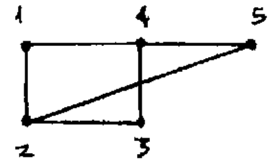
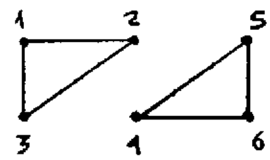
Serie 8: Gases reales

1.

a) $f_{12} \cdot f_{23} \cdot f_{34} \cdot f_{45} \cdot f_{14} \cdot f_{25}$



b) $f_{12} \cdot f_{23} \cdot f_{13} \cdot f_{45} \cdot f_{46} \cdot f_{56}$



2.

$$Z_{GC} = e^{\sum_\ell b_\ell z^\ell \frac{V}{\lambda^3}}$$

$$\ln Z_{GC} = \sum_\ell b_\ell z^\ell \frac{V}{\lambda^3}$$

$$\frac{PV}{kT} = \sum_\ell b_\ell z^\ell \frac{V}{\lambda^3} \quad \Rightarrow \quad \frac{P}{kT} = \frac{1}{\lambda^3} \sum_\ell b_\ell z^\ell$$

$$N = \sum_\ell b_\ell z^\ell \frac{V}{\lambda^3} \ell \quad \Rightarrow \quad \frac{N}{V} = \frac{1}{\lambda^3} \sum_\ell b_\ell \, \ell \, z^\ell$$

En el límite termodinámico será:

$$\begin{cases} \dfrac{P}{kT} = \dfrac{1}{\lambda^3} \sum_\ell \bar{b}_\ell z^\ell \\ \dfrac{1}{v} = \dfrac{1}{\lambda^3} \sum_\ell \bar{b}_\ell \, \ell \, z^\ell \end{cases}$$

$$z = \sum_\ell^\infty c_\ell \left(\frac{1}{v}\right)^\ell \qquad \text{donde} \quad c_\ell = \lambda^3 K \quad \text{para que sea adimensional } z$$

$$\frac{P}{kT} = \frac{1}{\lambda^3} \sum_\ell^\infty \bar{b}_\ell \left(\sum_k^\infty c_k \left(\frac{1}{v}\right)^k \right)^\ell = \sum_\ell^\infty \bar{b}_\ell \left(\sum_k c_k \left(\frac{1}{v}\right)^{k-1} \frac{N}{V} \right)^\ell \frac{1}{\lambda^3}$$

hasta O_2 en k y ℓ

$$\frac{P}{kT} = \left\{ \bar{b}_1 \left(c_1 + c_2 \left[\frac{1}{v}\right] \right) \frac{N}{V} + \bar{b}_2 \left(c_1 + c_2 \left[\frac{1}{v}\right] \right)^2 \left(\frac{N}{V}\right)^2 \right\} \frac{1}{\lambda^3}$$

$$\frac{PV}{NkT} = \left\{ \bar{b}_1 c_1 + \bar{b}_1 c_2 \left(\frac{1}{v}\right) + \frac{\bar{b}_2}{v} \cdot \left(c_1^2 + 2 c_1 c_2 \left(\frac{1}{v}\right) + c_2^2 \left(\frac{1}{v}\right)^2 \right) \right\} \frac{1}{\lambda^3}$$

$$\frac{PV}{NkT} = \frac{Pv}{kT} = \underbrace{\bar{b}_1 c_1 \frac{1}{\lambda^3}}_{B_1} + \underbrace{\left[\frac{\bar{b}_1 c_2 + \bar{b}_2 c_1^2}{\lambda^3}\right]}_{B_2} \left(\frac{1}{v}\right) + \bar{b}_2 \frac{2 c_1 c_2}{\lambda^3} \left(\frac{1}{v}\right)^2 + \cdots$$

$$\Rightarrow \quad \frac{Pv}{kT} = \sum_{\ell=1}^\infty B_\ell \left(\frac{1}{v}\right)^{\ell-1}$$

$$\frac{PV}{NkT} = \sum_{l=1}^{\infty} B_l \left(\frac{1}{v}\right)^{l-1}$$

$$\frac{P}{kT} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l$$

$$\frac{1}{v} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l . l . z^l \rightarrow \int_0^z \frac{1}{v} . \frac{dz}{z} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l \, l \int_0^z z^{l-1} dz$$

$$\int_0^z \frac{1}{v} \cdot \frac{dz}{z} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l \quad z^l$$

