1 (a) $$\left.\begin{array}{l} N = N_0 + N_\epsilon \\ \\ E = \epsilon N_\epsilon \end{array}\right\} \Longrightarrow N_\epsilon = \frac{E}{\epsilon}, \quad N_0 = N - \frac{E}{\epsilon}$$

$\Omega(E,N) = \Omega(N_0, N_\epsilon) =$ (número de formas en que puedo elegir N_0 partículas de las N que tengo) $\times$ (número de formas en que puedo repartir las N_ϵ restantes en 3 estados)

$$\Longrightarrow \Omega(E,N) = \binom{N}{N_0} 3^{N_\epsilon}$$

$$\Longrightarrow S(E,N) = k \left\{ N_\epsilon \log 3 + \log \binom{N}{N_0} \right\}$$

$$\underset{\text{Stirling}}{=} k \left\{ N_\epsilon \log 3 + N \log N - N_0 \log N_0 - N_\epsilon \log N_\epsilon \right\}$$

$$= k \left\{ N_\epsilon \log \frac{3N}{N_\epsilon} + N_0 \log \frac{N}{N_0} \right\}$$

$$= Nk \left\{ \frac{N_\epsilon}{N} \log \frac{3N}{N_\epsilon} + \frac{N_0}{N} \log \frac{N}{N_0} \right\}$$

$$= -Nk \left\{ \frac{N_\epsilon}{N} \log \frac{N_\epsilon}{3N} + \frac{N_0}{N} \log \frac{N_0}{N} \right\}$$

$$= \boxed{-Nk \left\{ \frac{E}{N\epsilon} \log \frac{E}{3N\epsilon} + \left(1 - \frac{E}{N\epsilon}\right) \log \left(1 - \frac{E}{N\epsilon}\right) \right\} = S(E,N)}$$

Para graficar, notemos: $0 \leq E \leq N\epsilon \implies S \geq 0$.

$$S(E=0) = 0 \quad ; \quad S(E=N\epsilon) = -Nk \log \frac{1}{3} = Nk \log 3$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = -Nk \left\{ \frac{1}{N\epsilon} \log \frac{E}{3N\epsilon} + \cancel{\frac{1}{N\epsilon}} \right.$$

$$\left. - \frac{1}{N\epsilon} \log \left(1 - \frac{E}{N\epsilon}\right) - \cancel{\frac{1}{N\epsilon}} \right\}$$

$$= \frac{k}{\epsilon} \log \left[\frac{3N\epsilon}{E} \left(1 - \frac{E}{N\epsilon}\right) \right] = \boxed{\frac{k}{\epsilon} \log \left[3 \left(\frac{N\epsilon}{E} - 1 \right) \right] = \frac{1}{T}}$$

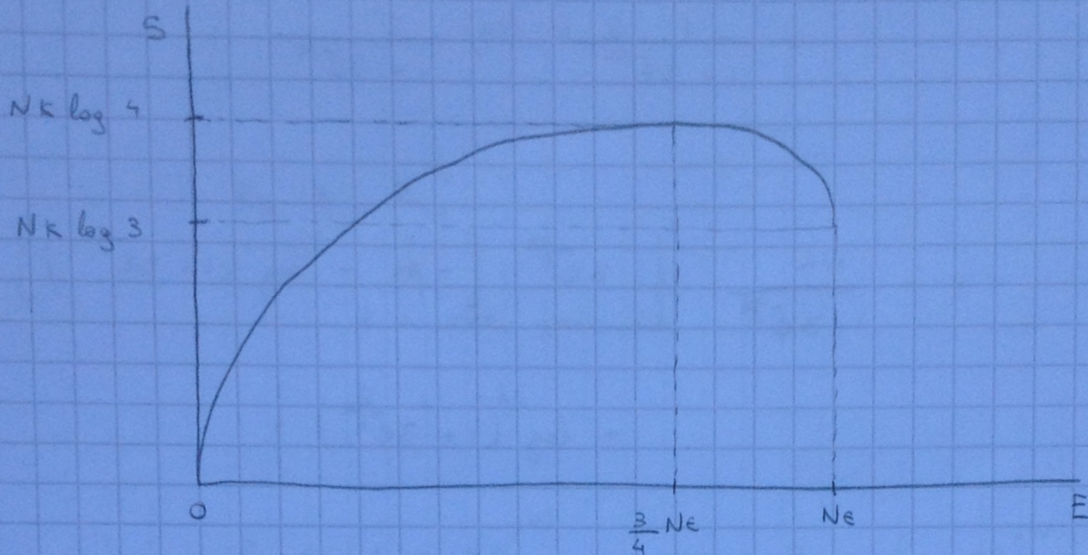
$$\Rightarrow \left.\frac{\partial S}{\partial E}\right|_{E=0} = \infty \quad , \quad \left.\frac{\partial S}{\partial E}\right|_{E=N\epsilon} = -\infty$$

