Gases ideais quânticos.

variáveis

$$\begin{cases} E = \sum_i n_i \varepsilon_i \Longrightarrow U = \sum \langle n_i \rangle \varepsilon_i = \int_0^\infty \varepsilon\, g(\varepsilon) \langle n_\varepsilon \rangle \, d\varepsilon \\ \mathcal{N} = \sum_i n_i \Longrightarrow N = \sum_i \langle n_i \rangle = \int_0^\infty g(\varepsilon) \langle n_\varepsilon \rangle \, d\varepsilon \end{cases}$$

n_i: população do estado c/energia ε_i

· as propriedades térmicas do gás podem ser determinadas a partir da população média dos estados.

$$Z_G = \sum_{\{n_i\}} e^{-\sum_i \beta(\varepsilon_i - \mu) n_i} = \underbrace{\sum_{n_1} \left[e^{\beta(\mu - \varepsilon_1)} \right]^{n_1} \sum_{n_2} \left[e^{\beta(\mu - \varepsilon_2)} \right]^{n_2} \cdots}_{\text{independente}} \Longrightarrow \prod_i \underbrace{Z_i}_{\text{independentes}}$$

· **férmions**. ($n_i = 0$ ou 1) $\Longrightarrow Z_i = 1 + e^{\beta(\mu - \varepsilon_i)} \Longrightarrow \boxed{\ln Z_G = \sum_i \left[1 + e^{\beta(\mu - \varepsilon_i)} \right]}$ (férmions)

· **bósons** ($n_i = 0 - \infty$) $\Longrightarrow Z_i = \sum_{n_i=0}^{\infty} \left[e^{\beta(\mu - \varepsilon_i)} \right]^n = \dfrac{1}{1 - e^{\beta(\mu - \varepsilon_i)}} \Longrightarrow \boxed{\ln Z_G = -\sum_i \left[1 - e^{\beta(\mu - \varepsilon_i)} \right]}$ (bósons)

Relação entre a pressão e a energia

$$g(\varepsilon) = C\,\varepsilon^n \quad \begin{cases} n = 1/2 & \text{(massivas não-relativísticas)} \\ n = 2 & \text{(ultra-relativísticas ou não-massivas)} \end{cases}$$

$$\begin{cases} \ln Z_G = \pm C \displaystyle\int_0^\infty \varepsilon^n \ln\left[1 \pm e^{(\mu-\varepsilon)/kT}\right] d\varepsilon \\ \ln Z_G = \dfrac{C}{n+1}\dfrac{1}{kT}\displaystyle\int_0^\infty \dfrac{\varepsilon^{n+1}}{\lambda^{-1} e^{\varepsilon/kT} \pm 1}\, d\varepsilon \end{cases}$$

$$\boxed{\begin{array}{l} dv = \varepsilon^n d\varepsilon \implies v = \dfrac{\varepsilon^{n+1}}{n+1} \quad (v(0)=0) \\ u = \ln f(\varepsilon) \implies u(\infty) = 0 \\ \dfrac{dU}{d\varepsilon} = \dfrac{f'(\varepsilon)}{f(\varepsilon)} \qquad f'(\varepsilon) = \mp \dfrac{1}{kT} e^{(\mu-\varepsilon)/kT} \\ dU = \mp \dfrac{1}{kT} \dfrac{e^{(\mu-\varepsilon)/kT}}{1 \pm e^{(\mu-\varepsilon)/kT}} d\varepsilon = \mp \dfrac{1}{kT} \dfrac{1}{e^{(\varepsilon-\mu)/kT} \mp 1} d\varepsilon \end{array}}$$

$$\begin{cases} PV = -\Omega = kT \ln Z_G = \dfrac{C}{n+1}\displaystyle\int_0^\infty \dfrac{\varepsilon^{n+1}}{\lambda^{-1} e^{\varepsilon/kT} \pm 1}\, d\varepsilon \\ U = \displaystyle\sum_i \langle n_i \rangle \varepsilon_i = C \int \dfrac{\varepsilon^{n+1}}{\lambda^{-1} e^{\varepsilon/kT} \pm 1}\, d\varepsilon \end{cases}$$

$$\boxed{PV = \frac{1}{n+1} U \quad \begin{cases} \dfrac{2}{3} U \\ \dfrac{U}{3} \end{cases}}$$

(massivas não-relativísticas)

(ultra-relativísticas ou não-massivas)