$l+1 = j$

$$\int_0^z \frac{1}{v} \frac{dz}{z} = \frac{P}{kT}$$

$$\int_0^z \frac{1}{v} \frac{dz}{z} = \int_0^z \sum_{l=1}^{\infty} b_l . \frac{l . z^{l-1}}{\lambda^3} . dz = \frac{P}{kT}$$

$$E = -\frac{\partial}{\partial \beta}\left(\frac{PV}{kT}\right) = -\frac{\partial T}{\partial \beta} \frac{\partial}{\partial T}\left(\frac{PV}{kT}\right) = kT^2 \frac{\partial}{\partial T}\left(\frac{PV}{kT}\right) = NkT^2 \sum_{l=1}^{\infty} \frac{\partial B_l}{\partial T}\left(\frac{1}{v}\right)^{l-1}$$

$$\frac{3/2\, PV}{NkT} = T \sum_{l=1}^{\infty} \frac{\partial B_l}{\partial T}\left(\frac{1}{v}\right)^{l-1}$$

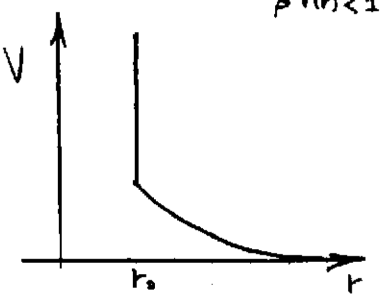
$$\frac{P}{kT} = \frac{T}{v} \frac{2}{3} \sum_{l=1}^{\infty} \frac{\partial B_l}{\partial T}\left(\frac{1}{v}\right)^{l-1}$$

$$\frac{PV}{NkT} = \frac{2}{3} \sum_{l=1}$$

$$\frac{3/2\, PV}{NkT} = T \frac{\partial B}{\partial T} + \frac{2}{3} \sum_{l=1}$$

3.

$$\left\{\begin{array}{ll} V(r) = \infty & r < r_0 \\ e^{-\beta V(r)} \underset{\beta V(r) < 1}{\approx} 1 - \beta V(r) & r > r_0 \end{array}\right\} \leftarrow \text{Van der Waals aproximation}$$



$$Z_{GC} = e^{\sum_{\ell=1}^{\infty}\left(b_\ell z^\ell \frac{V}{\lambda^3}\right)}$$

Donde b_ℓ es la integral configuracional para los ℓ-clusters

$$[①] \quad b_1 = \frac{1}{1!\,\lambda^{3(0)}\,V}\int_0^\infty d^3r_1\, f_{11} = 1$$

$$[①—②] \quad b_2 = \frac{1}{2.\lambda^3.V}\int_0^\infty d^3r_1\, d^3r_2\, f_{12} \simeq \frac{1}{2\lambda^3}\int d^3r\, f(r)\, r^2$$

$$b_2 \approx \frac{2\pi}{\lambda^3}\int_0^\infty r^2\, dr\, f_{12}$$

$$f_{ij} = e^{-\beta V_{ij}} - 1$$

$$f_{ij} = \begin{cases} -1 & r < r_0 \\ -\beta V(r) & r > r_0 \end{cases}$$

$$\ln Z_{GC} = \sum_{\ell=1}^{\infty} b_\ell z^\ell \frac{V}{\lambda^3}$$

$$\frac{PV}{kT} = \ln Z_{GC} = \sum_{\ell=1}^{\infty} b_\ell z^\ell \frac{V}{\lambda^3} \rightarrow \frac{P}{kT} = \frac{1}{\lambda^3}\sum_{\ell=1}^{\infty} b_\ell z^\ell$$

