu_B H)}_{\text{expansão em série}}\right]$

→ $f(\varepsilon \mp \mu_B H) \approx f(\varepsilon) \mp \mu_B H f'(\varepsilon)$ ⇒ $M \approx -2\mu_B^2 VCH\int_0^\infty f'(\varepsilon)\varepsilon^{\frac{1}{2}}d\varepsilon \overset{\text{Int. partes}}{=} VC\mu_B^2 H\underbrace{\int_0^\infty \varepsilon^{-\frac{1}{2}}f(\varepsilon)d\varepsilon}_{\text{expansão de Sommerfeld}} = VC\mu_B^2 H\left[2\mu^{\frac{1}{2}} - \frac{\pi^2}{12}(k_B T)^2\mu^{-\frac{3}{2}}\right]$

$\rightarrow$ $N = VC\int_0^\infty d\varepsilon\, \varepsilon^{\frac{1}{2}} \left[f(\varepsilon - \mu_B H) + f(\varepsilon + \mu_B H)\right] \approx 2VC\int_0^\infty d\varepsilon\, \varepsilon^{\frac{1}{2}} f(\varepsilon)$

$\rightarrow$ queremos termos de até 1ª ordem em H, mas $f(\varepsilon + \mu_B H) + f(\varepsilon - \mu_B H)$ é par em H $\Rightarrow$ não há termos ímpares na expansão

$$\therefore \boxed{N = \frac{4}{3} VC\mu^{\frac{3}{2}}\left[1 + \frac{\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2\right]}, \quad \mu = \varepsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]$$

$\rightarrow$ Escrevendo M em termos de N: $\boxed{M = \frac{3}{2}\frac{N\mu_B^2 H}{\varepsilon_F}\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]}$

* $T \gg T_F$

$\rightarrow$ $f(\varepsilon \mp \mu_B H) = \left[e^{\beta(\varepsilon \mp \mu_B H - \mu)} + 1\right]^{-1} \xrightarrow{\varepsilon \gg \mu} f(\varepsilon \mp \mu_B H) \approx e^{-\beta(\varepsilon \mp \mu_B H - \mu)}$ $\rightarrow$ dist. Boltzmann

$\rightarrow$ $M = \mu_B VC\int_0^\infty \varepsilon^{\frac{1}{2}} d\varepsilon \left[e^{-\beta(\varepsilon - \mu_B H - \mu)} - e^{-\beta(\varepsilon + \mu_B H - \mu)}\right] = 2\,\text{senh}(\beta\mu_B H)\,\mu_B VC\int_0^\infty \cdots$

mesma integral $\rightarrow$ não precisamos calcular porque queremos $m = \frac{M}{N}$

$\rightarrow$ $N = VC\int_0^\infty \varepsilon^{\frac{1}{2}} d\varepsilon \left[e^{-\beta(\varepsilon - \mu_B H - \mu)} + e^{-\beta(\varepsilon + \mu_B H - \mu)}\right] = 2\cosh(\beta\mu_B H)\, VC\int_0^\infty \cdots$

$\rightarrow$ $m = \frac{M}{N} \Rightarrow \boxed{m = \mu_B \tanh(\beta\mu_B H)}$ $\rightarrow$ resultado clássico

$\rightarrow$ não há restrição sobre H, desde que $T \gg T_F$

$\rightarrow$ devemos interpretar $\mu_B \rightarrow \mu_{mag}$, um momento de dipolo magnético permanente

14/08/24

Bósons livres

→ $\ln \Xi_{BE} = -\sum_j \ln\left[1-e^{-\beta(\epsilon_j-\mu)}\right]$

→ $p = -\frac{k_BT}{V}\ln\Xi$ → $pV = -\Phi = -\frac{1}{\beta}\ln\Xi$

→ $\langle n_j\rangle = \frac{1}{e^{\beta(\epsilon_j-\mu)}-1} > 0$

↳ $e^{\beta(\epsilon_j-\mu)} > 1 \ \forall_j \Rightarrow \epsilon_j > 0$

$e^{-\beta\mu} > 1$

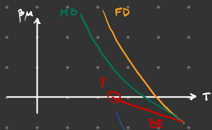
$\therefore \boxed{\mu<0}$ → a distribuição de Bose-Einstein impõe uma condição sobre o potencial químico

* Limite clássico:

→ $\langle n_j\rangle \approx e^{-\beta(\epsilon_j-\mu)}$ → Maxwell-Boltzmann

→ $N = \gamma VC\int_0^\infty \epsilon^{\frac12}d\epsilon\, e^{-\beta(\epsilon-\mu)} \Rightarrow \beta\mu = \ln\left(\frac{\rho\Lambda^3}{\gamma}\right)$

$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$, $\rho = \frac{N}{V}$



↳ $\mu<0$ → não pode cruzar o eixo

→ Sabemos que $\underbrace{\frac{\partial^2F}{\partial N^2} = \frac{\partial\mu}{\partial N} \geq 0}_{\text{estabilidade termodinâmica}}$ → qual o comportamento de N para $\mu\to0$?