Distribuições de Fermi-Dirac, Bose-Einstein e Maxwell-Boltzmann

$$\ln Z_G = \pm \sum_i \ln\left[1 \pm e^{\beta(\mu-\varepsilon_i)}\right] \qquad \begin{cases} (+) & \text{férmions} \\ (-) & \text{bósons} \end{cases}$$

$$N = kT \left.\frac{\partial \ln Z_G}{\partial \mu}\right|_{T,V} = \sum_i \frac{e^{\beta(\mu-\varepsilon_i)}}{1 \pm e^{\beta(\mu-\varepsilon_i)}} = \sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1} = \sum \langle n_i \rangle$$

$$\boxed{\langle n_i \rangle = \frac{1}{\lambda^{-1} e^{\varepsilon_i/kT} \pm 1}} \qquad \begin{cases} (+) & \underline{\text{distribuição de Fermi-Dirac}} \\ (-) & \underline{\text{distribuição de Bose-Einstein}} \end{cases}$$

fugacidade $\leftarrow$ $\boxed{\lambda = e^{\mu/kT}}$

- <u>gases não-degenerados</u> $(\langle n_i \rangle \ll 1) \Rightarrow 1 \mp \langle n_i \rangle = \dfrac{\lambda^{-1} e^{\beta\varepsilon_i}}{\lambda^{-1} e^{\beta\varepsilon_i} \pm 1} \Rightarrow \dfrac{\langle n_i \rangle}{\underbrace{1 \mp \langle n_i \rangle}_{1}} = \lambda e^{-\beta\varepsilon_i}$

$$\boxed{\langle n_i \rangle = \lambda e^{-\beta\varepsilon_i}}$$ <u>distribuição de Maxwell-Boltzmann</u>

- <u>fótons e fônons</u> $(\mu = 0 \Leftrightarrow \lambda = 1) \Rightarrow \boxed{\langle n_i \rangle = \dfrac{1}{e^{\varepsilon_i/kT} - 1}}$ <u>distribuição de Planck</u>

Gases quânticos não-relativísticos ligeiramente degenerados ($\lambda < 1$)

$$\left\{ \begin{array}{l} \langle n(\varepsilon)\rangle = \dfrac{1}{\lambda^{-1} e^{\beta\varepsilon} \pm 1} \qquad \left| \begin{array}{l} (+)\ \text{F.D.} \\ (-)\ \text{B.E.} \end{array} \right. \qquad \lambda = e^{\mu/kT} \\ g(\varepsilon) = \dfrac{3}{2} N \dfrac{\varepsilon^{1/2}}{(kT_d)^{3/2}} \qquad T_d = \left(\dfrac{3}{4\pi g}\right)^{2/3} \left(\dfrac{h^2}{2mk}\right) \left(\dfrac{N}{V}\right)^{2/3} \end{array} \right.$$

(massivos não-relativísticos)

$$N = \int_0^\infty g(\varepsilon)\, \langle n(\varepsilon)\rangle\, d\varepsilon = \frac{3}{2} \frac{N}{(kT_d)^{3/2}} \int_0^\infty \frac{\varepsilon^{1/2}}{\lambda^{-1} e^{\beta\varepsilon} \pm 1} d\varepsilon = \frac{3}{2} N \left(\frac{T}{T_d}\right)^{3/2} \lambda \int_0^\infty \frac{x^{1/2}}{e^{x} \pm \lambda}$$

$$\left\{ \begin{array}{l} x = \beta\varepsilon = \varepsilon/kT \\ d\varepsilon = kT\, dx \\ \varepsilon^{1/2} = (kT)^{1/2} x^{1/2} \end{array} \right.$$

$$\left\{ \begin{array}{l} f(\lambda) = \dfrac{1}{e^{x} \pm \lambda} = f(0) + \lambda f'(0) = e^{-x} \mp \lambda e^{-2x} \\ \displaystyle\int_0^\infty \frac{x^{1/2}}{e^{x} \pm \lambda} dx = \underbrace{\int_0^\infty x^{1/2} e^{-x} dx}_{\Gamma(3/2)} \mp \lambda \underbrace{\int_0^\infty x^{1/2} e^{\overbrace{-2x}^{y}} dx}_{\frac{1}{2^{3/2}} \Gamma(3/2)} = \Gamma(3/2)\left(1 \mp \frac{\lambda}{2^{3/2}}\right) \end{array} \right.$$

$$\boxed{\begin{array}{l} f(\lambda) = (e^{x} \pm \lambda)^{-1} \Rightarrow f(0) = e^{-x} \\ f'(\lambda) = \mp (e^{x} \pm \lambda)^{-2} \Rightarrow f'(0) = \mp e^{-2x} \end{array}}$$