$$\frac{P\lambda^3}{kT} = \sum_{\ell=1}^{\infty} a_\ell \left(\frac{\lambda^3}{v}\right)^\ell \qquad \lim_{\substack{V\to\infty \\ N\to\infty}}\left(\frac{P}{kT}\right) = \sum_{\ell=1}^{\infty} b_\ell \frac{z^\ell}{\lambda^3}$$

$$\frac{Pv}{kT} = \sum_{\ell=1}^{\infty} a_\ell \left(\frac{\lambda^3}{v}\right)^{\ell-1}$$

$$\frac{N}{V} = \sum_{\ell=1}^{\infty} b_\ell \frac{z^\ell}{\lambda^3}\,\ell \Rightarrow \lim_{\substack{V\to\infty \\ N\to\infty}} \frac{1}{v} = \frac{1}{\lambda^3}\sum_{\ell=1}^{\infty} b_\ell z^\ell\,\ell$$

Podemos invertir la serie y despejar: $z = \sum_{\ell=1}^{\infty} c_\ell \left(\frac{\lambda^3}{v}\right)^\ell$

$$\mathcal{O}_1: \quad \frac{\lambda^3}{v} = b_1 1 z \qquad z = c_1 \frac{\lambda^3}{v}$$

$$\mathcal{O}_2: \quad \frac{\lambda^3}{v} = b_1 z + b_2 2 z^2 \qquad z = c_1 \frac{\lambda^3}{v} + c_2\left(\frac{\lambda^3}{v}\right)^2$$

hasta $\mathcal{O}_2$ es: $\frac{P\lambda^3}{kT} = b_1 z + b_2 z^2 = b_1 c_1 \frac{\lambda^3}{v} + b_1 c_2 \left(\frac{\lambda^3}{v}\right)^2 + b_2\left(c_1 \frac{\lambda^3}{v} + c_2\left[\frac{\lambda^3}{v}\right]^2\right)^2$

$$\frac{P\lambda^3}{kT} = b_1 c_1 \frac{\lambda^3}{v} + b_1 c_2\left(\frac{\lambda^3}{v}\right)^2 + b_2 c_1^2\left(\frac{\lambda^3}{v}\right)^2 + b_2 c_2^2\left(\frac{\lambda^3}{v}\right)^4 + b_2 2 c_1 c_2\left(\frac{\lambda^3}{v}\right)^3$$

$$\frac{Pv}{kT} = b_1 c_1 + b_1 c_2\left(\frac{\lambda^3}{v}\right) + b_2 c_1^2\left(\frac{\lambda^3}{v}\right) + b_2 c_2^2\left(\frac{\lambda^3}{v}\right)^3 + b_2 2 c_1 c_2\left(\frac{\lambda^3}{v}\right)^2$$

$$\Rightarrow a_1 = b_1 c_1 \qquad \Rightarrow a_2 = b_1 c_2 + b_2 c_1^2$$

$$\frac{\lambda^3}{v} = \bar{b}_1 c_1 \left(\frac{\lambda^3}{v}\right) + \bar{b}_1 c_2 \left(\frac{\lambda^3}{v}\right)^2 + 2\bar{b}_2 \left(\frac{\lambda^3}{v}\right)^2 c_1^2 + 2\bar{b}_2 c_2^2 \left(\frac{\lambda^3}{v}\right)^4 + 4\bar{b}_2 c_1 c_2 \left(\frac{\lambda^3}{v}\right)^3$$

$$0 = \underbrace{(\bar{b}_1 c_1 - 1)}_{=0} \frac{\lambda^3}{v} + \underbrace{\left[\bar{b}_1 c_2 + 2\bar{b}_2 c_1^2\right]}_{=0} \left(\frac{\lambda^3}{v}\right)^2 + \dots$$

$$\bar{b}_1 c_1 = 1 \qquad c_2 = \frac{-2\bar{b}_2 c_1^2}{\bar{b}_1} = -2\bar{b}_2$$

