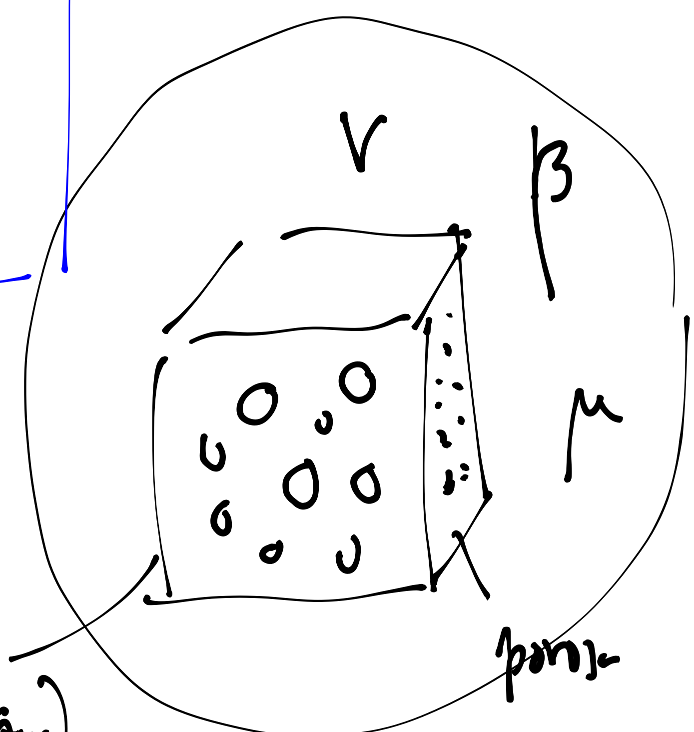
Ensemble gran canónico (cont.):

mié. 28 oct. 2020.

clase 12

- Para e.gr.

$$\boxed{\rho_{gc} = \frac{e^{-\beta(\mathcal{H}\,\underline{x},\,\mu N)}}{\mathcal{Z}(\beta,\mu)}}$$



$$\rho_{gc} = \rho_{gc}(q, p; N)$$

$q = (\vec{q}_1 \ldots q_N)$

$p = (p_1 \ldots p_N)$

∂ N partículas.

-

$$\Phi = \Phi(T, V, \mu)$$

$$\boxed{\Phi = -kT \ln \mathcal{Z}(T, V, \mu)}$$

$$\langle N \rangle = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \quad ; \quad -S = \left(\frac{\partial \Phi}{\partial T}\right) \quad \ldots$$

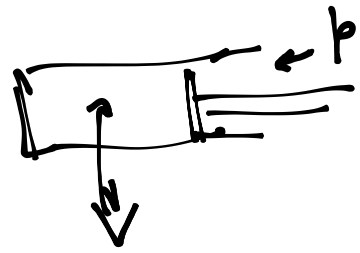
Ejemplos:

Prob. 2, Guía 5 — Muestre que en ensemble g.c. la compresibilidad isotérmica K_T es

$$K_T = \frac{v}{\langle N\rangle k_B T}\left(\langle N^2\rangle - \langle N\rangle^2\right) ; \quad v = \frac{V}{N}$$

$$K_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right) = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

• Y particularice al caso del gas ideal.



$$\frac{\Delta V}{\Delta p} \qquad pV = N k_B T$$

Sol: Obtengamos $\langle N\rangle$ y $\langle N^2\rangle$

$$\mathcal{Z} = \sum_{N,i} e^{-\beta(E_i - \mu N)} : \sum_N \int d\Gamma\, e^{-\beta(\mathcal{H} - \mu N)}$$

$$\langle N\rangle = -\frac{\partial \Phi}{\partial \mu} = \frac{kT}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu} \quad ; \text{ pues } \Phi = -kT\ln \mathcal{Z}$$

$$\langle N^2\rangle = \frac{1}{\mathcal{Z}}\sum_{i,N} N^2 e^{-\beta(E_i - \mu N)} = \frac{(kT)^2}{\mathcal{Z}}\frac{\partial^2}{\partial \mu^2}\mathcal{Z}$$

usando que $kT \frac{\partial \mathcal{Z}}{\partial \mu} = \mathcal{Z} \langle N \rangle$

$$\Rightarrow \langle N^2 \rangle = \frac{kT}{\mathcal{Z}} \frac{\partial}{\partial \mu}\left(\mathcal{Z}\langle N \rangle\right) = \langle N \rangle^2 + kT \frac{\partial \langle N \rangle}{\partial \mu}$$

$$\therefore \boxed{\langle N^2 \rangle - \langle N \rangle^2 = kT \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V}}$$