Máximo. $\frac{1}{T} = 0 \iff \frac{N\epsilon}{E} - 1 = \frac{1}{3} \iff \frac{N\epsilon}{E} = \frac{4}{3} \iff E = \frac{3}{4} N\epsilon$

$$S\left(E = \frac{3}{4} N\epsilon\right) = -Nk \left\{ \frac{3}{4} \log \frac{1}{4} + \frac{1}{4} \log \frac{1}{4} \right\}$$

$$= Nk \log 4$$

Así pues,



(b) Del ítem anterior,

$$\frac{1}{T} = \frac{k}{\epsilon} \log\left[3\left(\frac{N\epsilon}{E} - 1\right)\right]$$

$$\Rightarrow \beta\epsilon = \log\left[3\left(\frac{N\epsilon}{E} - 1\right)\right] \Rightarrow e^{\beta\epsilon} = 3\left(\frac{N\epsilon}{E} - 1\right)$$

$$\Rightarrow \frac{N\epsilon}{E} = \frac{1}{3} e^{\beta\epsilon} + 1 \Rightarrow E = \frac{N\epsilon}{\frac{1}{3} e^{\beta\epsilon} + 1}$$

$$\Rightarrow E = N\epsilon \frac{3e^{-\beta\epsilon}}{1 + 3e^{-\beta\epsilon}}$$ ok con canónico

$$\Rightarrow c = \frac{1}{N} \frac{\partial E}{\partial T} = \epsilon \frac{\epsilon \frac{1}{3} e^{\beta\epsilon}}{\left(\frac{1}{3} e^{\beta\epsilon} + 1\right)^2} \frac{1}{kT^2}$$

$$= \boxed{\left(\frac{\epsilon}{kT}\right)^2 \frac{3e^{-\beta\epsilon}}{\left(1 + 3e^{-\beta\epsilon}\right)^2} k = c}$$

(c) $$S(T,N) = -Nk\left\{ \frac{3e^{-\beta\epsilon}}{1+3e^{-\beta\epsilon}} \log \frac{e^{-\beta\epsilon}}{1+3e^{-\beta\epsilon}} + \frac{1}{1+3e^{-\beta\epsilon}} \log \frac{1}{1+3e^{-\beta\epsilon}} \right\}$$

$$= -\frac{Nk}{1+3e^{-\beta\epsilon}} \left\{ 3e^{-\beta\epsilon}\left[-\beta\epsilon - \log\left(1+3e^{-\beta\epsilon}\right)\right] - \log\left(1+3e^{-\beta\epsilon}\right) \right\}$$

$$= \frac{1}{T} N\epsilon \frac{3e^{-\beta\epsilon}}{1+3e^{-\beta\epsilon}} + \frac{Nk}{1+3e^{-\beta\epsilon}}\left(1+3e^{-\beta\epsilon}\right)\log\left(1+3e^{-\beta\epsilon}\right)$$

$$= \frac{E}{T} + Nk\log\left(1+3e^{-\beta\epsilon}\right)$$

$$\Rightarrow \boxed{F(T,N) = E - TS = -NkT\log\left(1+3e^{-\beta\epsilon}\right)}$$

Ok con canónica

2. (a) $Z_{A,B}$ f. de partición grancanónica del conjunto de sitios

de tipo A, B

$$Z_A = Z_{1A}^{N_A}$$

$\uparrow$

f. de part. grancanónica

de 1 sitio

$$Z_{1A} = 1 + z e^{\beta W} \Rightarrow Z_A = \left(1 + z e^{\beta W}\right)^{N_A}$$

$$Z_B = Z_{1B}^{N_B}$$

$$Z_{1B} = 1 + z e^{\beta W} + z^2 e^{2\beta W} \Rightarrow Z_B = \left(1 + z e^{\beta W} + z^2 e^{2\beta W}\right)^{N_B}$$