$$c_1 = 1$$

$$\boxed{a_1 = \bar{b}_1}$$

$$a_2 = c_2 + \bar{b}_2 = -\bar{b}_2 \qquad \boxed{a_2 = -\bar{b}_2}$$

2^{do} coeficiente del virial

$$B_2 = -\bar{b}_2 \lambda^3$$

$$E - E_{ideal} = -NkT^2 \sum_{l=1}^{\infty} \frac{1}{l} \frac{\partial B_{l+1}}{\partial T} \left(\frac{1}{v}\right)^l$$

$$E - E_{ideal} = -NkT^2 \frac{\partial B_2}{\partial T} \left(\frac{1}{v}\right)$$

$$\bar{b}_2 = \lim_{V\to\infty} b_2 = \lim_{V\to\infty} \frac{1}{2\lambda^3} \int_0^\infty dr\, f_{12} = \frac{2\pi}{\lambda^3} \int_0^\infty dr \left(e^{-\beta V(r)} - 1\right) r^2$$

$$-\bar{b}_2 \lambda^3 = 2\pi \int_0^\infty \left(1 - e^{-\beta V(r)}\right) r^2 \, dr$$

$$B_2 = 2\pi \left(\int_0^{r_0} r^2 \, dr + \int_{r_0}^\infty \left(1 - e^{-\beta V(r)}\right) r^2 dr \right)$$

$$B_2 = 2\pi \left(\frac{r_0^3}{3} + \int_{r_0}^\infty \left(1 - e^{-\beta V}\right) r^2 dr \right)$$

$$\frac{\partial B_2}{\partial T} = 2\pi \int_{r_0}^\infty -e^{-\beta V} \frac{+V}{kT^2} r^2 dr = \frac{-2\pi}{kT^2} \int_{r_0}^\infty e^{-\beta V(r)} V(r)\, r^2 dr$$

$$E - E_{ideal} = -Nk\cancel{T^2} \cdot \frac{N}{V} \frac{(-2\pi)}{\cancel{kT^2}} \int_{r_0}^\infty e^{-\beta V(r)} V(r) r^2 dr$$

$$= \frac{N^2}{2} \frac{4\pi}{V} \int_{r_0}^\infty e^{-\beta V(r)} V(r)\, r^2 dr$$

$$\boxed{E - E_{ideal} = n_{pares} \langle V(r) \rangle}$$

4.

$$S \sim S_{ideal} - Nk\,\frac{\partial(TB_2)}{\partial T}\cdot\frac{N}{V}$$

$$\frac{\partial(TB_2)}{\partial T} = T\cdot\frac{\partial B_2}{\partial T} + B_2 =$$

$$\frac{\partial(T.B_2)}{\partial T} = T\left(\frac{+2\pi}{kT^2}\right)\int_{r_0}^{\infty} V(r)\,r^2.dr + 2\pi\left(\frac{r_0^3}{3} - \int_{r_0}^{\infty}\beta.V(r)\,r^2.dr\right)$$

$$-Nk\,\frac{\partial(TB_2)}{\partial T}\cdot\frac{N}{V} = -\left(\beta 2\pi\cancel{\int_{r_0}^{\infty} V(r)\,r^2.dr} + \frac{2\pi r_0^3}{3} - \beta 2\pi\cancel{\int_{r_0}^{\infty} V(r).r^2.dr}\right)\frac{1}{v}Nk$$

$$S - S_{ideal} \approx -Nk\,\frac{1}{v}\,\frac{2\pi}{3}r_0^3 = -\frac{N^2k}{V}\,\frac{2\pi r_0^3}{3} < 0 \Rightarrow$$

$$S - S_{ideal} < 0 \quad\Rightarrow\quad \boxed{S < S_{ideal}}$$

5.

$$B_2(T) = 2\pi\int_0^{\infty}(1 - e^{-\beta V})\,r^2.dr$$

$$B_2(T) = 2\pi\Big[\underbrace{\int_0^{L}(1-e^{-\beta V})\,r^2.dr}_{①} + \underbrace{\int_L^{\infty}(1-e^{-\beta V})\,r^2.dr}_{②}\Big]$$