{para determinar se uma integral converge, podemos analisar o comportamento do integrando nos limites de integração

↳ Colocando na integral: $N = \gamma VC\int_0^\infty \frac{\epsilon^{\frac12}}{e^{\beta(\epsilon-\mu)}-1}d\epsilon \Rightarrow N_{max} = \gamma VC\int_0^\infty\frac{\epsilon^{\frac12}}{e^{\beta\epsilon}-1}d\epsilon$ } bem-comportada no limite superior e inferior

↳ Como chegamos em um número máximo de partículas para bósons ideais, sem o princípio da exclusão?

→ $z = e^{\beta\mu} \Rightarrow N = \sum_j\frac{1}{z^{-1}e^{\beta\epsilon_j}-1} = \frac{1}{z^{-1}-1} + \sum_{j>0}\frac{1}{z^{-1}e^{\beta\epsilon_j}-1}$

↳ $\mu\to0 \Rightarrow z\to1$ → divergência ⇒ demais partículas vão para o estado fundamental

↳ $\epsilon_0 = 0$

→ Em termos da densidade: $\rho = \frac{N}{V} = \rho_0 + \frac{1}{V}\frac{1}{z^{-1}e^{\beta\epsilon_j}-1}$, $\rho_0 = \frac{1}{V}\frac{1}{z^{-1}-1}$

$\rho_0 \to \infty$ para $\mu\to0$

→ Partículas excitadas: $N_e = \gamma VC\int_0^\infty\frac{\epsilon^{\frac12}}{z^{-1}e^{\beta\epsilon}-1}d\epsilon$

↳ na integral, o estado fundamental não contribui

→ Partículas no estado fundamental: $\rho_0 = \frac{N_0}{V} = \lim_{z\to1}\frac{1}{V}\frac{1}{z^{-1}-1}$

→ No limite $z\to1$: iniciamos o sistema e baixamos a temperatura até uma temperatura crítica

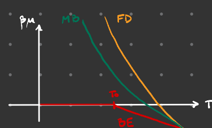
↳ Abaixo dessa temperatura uma fração finita das partículas excitadas vai para o estado fundamental → Condensação de Bose-Einstein

$x \equiv \beta_0\epsilon \to N = \gamma VC\int_0^\infty\frac{\epsilon^{\frac12}}{e^{\beta_0\epsilon}-1}d\epsilon = \frac{\gamma VC}{\beta_0^{\frac32}}\int_0^\infty\frac{x^{\frac12}}{e^x-1}dx = \frac{\gamma VC}{\beta_0^{\frac32}}\Gamma\left(\tfrac32\right)\zeta\left(\tfrac32\right)$

zeta de Riemann

$\therefore \boxed{T_0 = \frac{\hbar^2}{2mk_B}\left[\frac{4\pi^2}{\gamma\Gamma\left(\frac32\right)\zeta\left(\frac32\right)}\right]^{\frac23}\left(\frac{N}{V}\right)^{\frac23}}$

↳ N define a temperatura crítica



→ $N_0 = N - N_e = N\left(1-\frac{N_e}{N}\right)$

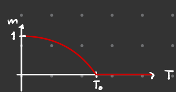
→ $N_e = \frac{\gamma VC}{\beta^{\frac32}}\Gamma\left(\tfrac32\right)\zeta\left(\tfrac32\right)$

→ $N = \frac{\gamma VC}{\beta_0^{\frac32}}\Gamma\left(\tfrac32\right)\zeta\left(\tfrac32\right)$ } $\frac{N_e}{N} = \left(\frac{\beta_0}{\beta}\right)^{\frac32} \Rightarrow \boxed{N_0 = N\left[1-\left(\frac{\beta_0}{\beta}\right)^{\frac32}\right] = N\left[1-\left(\frac{T}{T_0}\right)^{\frac32}\right]}$

teoria não é realista (partículas não interagem)

→ "Transição de fase": $m = \frac{N_0}{N}$

{não é transição de fato porque o eixo $\mu=0$ não pode ser cruzado para $\mu>0$



$m = \left(\frac{T_0-T}{T}\right)^{\bar\beta}$ → expoente crítico

$\delta \equiv \frac{T_0-T}{T_0} \Rightarrow T = T_0(1-\delta) \Rightarrow N_0 = N\left(1-(1-\delta)^{\frac32}\right) \approx \frac32 N\delta = \frac32 N\left(\frac{T_0-T}{T_0}\right)^1 \Rightarrow \bar\beta = 1$

