4302401 – Mecânica Estatística

Gás Ideal Monoatômico – II

Referências: Reif, Sec. 2.5
Salinas, Sec. 4.4

Gás Monoatômico: Número de Microestados

– **Energia**. Por definição, no gás ideal não interações entre as partículas (átomos):

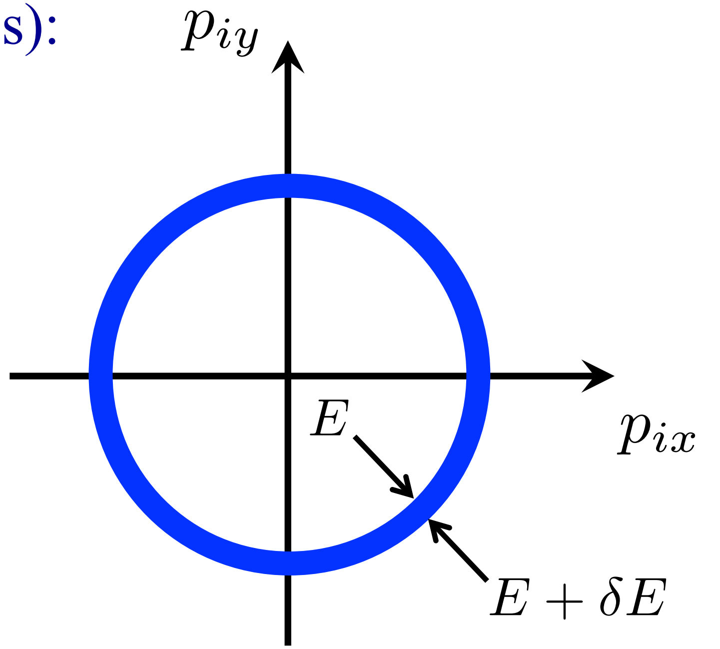
$$E = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} = \sum_{i=1}^{N} \left[\frac{1}{2m} (p_{ix}^2 + p_{iy}^2 + p_{iz}^2) \right] = \sum_{i=1}^{N} \sum_{\alpha=1}^{3} \frac{1}{2m} p_{i\alpha}^2$$

– Gás monoatômico com volume V energia entre E e $E + \delta E$:

$$\Omega(E) \propto \mathcal{V} = \overbrace{\int d^3\mathbf{r}_1 \cdots \int d^3\mathbf{r}_N}^{= V \times V \cdots \times V = V^N} \underbrace{\int d^3\mathbf{p}_1 \cdots \int d^3\mathbf{p}_N}_{\text{em } 2mE \leq \sum_{i=1}^{N} \sum_{\alpha=1}^{3} p_{i\alpha}^2 \leq 2m(E+\delta E)}$$

ii) As componentes Cartesianas de momento linear ($p_{i\alpha}$) estão restritas a uma casca hiperesférica (3N-dimensional), entre os raios $R = (2mE)^{1/2}$ e $R' = [2m(E+\delta E)]^{1/2}$. A figura abaixo ilustra o caso bidimensional (1 partícula em 2 dimensões):

$$2mE = \sum_{i=1}^{N} \sum_{\alpha=1}^{3} p_{i\alpha}^2$$



– Número de Microestados:

$$\Omega(E) \propto \mathcal{V} = \overbrace{\int d^3\mathbf{r}_1 \cdots \int d^3\mathbf{r}_N}^{= V \times V \cdots \times V = V^N} \underbrace{\int d^3\mathbf{p}_1 \cdots \int d^3\mathbf{p}_N}$$

$$\text{em } 2mE \leq \sum_{i=1}^{N} \sum_{\alpha=1}^{3} p_{i\alpha}^2 \leq 2m(E + \delta E)$$

Gás Monoatômico: Equação de Estado

$$\boxed{\Omega(N,V,E) \;=\; \frac{3N}{2}\,\frac{C_{3N}}{h_0^{3N}}\,(2m)^{\frac{3N}{2}}\;E^{\left(\frac{3N}{2}-1\right)}\,V^N\delta E}$$