- Demostremos que $\frac{\partial \langle N \rangle}{\partial \mu}$ está relacionado con $K_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{T N}$

Eso viene de Termodinámica:

Gibbs-Duhem : $d\mu = v\,dp - s\,dT$

a T = cte : $\left(\frac{\partial \mu}{\partial v}\right)_T = v \frac{\partial p}{\partial v}$

$pV = N k_B T$

$p = \frac{N}{V} k_B T$

- $p = p(T, V, N)$: variables extensivas V, N.

p como func. de variables intensivas : $p = p(T, v)$

$\frac{\partial p}{\partial v}$ se puede calcular como derivada de $\frac{\partial p}{\partial V}$ o $\frac{\partial p}{\partial N}$

$$\left(\frac{\partial p}{\partial N}\right)_{T,V} = \frac{\partial}{\partial N} p(T, V/N) = \frac{\partial}{\partial v} p \frac{\partial v}{\partial N} = -\frac{V}{N^2}\left(\frac{\partial}{\partial v} p\right)_T$$

$$\left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{\partial}{\partial V}\left(p(T, V/N)\right) = \frac{\partial}{\partial v} p \frac{\partial v}{\partial V} = \frac{1}{N}\left(\frac{\partial}{\partial v} p\right)_T$$

Combinando: $\left(\frac{\partial p}{\partial N}\right)_{T,V} = -\frac{V}{N}\left(\frac{\partial p}{\partial V}\right)_{T,V}$

De $(*)$ temos

$$\left(\frac{\partial \mu}{\partial v}\right) = \frac{\partial \mu}{\partial N}\frac{\partial N}{\partial v} = -\frac{N^2}{V}\left(\frac{\partial \mu}{\partial N}\right)_T = v\left(\frac{\partial p}{\partial v}\right)_T$$

$$\Rightarrow -\frac{V}{N^2}\left(\frac{\partial N}{\partial \mu}\right) = \boxed{\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = -K_T}$$

$$\Rightarrow \boxed{K_T = \frac{v}{N}\left(\frac{\partial N}{\partial \mu}\right)_T} \quad \text{: termodinámica.}$$

$$\therefore \langle N^2\rangle - \langle N\rangle^2 = \frac{kT\langle N\rangle}{v} K_T \quad \text{o} \quad \boxed{K_T = \frac{v}{\langle N\rangle k_B T}\left(\langle N^2\rangle - \langle N\rangle^2\right)}$$

▷ Caso gas ideal

$$\frac{\partial \langle N \rangle}{\partial \mu} = \; ? \quad ; \quad \mathcal{Z}_{gi} = \exp\left\{ e^{\beta\mu} V \left(\frac{2 m k_B T}{h^2} \right)^{3/2} \right\} \rightarrow \exp(e^{\beta\mu} Z_1)$$

$$\langle N \rangle = -\frac{\partial \phi}{\partial \mu} = kT \frac{\partial}{\partial \mu} \ln \mathcal{Z} \overset{\text{gas ideal}}{=} e^{\beta\mu} V \left(\frac{2 m k_B T}{h^2} \right)^{3/2}$$

luego $\displaystyle \frac{\partial \langle N \rangle}{\partial \mu} = \beta \langle N \rangle$

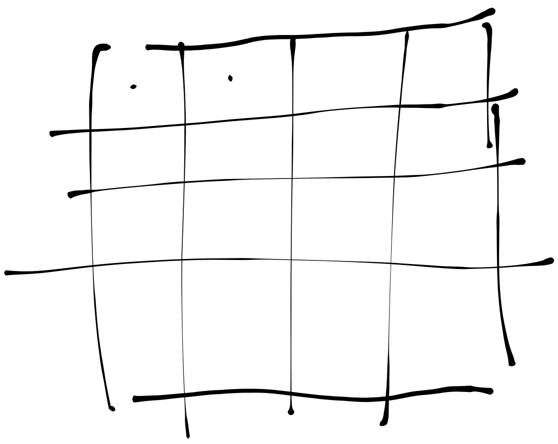
$$\therefore \quad \langle N^2 \rangle - \langle N \rangle^2 = kT \frac{\partial \langle N \rangle}{\partial \mu} \overset{\text{gas ideal}}{=} \langle N \rangle$$

$$\therefore \quad K_T = \frac{V}{\langle N \rangle k_B T} \left(\langle N^2 \rangle - \langle N \rangle^2 \right) \overset{\text{g. ideal}}{=} \frac{V}{N k_B T}$$

y como $pV = N k_B T \Rightarrow \dfrac{V}{\langle N \rangle k_B T} = \dfrac{1}{p}$

$$\boxed{K_T = \frac{1}{p}}$$

Prob. 5, Guía 5



O_2, CO ; dados "fugacidad"