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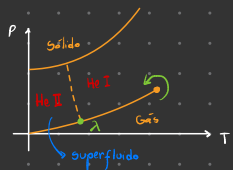
→ Exemplo: He^4

$$T_0 = \frac{h^2}{2mk_B}\left[\frac{4\pi^2}{\gamma\Gamma(\frac{3}{2})\zeta(\frac{3}{2})}\right]^{\frac{2}{3}}\left(\frac{N}{V}\right)^{\frac{2}{3}}$$



$T_\lambda = 2{,}17\,K$

$T_0 = 3{,}14\,K$

→ Precisamos de uma teoria mais sofisticada

* $T > T_0$:

→ $$\frac{\ln \Xi}{V} = -\gamma C \int_0^\infty \varepsilon^{\frac{1}{2}} \ln(1 - z e^{-\beta\varepsilon})\, d\varepsilon, \quad z = e^{\beta\mu}, \quad \mu < 0$$

→ $z < 1$: $\ln(1-x) = -x - \frac{x^2}{2} - \ldots \Rightarrow \frac{\ln \Xi}{V} = \gamma C \int_0^\infty \varepsilon^{\frac{1}{2}}\left[z e^{-\beta\varepsilon} + \frac{z^2}{2} e^{-2\beta\varepsilon}\right] = \gamma C \sum_{n=1}^{\infty} \frac{z^n}{n^{\frac{5}{2}}}$

→ Definimos: $g_\alpha(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^\alpha}$

$$\therefore \boxed{\frac{\ln \Xi}{V} = \gamma C g_{\frac{5}{2}}(z)}$$

* $N = z \frac{\partial}{\partial z} \ln \Xi \Big|_\beta$

→ $\frac{\partial}{\partial z} g_\alpha(z) = \sum_{n=1}^{\infty} \frac{n z^{n-1}}{n^\alpha} = \sum_{n=1}^{\infty} \frac{z^{n-1}}{n^{\alpha-1}} \Rightarrow z \frac{\partial}{\partial z} g_\alpha(z) = g_{\alpha-1}(z)$

$$\therefore \boxed{N = \frac{\gamma V}{\Lambda^3} g_{\frac{3}{2}}(z)}$$

* $U = -\frac{\partial}{\partial \beta} \ln \Xi \Big|_z$, $\quad \frac{\partial \Lambda}{\partial \beta} = \frac{\Lambda}{2\beta}$ $\Bigg\}$ $\quad U = \frac{3\gamma}{\Lambda^4}\frac{\Lambda}{2\beta} g_{5/2}$

$$\boxed{U = \frac{3}{2}\frac{\gamma V}{\Lambda^3 \beta} g_{5/2}(z)}$$

* $c_v = \frac{1}{N} \frac{\partial U}{\partial T}\Big|_{V,N}$

→ $U(\beta, z) = U(\beta, z(\beta, N)) \rightarrow \frac{\partial U}{\partial \beta}\Big|_N = \frac{\partial U}{\partial \beta}\Big|_z + \frac{\partial U}{\partial z}\Big|_\beta \frac{\partial z}{\partial \beta}\Big|_N$

→ $\frac{\partial z}{\partial \beta}\Big|_N \frac{\partial \beta}{\partial N}\Big|_z \frac{\partial N}{\partial z}\Big|_\beta = -1 \Rightarrow \frac{\partial z}{\partial \beta}\Big|_N = -\frac{\frac{\partial N}{\partial \beta}\big|_z}{\frac{\partial N}{\partial z}\big|_\beta}$

→ $\frac{\partial U}{\partial \beta}\Big|_z = -\frac{15}{4}\frac{\gamma V}{\beta^2 \Lambda^3} g_{5/2}(z)$

→ $\frac{\partial U}{\partial z}\Big|_\beta = \frac{1}{z}\left(z \frac{\partial U}{\partial z}\right)\Big|_\beta = \frac{3}{2}\frac{\gamma V}{\beta \Lambda^3 z} g_{3/2}(z)$

→ $\frac{\partial N}{\partial \beta}\Big|_z = -\frac{3}{2}\frac{\gamma V}{\beta \Lambda^3} g_{3/2}(z)$

→ $\frac{\partial N}{\partial z}\Big|_\beta = \frac{\gamma V}{\Lambda^3 z} g_{1/2}(z)$

$$\therefore \boxed{c_v = \frac{3}{2} k_B \left\{\frac{5}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{3}{2}\frac{g_{3/2}(z)}{g_{1/2}(z)}\right\}}$$

↳ Limite clássico: $z \ll 1 \Rightarrow g_\alpha(z) \approx z \Rightarrow \boxed{c_v = \frac{3}{2} k_B}$