– Iremos reescrever a expressão acima na forma abaixo (N>>1):

$$\Omega(N,V,E) \;=\; B(N,E)\,V^N\,\delta E$$

$$\frac{1}{N}\ln[\Omega(E)] \;=\; \frac{1}{N}\ln[B(E,N)] \;+\; \underbrace{\left[\ln(V)+\frac{1}{N}\ln(\delta E)\right]}_{=\,\ln(V)\;,\;\;\text{pois}\;\;N\sim 10^{23}}$$

$$=\;\frac{1}{N}\ln[B(E,N)] \;+\; \ln(N) + \underbrace{\ln(v)}_{v=V/N}$$

Tomando o limite termodinâmico:

$$\beta p = \lim_{N\to\infty;\frac{V}{N}=v} \frac{1}{N} \frac{\partial \ln[\Omega(N,V,E)]}{\partial v}$$

$$= \frac{1}{v}$$

$$\boxed{pV = Nk_BT = \left(\frac{N}{N_A}\right)(k_BN_A)T = nRT}$$

Gás Monoatômico: Energia Interna e Calor Específico

– Vamos reescrever o número de microestados:

$$\Omega(N,V,E) \;=\; B'(V,N)\, E^{\frac{3N}{2}}\; \frac{\delta E}{E}$$

$$\ln[\Omega(N,V,E)] \;=\; \ln[B'(V,N)] \;+\; \frac{3}{2}\ln(E) \;+\; \ln\left(\frac{\delta E}{E}\right)$$

$$\frac{1}{N}\ln[\Omega(N,V,E)] \;=\; \frac{1}{N}\ln[B'(V,N)] \;+\; \frac{3}{2}\ln(N) \;+\; \frac{3}{2}\ln(u)$$

$$+\underbrace{\frac{1}{N}\ln\left(\frac{\delta u}{u}\right)}_{\longrightarrow 0}$$

Tomando o limite termodinâmico:

$$\beta = \lim_{N\to\infty;\frac{E}{N}=u} \frac{1}{N}\frac{\partial \ln[\Omega(N,V,E)]}{\partial u}$$

$$= \frac{3}{2u}$$

$$E(T) = \frac{3}{2}Nk_BT = \frac{3}{2}nRT$$

– **Calor específico a volume constante (c_V).** Uma vez que $dW = 0$, temos $dE = dQ$:

$$c_V = \underbrace{\frac{1}{N} \lim_{\Delta T \to 0} \left(\frac{\Delta Q}{\Delta T} \right)_{N,V}}_{\text{(por partícula)}} = \frac{1}{N} \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{3}{2} k_B$$

$$C_V = \underbrace{\frac{1}{n} \lim_{\Delta T \to 0} \left(\frac{\Delta Q}{\Delta T} \right)_{N,V}}_{\text{(por mol)}} = \frac{1}{n} \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{3}{2} R$$

$$C_V = N_A c_V$$

Gás Monoatômico: Entropia

$$\Omega(N,V,E) \;=\; \frac{3N}{2}\,\frac{C_{3N}}{h_0^{3N}}\,(2m)^{\frac{3N}{2}}\;E^{\left(\frac{3N}{2}-1\right)}\;V^N\delta E$$

$$\ln[\Omega(N,V,E)] = \;\ln\left(\frac{3N}{2}C_{3N}\right)\;+\;\frac{3N}{2}\ln\left(\frac{2m}{h_0^2}\right)\;+$$

$$+\;\left(\frac{3N}{2}\right)\ln(E)\;+\;N\ln(V)\;+\;\ln\left(\frac{\delta E}{E}\right)$$

$$\frac{1}{N}\ln[\Omega(N,V,E)] = \;\frac{1}{N}\ln\left(\frac{3N}{2}C_{3N}\right)\;+\;\frac{3}{2}\ln\left(\frac{2m}{h_0^2}\right)\;+$$

$$+\;\ln(E^{\frac{3}{2}}V)\;+\;\frac{1}{N}\ln\left(\frac{\delta E}{E}\right)$$

– Em termos das densidades de volume e energia interna:

$$\frac{1}{N}\ln[\Omega(N,V,E)] = \frac{1}{N}\ln\left(\frac{3N}{2}C_{3N}N^{\frac{5N}{2}}\right) + \frac{3}{2}\ln\left(\frac{2m}{h_0^2}\right) + $$

$$+ \ln\left(u^{\frac{3}{2}}v\right) + \frac{1}{N}\ln\left(\frac{\delta u}{u}\right)$$

– Tomando o limite termodinâmico em cada termo:

$$\lim_{N\to\infty;u=\frac{E}{N}} \frac{1}{N}\ln\left(\frac{\delta u}{u}\right) = 0$$

$$\lim_{N\to\infty;u=\frac{E}{N}} \frac{3}{2}\ln\left(\frac{2m}{h_0^2}\right) + \ln\left(u^{\frac{3}{2}}v\right) = \frac{3}{2}\ln\left(\frac{2m}{h_0^2}\right) + \ln\left(u^{\frac{3}{2}}v\right)$$