Sea ahora $L \ggg 1$ y $V(r) \lll 1$

Como $V(r) = \frac{q}{r^3} \rightarrow 1 - e^{-\beta V} \approx \beta V + \frac{(\beta V)^2}{2} \Rightarrow$ a $\mathcal{O}(1)$ es

$$1 - e^{-\beta V} \sim \frac{q}{kTr^3}$$

$$\int_L^{\infty}\frac{q}{kTr^3}\,r^2dr = \frac{q}{kT}\int_L^{\infty}\frac{1}{r}.dr = \frac{q}{kT}\ln(r)\Big|_L^{M\to\infty} = \frac{q}{kT}\ln\left(\frac{M}{L}\right) \not< \infty$$

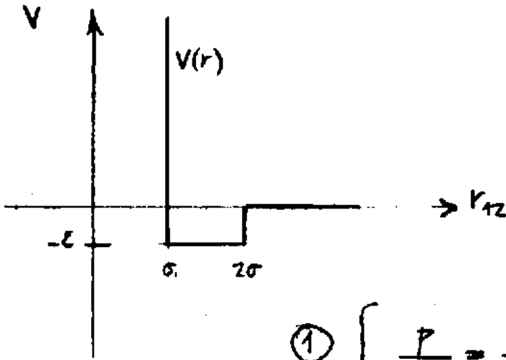
$\Rightarrow$ No está acotada

La integral ② no converge con $V(r) \propto r^{-3}$

La integral ① converge porque el integrando se comporta bien y el dominio es finito.

6.

$$V(r_{12}) = \begin{cases} \infty & 0 \leq r_{12} < \sigma \\ -\varepsilon & \sigma \leq r_{12} \leq 2\sigma \\ 0 & 2\sigma \leq r_{12} \end{cases}$$



gas con N moléculas

$$\frac{Pv}{kT} = \sum_{l=1}^{\infty} B_l \left(\frac{1}{v}\right)^{l-1}$$

$$\begin{cases} ① & \dfrac{P}{kT} = \dfrac{1}{\lambda^3} \sum_l b_l z^l \\ ② & \dfrac{1}{v} = \dfrac{1}{\lambda^3} \sum_l b_l l z^l \end{cases}$$

Invertimos la serie (2) $\rightarrow$ $z = \sum_{l=1}^{\infty} c_l \left(\frac{1}{v}\right)^l$

O_2: $\quad \frac{1}{v} = \frac{1}{\lambda^3}\left(b_1 z + b_2 2 z^2\right) \qquad z = c_1\left(\frac{1}{v}\right) + c_2\left(\frac{1}{v}\right)^2$

$$z = \frac{c_1}{\lambda^3}\left(b_1 z + b_2 2 z^2\right) + \frac{c_2}{(\lambda^3)^2}\left(b_1^2 z^2 + b_2^2 4 z^4 + 4 b_1 z^3 b_2\right)$$

$$z = \underbrace{\left[\frac{c_1}{\lambda^3} b_1\right]}_{=1} z + \underbrace{\left[\frac{c_1}{\lambda^3} b_2 2 + \frac{c_2}{(\lambda^3)^2} b_1^2\right]}_{=0} z^2$$

$$c_1 = \frac{\lambda^3}{b_1} = \lambda^3 \qquad c_2 = -\frac{c_1 b_2 2 (\lambda^3)^2}{\cancel{\lambda^3}\, b_1^2}$$

$$c_2 = -\frac{(\lambda^3)^2 b_2 2}{b_1^3} = -2 b_2 (\lambda^3)^2$$

Usamos resultados problema 2

$$B_2 = \frac{b_1 c_2 + b_2 c_1^2}{\lambda^3} = \frac{-2b_2(\lambda^3)^2 + b_2(\lambda^3)^2}{\lambda^3} = -b_2 \lambda^3 = a_2 \lambda^3$$