$O_2 \to \varepsilon_1$, $CO \to \varepsilon_2$

$$z_{1, O_2} = e^{\beta\mu_1} = 10^{-5}$$

$$z_{2, CO} = e^{\beta\mu_2} = 10^{-7}$$

a) Solo hay 2 estados por sitio

estado ψ	ε	n
vacío ψ_0	0	0
ocup. por O_2 ψ_1	ε_1	1

• Son sitios independientes:

$$\mathcal{Z} = \zeta^N$$

$$\zeta = \sum_{\{estado\}} e^{-\beta(\varepsilon_n - \mu N)}$$

$$\Rightarrow \zeta(\beta,\mu) = 1 + e^{-\beta(\varepsilon_1 - \mu)} = \left(1 + z_1 e^{-\beta\varepsilon_1}\right)$$

$$\mathcal{Z} = \zeta^N = \left(1 + z_1 e^{-\beta\varepsilon_1}\right)^N$$

• Para obtener ε_1, usamos que está el 90% de los sitios ocupados: dato del problema $f : 0{,}9$.

$$\frac{\langle N_1 \rangle}{N} = 0.9 = \frac{1}{N} \left(z_1 \frac{\partial}{\partial z_1} \ln \mathcal{Z} \right)$$

sitios ocup.

total sitios

fracción sitios ocupados

recordar

$$\langle N_1 \rangle = kT \frac{\partial \ln \mathcal{Z}}{\partial \mu_1} = z_1 \frac{\partial}{\partial z_1} \ln \mathcal{Z}$$

¡demostrarlo!

$$0.9 = \frac{z_1}{N} \frac{N e^{-\beta \varepsilon_1}}{(1 + z_1 e^{-\beta \varepsilon_1})} = \frac{1}{(z^{-1} e^{\beta \varepsilon_1} + 1)} = f^{\,0.9}$$

$$\Rightarrow \boxed{\varepsilon_1 = k_B T \ln \frac{z_1 (1-f)}{f} \Bigg|_{\substack{f=0.9 \\ z_1 = 10^{-5} \\ T = 310\,K}} = -0.37\,eV}$$

b) Aquí todos los sitios podrían estar ocupados.

Los estados son

ψ	ε	n
vacío ψ_0	0	0
ocup. O_2 ψ_1	ε_1	1
ocup. CO ψ_2	ε_2	1

$$\mathcal{Z} = \mathfrak{z}^N$$

$$\mathfrak{z} = \sum_{\{estados\}} e^{-\beta(\varepsilon_i - \mu n)}$$

$$\Rightarrow \mathcal{Z}(\beta,\mu) = \left(1 + z_1 e^{-\beta\varepsilon_1} + z_2 e^{-\beta\varepsilon_2}\right)$$

tasa de rendimiento (ó llenado) : O_2 : 10% : $f_{O_2} = 0.1$

$$\frac{\langle N_1\rangle}{N} = f_{O_2}$$: y suponemos conocido $\varepsilon_1 = 0.37\,eV$.

- Solo queda ε_2 como incógnita:

$$\frac{\langle N_1\rangle}{N} = \frac{z_1}{N}\frac{\partial \mathcal{Z}}{\partial z_1} = \frac{z_1 e^{-\beta\varepsilon_1}}{\left(1+z_1 e^{-\beta\varepsilon_1}+z_2 e^{-\beta\varepsilon_2}\right)} = 0.1$$

poniendo $\varepsilon_1 = 0{,}37\,eV$; $z_1 = 10^{-5}$; $z_2 = 10^{-7}$; y $T = 300K$

$$\varepsilon_2 = -k_B T \ln\left[\frac{z_1 e^{-\beta\varepsilon_1}(1-f_{O_2}) - f_{O_2}}{z_1 f_{O_2}}\right]$$

$$\boxed{\varepsilon_2 \simeq -0.55\,eV}$$

- Próxima clase Viernes: • Resumen Mec. Est. clásica: otros ensembles.
  - Revisión Prueba 1.