– Lembrando que $$C_{3N} = \frac{2\,\pi^{\frac{3N}{2}}}{(3N)\,\Gamma\left(\frac{3N}{2}\right)} = \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}$$

teremos:

$$\frac{1}{N}\ln\left(\frac{3N}{2}\,C_{3N}\,N^{\frac{5N}{2}}\right) = \frac{1}{N}\ln\left(\frac{3N}{2}\,\frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}\,N^{\frac{5N}{2}}\right) =$$

$$= \frac{3}{2}\ln(\pi) + \frac{5}{2}\ln(N) + \frac{1}{N}\ln\left(\frac{3N}{2}\right) - \frac{1}{N}\ln\left[\left(\frac{3N}{2}\right)!\right]$$

$$= \frac{3}{2}\left[\ln(\pi) - \ln\left(\frac{3}{2}\right) + 1\right] + \left(\frac{5}{2} - \frac{3}{2}\right)\ln(N) + \frac{1}{N}\ln\left(\frac{3N}{2}\right)$$

$$= \frac{3}{2}\ln\left(\frac{2\pi e}{3}\right) + \ln(N) + \frac{1}{N}\ln\left(\frac{3N}{2}\right)$$

$$\lim_{N\to\infty} \frac{1}{N} \ln\left(\frac{3N}{2} C_{3N} N^{\frac{5N}{2}}\right) = \lim_{N\to\infty} \left[\frac{3}{2} \ln\left(\frac{2\pi e}{3}\right) + \right.$$

$$\left. + \underbrace{\frac{1}{N} \ln\left(\frac{3N}{2}\right)}_{\longrightarrow 0} + \underbrace{\ln(N)}_{\longrightarrow \infty}\right] \longrightarrow \infty$$

– Ainda que nos conformássemos com *N* grande mas finito ($\sim 10^{23}$), haveria o problema da extensividade:

$$s_0' = \frac{3k_B}{2} \ln\left(\frac{4\pi m e}{3h_0^2}\right)$$

$$s(N,V,E) = s_0' + k_B \left[\frac{3}{2} \ln(u) + \ln(v) + \ln(N)\right]$$

$$s(\alpha N, \alpha V, \alpha E) \neq s(N,V,E)$$

$$S(\alpha N, \alpha V, \alpha E) \neq \alpha S(N,V,E)$$

– Esse problema é relacionado ao **Paradoxo de Gibbs**, e a seguir apresentaremos o **Fator de Correção de Boltzmann**. Vamos retomar o desenvolvimento anterior e perceber que:

$$\frac{1}{N}\ln\left(\frac{3N}{2}C_{3N}\,N^{\frac{5N}{2}}\right) = \frac{1}{N}\ln\left(\frac{3N}{2}\frac{\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!}\,N^{\frac{5N}{2}}\times\frac{1}{N!}\right) =$$

$$= \frac{3}{2}\ln(\pi) + \frac{5}{2}\ln(N) + \frac{1}{N}\ln\left(\frac{3N}{2}\right) - \frac{1}{N}\ln\left[\left(\frac{3N}{2}\right)!\,N!\right]$$

$$= \frac{3}{2}\left[\ln(\pi) - \ln\left(\frac{3}{2}\right) + \frac{5}{3}\right] + \left(\frac{5}{2} - \frac{3}{2} - 1\right)\ln(N) + \frac{1}{N}\ln\left(\frac{3N}{2}\right)$$

$$= \frac{3}{2}\ln\left(\frac{2\pi}{3}\right) + \frac{5}{2} + \underbrace{\frac{1}{N}\ln\left(\frac{3N}{2}\right)}_{\longrightarrow 0}$$

– A correção abaixo torna a entropia extensiva no limite termodinâmico:

$$C_{3N} \longrightarrow \frac{C_{3N}}{N!} \quad \text{ou} \quad \Omega \longrightarrow \frac{\Omega}{N!}$$

$$\boxed{s(N,V,E) \;=\; s_0 + k_B \left[\frac{3}{2}\ln(u) + \ln(v)\right]}$$

$$s_0 \;=\; k_B \left[\frac{3}{2}\ln\left(\frac{4\pi m}{3h_0^2}\right) + \frac{5}{2}\right]$$

$$s(\alpha N, \alpha V, \alpha E) \;=\; s(N,V,E)$$

$$S(\alpha N, \alpha V, \alpha E) \;=\; \alpha S(N,V,E)$$