$$B_2 = -b_2\lambda^3 \simeq -\cancel{\lambda^3}\left(\frac{2\pi}{\cancel{\lambda^3}} \int_0^{\infty} r^2 f(r)\, dr\right)$$

$$f_{12} = \begin{cases} -1 & 0 \leq r \leq \sigma \\ e^{+\beta\varepsilon} - 1 & \sigma \leq r \leq 2\sigma \\ 0 & 2\sigma < r \end{cases}$$

$$B_2 = -2\pi\left[\int_0^{\sigma} -r^2 dr + \int_{\sigma}^{2\sigma} r^2 (e^{\beta\varepsilon} - 1)\, dr\right]$$

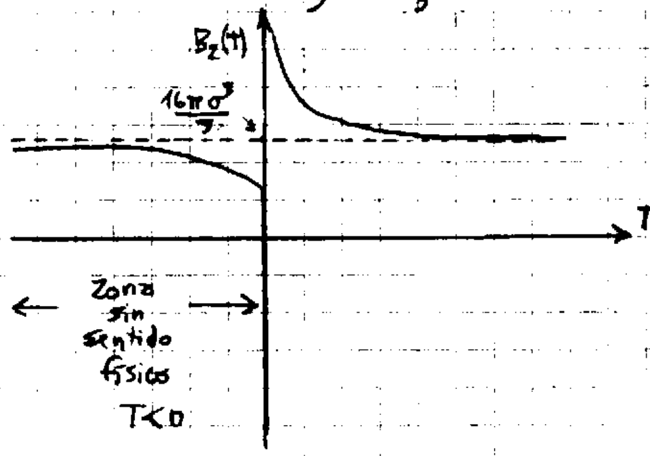
$$B_2 = -2\pi\left(-\frac{r^3}{3}\Big|_0^{\sigma} + \frac{r^3}{3}\Big|_{\sigma}^{2\sigma}(e^{\beta\varepsilon} - 1)\right)$$

$$\boxed{B_2 = -2\pi\left(\frac{1}{3}\left[-\sigma^3 + (e^{\beta\varepsilon} - 1)\, 7\sigma^3\right]\right)}$$

b)

$$B_2(T) = -\frac{2\pi}{3}\sigma^3\left[-1 + 7e^{\beta\varepsilon} - 7\right] = -\frac{2\pi\sigma^3}{3}\left(-8 + 7e^{\beta\varepsilon}\right) = \frac{2\pi\sigma^3}{3}\left(8 - 7e^{\beta\varepsilon}\right)$$

$$B_2(T) = \frac{16\pi\sigma^3}{3} - \frac{14\pi\sigma^3}{3}e^{\frac{\varepsilon}{kT}}$$



c)

$$V(\text{esfera } 2\sigma) = \frac{8\cdot 4\pi\sigma^3}{3}$$
$$V(\text{esfera } \sigma) = \frac{4}{3}\pi\sigma^3$$
$$= \frac{7\cdot 4\pi\sigma^3}{3} = \frac{28\pi\sigma^3}{3}$$

El volumen en el cual $V = -\varepsilon$ es $V_0 = \frac{28}{3}\pi\sigma^3 \rightarrow$

Usando el resultado del Problema 2 es $\rightarrow$

$$E - E_{ideal} = -NkT^2\frac{\partial B_2}{\partial T}\frac{1}{v} = -N\cancel{kT^2}\left(-\frac{14\pi\sigma^3}{3}\right)e^{\beta\varepsilon}\frac{-\varepsilon}{\cancel{kT^2}}\frac{1}{v} = \frac{N^2}{2}\left(\frac{28\pi\sigma^3}{3}\right)\frac{1}{V}e^{\beta\varepsilon}(-\varepsilon)$$

$$\boxed{E - E_{ideal} = n\left(\frac{V_0}{V}\right)e^{\beta\varepsilon}(-\varepsilon)}$$

donde $n \equiv$ el número de pares es $\frac{N^2}{2}$

d)