$$1 = \frac{3}{2} \frac{\Gamma(3/2)}{T_d^{3/2}} T^{3/2} \left(1 \mp \frac{\lambda}{2^{3/2}}\right) \lambda \Longrightarrow \lambda = \underbrace{\left(\frac{2}{3} \frac{T_d^{3/2}}{\Gamma(3/2)}\right)}_{T_c^{3/2}} \frac{1}{T^{3/2}} \frac{1}{\left(1 \mp \lambda/2^{3/2}\right)} = \boxed{\left(\frac{T_c}{T}\right)^{3/2} \left(1 \pm \frac{\lambda}{2^{3/2}}\right) = \lambda} \quad (T > T_c)$$

$$\boxed{T_c = \frac{T_d}{\left[\frac{3}{2}\Gamma(3/2)\right]^{2/3}} = \frac{T_d}{\left[\Gamma(5/2)\right]^{2/3}}}$$

$$U = \int_0^\infty \varepsilon\, g(\varepsilon)\, \langle n(\varepsilon)\rangle\, d\varepsilon = \frac{3}{2}\frac{N}{(kT_d)^{3/2}} \int \frac{\varepsilon^{3/2}}{\lambda^{-1} e^{\beta\varepsilon} \pm 1} d\varepsilon = \underbrace{\frac{3}{2} NkT \left(\frac{T}{T_d}\right)^{3/2} \lambda \int_0^\infty \frac{x^{3/2}}{e^x \pm \lambda} dx}_{PV}$$

$$\begin{cases} x = \beta\varepsilon = \varepsilon/kT \\ d\varepsilon = kT\, dx \\ \varepsilon^{3/2} = (kT)^{3/2} x^{3/2} \end{cases}$$

$$PV = NkT \left(\frac{T}{T_d}\right)^{3/2} \lambda \left[\underbrace{\int_0^\infty x^{3/2} e^{-x} dx}_{\Gamma(5/2)} \mp \lambda \underbrace{\int_0^\infty x^{3/2} e^{-2x} dx}_{\frac{1}{2^{5/2}}\Gamma(5/2)} \right]$$

$$\boxed{\frac{1}{e^x \pm \lambda} = e^{-x} \mp \lambda e^{-2x}}$$

$$PV = NkT \left(\frac{T}{T_d}\right)^{3/2} \Gamma(5/2)\, \lambda \left(1 \mp \frac{\lambda}{2^{5/2}}\right) = NkT\, \cancel{\left(\frac{T}{T_c}\right)^{3/2}} \underbrace{\left(1 \pm \frac{\lambda}{2^{3/2}}\right)\left(1 \mp \frac{\lambda}{2^{5/2}}\right)}$$

$$\boxed{T_c^{3/2} = \frac{T_d^{3/2}}{\Gamma(5/2)}}$$

$$1 \pm \frac{\lambda}{2^{3/2}} \mp \frac{\lambda}{2^{5/2}} = 1 \pm \frac{\lambda}{2^{3/2}} \underbrace{\left(1 - \frac{1}{2}\right)}_{1/2} = 1 \pm \frac{\lambda}{2^{5/2}}$$

$$\boxed{PV = NkT \left(1 \pm \frac{\lambda}{2^{5/2}}\right)} \qquad \boxed{T > T_c}$$

$$\lambda \simeq \left(\frac{T_c}{T}\right)^{3/2} \implies \boxed{PV = NkT \left[1 \pm \frac{1}{2^{5/2}} \left(\frac{T_c}{T}\right)^{3/2}\right]}$$