↳ Condensação de Bose-Einstein: $z \to 1 \Rightarrow$ $\left.\begin{array}{l} g_{5/2}(1) = \sum_{n=1}^{\infty} \frac{1}{n^{5/2}} = \zeta(\frac{5}{2}) \\ g_{3/2}(1) = \zeta(\frac{3}{2}) \\ g_{1/2}(1) \to \infty \end{array}\right\}$ $\boxed{c_v = \frac{15}{4} k_B \frac{\zeta(5/2)}{\zeta(3/2)}}$

→ $\beta p V = \ln \Xi$

$\beta p = \frac{\gamma}{\Lambda^3} g_{5/2}(z)$

→ $S = -\frac{\partial \Phi}{\partial T}\Big|_{V,\mu} = V \frac{\partial p}{\partial T}\Big|_{V,\mu}$

$z = e^{\beta\mu} \Rightarrow \frac{\partial z}{\partial \beta}\Big|_\mu = \mu e^{\beta\mu} = \frac{z \ln z}{\beta}$

$\frac{\partial g_{5/2}}{\partial z}\Big|_\beta \frac{\partial z}{\partial \beta}\Big|_\mu \ldots ?$

$$S = \frac{k_B \gamma V}{\Lambda^3}\left\{\frac{5}{2} g_{5/2}(z) - g_{3/2}(z) \ln z\right\}$$

$$\therefore \boxed{S = k_B N \left\{\frac{5}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \ln z\right\}}$$

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$\rightarrow \ln \Xi = -\gamma V C \int_0^\infty \varepsilon^{\frac{1}{2}} d\varepsilon \ln\left(1 - z e^{-\beta\varepsilon}\right) d\varepsilon = \frac{\gamma V}{\Lambda^3} g_{5/2}(z)$

$\rightarrow g_\alpha(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^\alpha}$

$*$ $T < T_0$:

→ Problema: abaixo de T_0, a energia não varia infinitesimalmente

$\rightarrow p = \frac{1}{\beta V} \ln \Xi = -\frac{1}{\beta V} \sum_j \ln\left(1 - \overset{z \to 1}{z} e^{-\beta\varepsilon_j}\right) = \lim_{z\to 1} \left[-\frac{\gamma \ln(1-z)}{\beta V} - \frac{\gamma C}{\beta V} \int_0^\infty \varepsilon^{\frac{1}{2}} \ln\left(1 - e^{-\beta\varepsilon}\right) d\varepsilon \right]$

$\rightarrow \frac{N}{V} = \frac{1}{V} \frac{1}{z^{-1}-1} + \sum_{j\neq 0} \frac{1}{z^{-1} e^{\beta\varepsilon} - 1} \rightarrow \rho_0 = \lim_{z\to 1} \frac{1}{V} \frac{1}{z^{-1}-1} = \lim_{z\to 1} \frac{1}{V} \frac{z}{1-z} \Rightarrow \rho_0 = \lim_{z\to 1} \frac{1}{V(1-z)}$

$\rightarrow \frac{1}{V\rho_0} = (1-z) \Rightarrow -\ln V\rho_0 = \ln(1-z)$

$\rightarrow p = \lim_{V\to\infty} \left[\frac{\gamma \ln(V\rho_0)}{\beta V} - \frac{\gamma C}{\beta V} \int_0^\infty \varepsilon^{\frac{1}{2}} \ln\left(1 - e^{-\beta\varepsilon}\right) d\varepsilon \right]$

$\therefore \boxed{p(T < T_0) = \frac{\gamma}{\beta \Lambda^3} g_{5/2}(1)}$ → só depende da temperatura

$*$ $T > T_0$: $U = \frac{3}{2} \frac{\gamma V}{\beta \Lambda^3} g_{5/2}(z)$

$*$ $T < T_0$: $U = \frac{3}{2} \frac{\gamma V}{\beta \Lambda^3} g_{5/2}(1)$

$c_v = \frac{1}{N} \frac{\partial U}{\partial T}\Big|_{V,N} = \frac{1}{N} k_B \beta^2 \frac{\partial U}{\partial \beta}\Big|_{V,N} = \frac{\gamma V}{2} g_{5/2}(1) \left[-\frac{1}{\beta^2 \Lambda^3} - \frac{3}{\Lambda^4} \cdot \frac{\Lambda}{2\beta^2} \right] \left(-\frac{k_B \beta^2}{N} \right)$

$c_v = \frac{15}{4} \frac{\gamma k_B}{\Lambda^3} \left(\frac{V}{N}\right) g_{5/2}(1) \sim \sigma T^{\frac{3}{2}}$ → He^4: $\propto T^3$ → teoria falha porque não há interação entre partículas