$n_{A,B}$ número medio de moléculas absorbidas en sitios tipo A, B.

$$n_A = z \frac{\partial}{\partial z} \log Z_A = \boxed{N_A \frac{z e^{\beta W}}{1 + z e^{\beta W}} = n_A}$$

$$n_B = z \frac{\partial}{\partial z} \log Z_B = \boxed{N_B \frac{z e^{\beta W} + 2 z^2 e^{2\beta W}}{1 + z e^{\beta W} + z^2 e^{2\beta W}} = n_B}$$

$$\left(z = e^{\beta \mu} \right)$$

(b) $\mathcal{Z}$ de partición canónica del gas.

$$Z = \frac{1}{N!} Z_1^N$$

$$Z_1 = Z_{tras} Z_{rot} Z_{vib}$$

$$T \sim 500 \text{ K} \ll T_{vib} \Rightarrow Z_{vib} \simeq 1$$

$$T_{rot} = \frac{hc\nu_{rot}}{k} = 1.4 \cdot 5 \text{ K} \ll T \Rightarrow Z_{rot} \simeq Z_{rot,\text{clásica}}$$

$$= 2\frac{T}{T_{rot}}$$

hetero

$$\Rightarrow Z_1 = \frac{V}{\lambda^3} 2\frac{T}{T_{rot}}$$

$$\Rightarrow F = -kT \log Z \underset{\text{Stirling}}{=} -kT\left[N \log\left(\frac{V}{\lambda^3} 2\frac{T}{T_{rot}}\right) - N\log N + N\right]$$

$$= -NkT\left[\log\left(\frac{v}{\lambda^3} 2\frac{T}{T_{rot}}\right) + 1\right]$$

$$p = \frac{NkT}{V} = \frac{kT}{v} \Rightarrow F = -NkT\left[\log\left(\frac{kT}{p\lambda^3} 2\frac{T}{T_{rot}}\right) + 1\right]$$

$$\Rightarrow G = F + pV = F + NkT = -NkT\log\left(\frac{kT}{p\lambda^3} 2\frac{T}{T_{rot}}\right)$$

$$\Rightarrow \boxed{\mu(p,T) = \frac{G}{N} = -kT \log\left(\frac{kT}{p\lambda^3} \, 2\frac{T}{T_{rot}}\right)}$$

$$p \to \infty \Rightarrow \mu \to \infty \Rightarrow n_A \to N_A$$

$$n_B \to 2N_B$$

$$p \to 0 \Rightarrow \mu \to -\infty \Rightarrow n_A, n_B \to 0$$

3. $$\epsilon(y, \vec{p}) = cp + eE_0 y$$

$$\log Z_{GC} = \underbrace{\sum_i}_{\text{estados monopart.}} \log\left(1 + z e^{-\beta\epsilon_i}\right) = \underbrace{2}_{\text{deg. spin}} \int \frac{d^3x \, d^3p}{h^3} \log\left[1 + z e^{-\beta(cp + eE_0 y)}\right]$$

$$\underset{z_y = z e^{-\beta e E_0 y}}{=} \frac{2A}{h^3} \int_0^\infty dy \int d^3p \, \log\left(1 + z_y e^{-\beta cp}\right)$$

$$\underset{\text{esféricas}}{=} \frac{8\pi A}{h^3} \int_0^\infty dy \int_0^\infty dp \, p^2 \log\left(1 + z_y e^{-\beta cp}\right)$$

$$\underset{x = \beta cp}{=} \frac{8\pi A}{(\beta hc)^3} \int_0^\infty dy \int_0^\infty dx \, x^2 \log\left(1 + z_y e^{-x}\right)$$

$$\Rightarrow \log Z_{GC} \underset{\text{partes}}{=} \frac{8\pi A}{(\beta h c)^3} \int_0^\infty dy \ \frac{1}{3} \left\{ \cancel{x^3 \log\left(1 + z_y e^{-x}\right) \Big|_0^\infty} + \int_0^\infty dx \ \frac{x^3}{z_y^{-1} e^x + 1} \right\}$$

$$\underset{\Gamma(4) = 3! = 6}{=} \frac{16\pi A}{(\beta h c)^3} \int_0^\infty dy \ f_4\left(z e^{-\beta e E_0 y}\right)$$