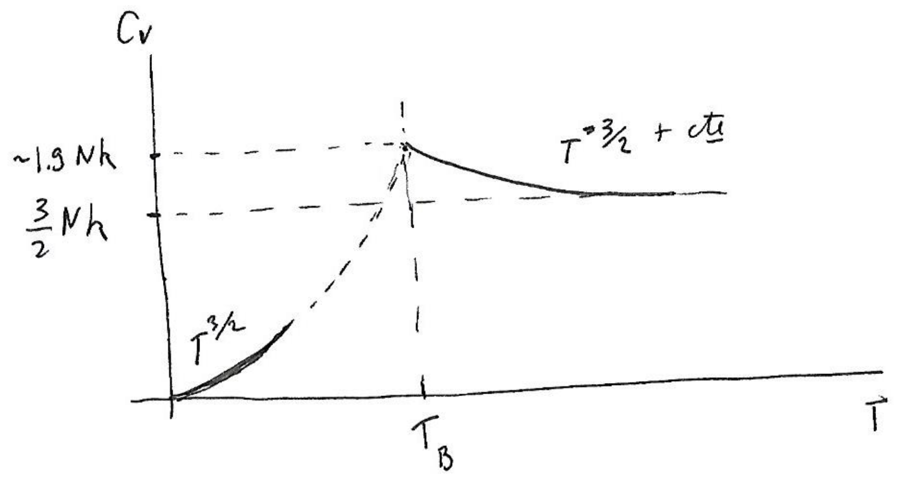
(+) férmions

(−) bósons

bósons massivos não-relativísticos ligeiramente degenerados

$$U = \frac{3}{2} NkT \left[1 - \frac{1}{2^{5/2}} \left(\frac{T_c}{T}\right)^{3/2} \right] = \frac{3}{2} NkT \left[1 - \frac{\overbrace{\zeta(3/2)}^{2.612}}{\underbrace{2^{5/2}}_{5,657}} \left(\frac{T_B}{T}\right)^{3/2} \right] \qquad T_B = \frac{T_c}{\left[\zeta(3/2)\right]^{2/3}}$$

$$\begin{cases} U = \frac{3}{2} NkT \left[1 - 0.462 \left(\frac{T_B}{T}\right)^{3/2} \right] & \text{(Einstein - 1924)} \qquad \left[- 0.0225 \left(\frac{T_B}{T}\right)^{3} \right] \\ C_v = \frac{3}{2} Nk \left[1 + 0.231 \left(\frac{T_B}{T}\right)^{3/2} \right] & (T > T_B) \qquad \left[+ 0.045 \left(\frac{T_B}{T}\right)^{3} \right] \end{cases}$$



gases não-degenerados $(\lambda \ll 1)$ $(T \gg T_c)$ $\lambda = e^{\mu/kT}$

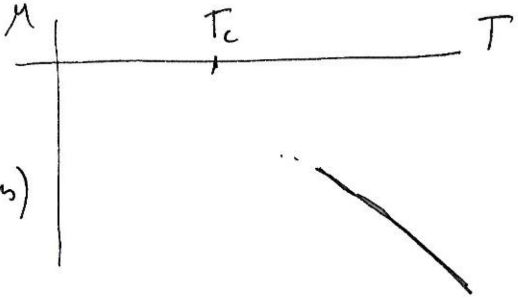
$$PV = NkT \underbrace{\left(\frac{T}{T_c}\right)^{3/2}}_{\approx 1} \lambda \implies \ln Z_G = N \left(\frac{T}{T_c}\right)^{3/2} e^{\mu/kT} \implies \left(\frac{\partial \ln Z_G}{\partial T}\right)_{\mu,V} = \frac{N\lambda}{T_c^{3/2}} \left(\frac{3}{2} T^{1/2} - \frac{\mu}{kT^2} T^{3/2}\right)$$

$$S = k \ln Z_G + kT \left(\frac{\partial \ln Z_G}{\partial T}\right)_{\mu,V} = Nk \underbrace{\left(\frac{T}{T_c}\right)^{3/2}}_{\approx 1} \lambda \left(\underbrace{1 + \frac{3}{2}}_{5/2} - \frac{\mu}{kT}\right) = Nk\left(\frac{5}{2} - \frac{\mu}{kT}\right)$$

$$\lambda = \left(\frac{T_c}{T}\right)^{3/2} = e^{\mu/kT} \implies \frac{\mu}{kT} = \frac{3}{2} \ln \frac{T_c}{T} \implies \boxed{\mu = -\frac{3}{2} kT \ln \frac{T}{T_c} < 0} \quad (T \gg T_c)$$

$$S = Nk\left(\frac{3}{2} \ln \frac{T}{T_c} + \frac{5}{2}\right) \qquad T_c = \left(\frac{h^2}{2\pi m k}\right)\left(\frac{N}{V}\right)^{2/3}$$

$f = 1$ (gases moleculares)



$$\boxed{S = Nk\left[\frac{3}{2} \ln T + \ln \frac{V}{N} + \frac{5}{2} + \frac{3}{2} \ln\left(\frac{2\pi m k}{h^2}\right)\right]} \quad (T \gg T_c)$$

(Sackur-Tetrode)

$$T_c^{3/2} = \frac{T_d^{3/2}}{\Gamma(5/2)} = \frac{T_d^{3/2}}{\frac{3}{2}\underbrace{\Gamma(3/2)}_{\sqrt{\pi}/2}} = \frac{T_d^{3/2}}{\frac{3}{4}\sqrt{\pi}}$$

$$T_d^{3/2} = \left(\frac{3}{4\pi f}\right)\left(\frac{N}{V}\right)\left(\frac{h^2}{2mk}\right)^{3/2} \implies T_c^{3/2} = \left(\frac{h^2}{2\pi m k}\right)^{3/2}\left(\frac{N}{fV}\right)$$