$$\underset{z e^{-\beta e E_0 y} = x}{=} \frac{16\pi A}{(\beta h c)^3} \frac{1}{\beta e E_0} \int_0^z dx \ \underbrace{\frac{f_4(x)}{x}}_{= f_5'(x)} = \frac{16\pi A}{(\beta h c)^3} \frac{1}{\beta e E_0} f_5(z)$$

$$\left(\begin{array}{l} z e^{-\beta e E_0 y} = x \\[1em] \Rightarrow dx = -\beta e E_0 \, z e^{-\beta e E_0 y} \, dy \\[1em] \Rightarrow dy = -\dfrac{1}{\beta e E_0} \dfrac{dx}{x} \\[1em] y = 0 \longrightarrow x = z \\[0.5em] y = \infty \longrightarrow x = 0 \end{array} \right)$$

$$\rightarrow \log Z_{GC} = \underbrace{\frac{16\pi A}{(2\pi \hbar c)^3}}_{= \frac{2A}{\pi^2 (\hbar c)^3}} \frac{(kT)^4}{e E_0} f_5(z) = \boxed{\frac{2A}{\pi^2} \frac{(kT)^4}{(\hbar c)^3 e E_0} f_5(z) = \log Z_{GC}}$$

(b) $$N = z \frac{\partial}{\partial z} \log Z_{GC} = \frac{2A}{\pi^2} \frac{(kT)^4}{(\hbar c)^3 e E_0} f_4(z)$$

$$U = -\left(\frac{\partial}{\partial \beta} \log Z_{GC}\right)_z = 4 \frac{2A}{\pi^2} \frac{(kT)^5}{(\hbar c)^3 e E_0} f_5(z)$$

Sommerfeld

$$f_n(z) = \frac{(\log z)^n}{\Gamma(n+1)} \left[1 + \frac{\pi^2}{6} \frac{n(n-1)}{(\log z)^2} + O\left((\log z)^{-3}\right) \right]$$

$$\Rightarrow N = \frac{2A}{\pi^2} \frac{(kT)^4}{(\hbar c)^3 e E_0} \frac{(\beta\mu)^4}{\Gamma(5)} \left[1 + \frac{2\pi^2}{(\beta\mu)^2} + O(T^3) \right]$$

$$= \frac{A}{12\pi^2} \frac{1}{(\hbar c)^3 e E_0} \mu^4 \left[1 + 2\pi^2 \left(\frac{kT}{\mu}\right)^2 + O(T^3) \right]$$

$\uparrow$

$\Gamma(5) = 4! = 24$

$$U = 4 \frac{2A}{\pi^2} \frac{(kT)^5}{(\hbar c)^3 e E_0} \frac{(\beta\mu)^5}{\Gamma(6)} \left[1 + O(T^2) \right]$$

$$= \frac{A}{15\pi^2} \frac{1}{(\hbar c)^3 e E_0} \mu^5 \left[1 + O(T^2) \right]$$

A $\quad T = 0, \quad \mu = \epsilon_F$

$$N = \frac{A}{12\pi^2} \frac{1}{(\hbar c)^3 e E_0} \epsilon_F^4 \Rightarrow \boxed{\epsilon_F = \left[\frac{12\pi^2}{A} (\hbar c)^3 e E_0 N \right]^{1/4}}$$

$$U = \frac{12}{15} N \epsilon_F = \boxed{\frac{4}{5} N \epsilon_F = U}$$

(c) Volvemos a la ec. para N que obtuvimos en el ítem anterior:

$$N = \frac{A}{12\pi^2} \frac{1}{(\hbar c)^3 e E_0} \mu^4 \left[1 + 2\pi^2 \left(\frac{kT}{\mu}\right)^2 + O(T^3) \right]$$

$$\underset{\mu = \epsilon_F (1 + O(T))}{=} \frac{A}{12\pi^2} \frac{1}{(\hbar c)^3 e E_0} \mu^4 \left[1 + 2\pi^2 \left(\frac{kT}{\epsilon_F}\right)^2 + O(T^3) \right]$$

$$\Rightarrow \mu^4 = \epsilon_F^4 \left[1 - 2\pi^2 \left(\frac{kT}{\epsilon_F}\right)^2 + O(T^3) \right]$$

$$\boxed{\mu = \epsilon_F \left[1 - \frac{\pi^2}{2} \left(\frac{kT}{\epsilon_F}\right)^2 + O(T^3) \right]}$$