GUÍA 6: Energía de cohesión

1. Energía de cohesión del neón $(a = 4{,}43\ \text{Å})$

a)

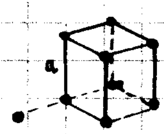
$$E = \frac{1}{2} N 4\epsilon \left[\sum_{ij} \left(\frac{\sigma}{p_{ij} r_{nn}}\right)^{12} - \sum_{ij} \left(\frac{\sigma}{p_{ij} r_{nn}}\right)^{6} \right]$$

$$\left[\left(\frac{\sigma}{r_{nn}}\right)^{12} \sum_{ij} \left(\frac{1}{p_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{nn}}\right)^{6} \sum_{ij} \left(\frac{1}{p_{ij}}\right)^{6} \right]$$

$$E = N 2 \epsilon \left[\left(\frac{\sigma}{r_{nn}}\right)^{12} A_{12} - \left(\frac{\sigma}{r_{nn}}\right)^{6} A_6 \right]$$

$$\varepsilon = 2\epsilon \left[\left(\frac{\sigma}{r_{nn}}\right)^{12} A_{12} - \left(\frac{\sigma}{r_{nn}}\right)^{6} A_6 \right] \quad \leftarrow \text{Energía por partícula}$$

* SC:



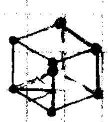
$$\varepsilon = 2(0{,}0031\ \text{eV}) \left[6{,}20 \left(\frac{\sigma}{a}\right)^{12} - 8{,}40 \left(\frac{\sigma}{a}\right)^{6} \right]$$

1V : 6
2V : 12

$$[0{,}0194336 - 0{,}4702841]$$

$$\boxed{\varepsilon \cong -0{,}0027\ \text{eV}}$$

* BCC:



$$\varepsilon = 2(0{,}0031\ \text{eV}) \left[9{,}11418 \left(\frac{\sigma}{\frac{\sqrt{3}a}{2}}\right)^{12} - 12{,}2553 \left(\frac{\sigma}{\frac{\sqrt{3}a}{2}}\right)^{6} \right]$$

1V : 8
2V : 6

$$[0{,}1605136 - 1{,}6263768]$$

$$\boxed{\varepsilon \cong -0{,}0090\ \text{eV}}$$

* FCC:

$$\varepsilon = 2(0{,}0031\ \text{eV}) \left[12{,}13188 \left(\frac{\sigma}{\frac{a}{\sqrt{2}}}\right)^{12} - 14{,}45392 \left(\frac{\sigma}{\frac{a}{\sqrt{2}}}\right)^{6} \right]$$

1V : 12
2V : 4

$$[2{,}4337172 - 6{,}4737609]$$

$$\boxed{\varepsilon \cong -0{,}0250\ \text{eV}}$$

* HCP:

$$\varepsilon = 2(0{,}0031\ \text{eV}) \left[12{,}13229 \left(\frac{\sigma}{a}\right)^{12} - 14{,}45489 \left(\frac{\sigma}{a}\right)^{6} \right]$$

1V : 12
2V : 18

$$[0{,}0380281 - 0{,}8092744]$$

$$\boxed{\varepsilon \cong -0{,}0047\ \text{eV}}$$

⇒ Esperamos encontrar al Ne en la estructura FCC, lo cual concuerda con el dato experimental contratapa Ashcroft. Dentro de las estructuras sólidas consideradas la de menor energía es la FCC $\Rightarrow$ será la más "estable".

$$\lim_{n\to\infty} A_n = \#\ 1^{\text{eros}}\text{ vecinos}$$

Existe un r de equilibrio, r_0, que minimiza la energía:

$$\phi(r) = 2\epsilon\left[A_{12}\left(\frac{\sigma}{r}\right)^{12} - A_6\left(\frac{\sigma}{r}\right)^{6}\right]$$

$$\frac{\partial\phi(r)}{\partial r} = 2\epsilon\left[A_{12}(-12)\,\sigma^{12} r^{-13} - A_6(-6)\,\sigma^6 r^{-7}\right] = 0$$

$$\cancel{+}A_{12}\,\cancel{12}^{\,2}\,\sigma^{\cancel{12}\,6}\, r^{\cancel{-13}\,-6} = \cancel{+}A_6\,\cancel{6}\,\cancel{\sigma^6}\,\cancel{r^{-7}}$$

$$\sigma^6\,\frac{2A_{12}}{A_6} = r^6$$

$$\boxed{\sigma\left(\frac{2A_{12}}{A_6}\right)^{1/6} = r_0}$$

* FCC

$$r_0 = \sigma\left(\frac{2\cdot 12{,}13188}{14{,}45392}\right)^{1/6} = \sigma\cdot 1{,}090173 \Rightarrow \quad r_0 = 2{,}98\ \text{Å}$$

$$\mathcal{E}_c = 2\epsilon\left[12{,}13188\left(\frac{1}{1{,}090173}\right)^{12} - 14{,}45392\left(\frac{1}{1{,}090173}\right)^{6}\right]$$

$$\mathcal{E}_c \cong 2\epsilon\,[4{,}305098 - 8{,}610196] \cong -8{,}6102\,\epsilon \quad\to\quad \boxed{\mathcal{E}_c = -0{,}0267\ \text{eV}}$$

* SC

$$r_0 = \sigma\cdot 1{,}0670 \Rightarrow$$

$$\mathcal{E}_c = 2\epsilon\left[6{,}20\left(\frac{1}{1{,}0670}\right)^{12} - 8{,}40\left(\frac{1}{1{,}0670}\right)^{6}\right]$$

$$\mathcal{E}_c \cong 2\epsilon\,[2{,}84516 - 5{,}6903] \cong -5{,}690\,\epsilon \qquad \boxed{\mathcal{E}_c = -0{,}0176\ \text{eV}}$$

* BCC

$$r_0 = \sigma\cdot 1{,}0684 \Rightarrow$$

* HCP

$$r_0 = \sigma\cdot 1{,}09018 \Rightarrow$$

$$\mathcal{E}_c = 2\epsilon\left[12{,}13229\left(\frac{1}{1{,}09018}\right)^{12} - 14{,}45489\left(\frac{1}{1{,}09018}\right)^{6}\right]$$

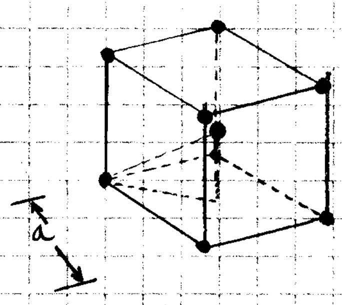
$$\mathcal{E}_c \approx 2\epsilon\,[4{,}3049 - 8{,}6105] \cong -8{,}611\,\epsilon \qquad \boxed{\mathcal{E}_c = -0{,}0267\ \text{eV}}$$

Los valores experimentales son de $r_0 = 3{,}13$ Å, $\mathcal{E}_c = -0{,}02$ eV/átomo, con lo cual no pega tan bien, después de todo, con la teoría.

HOJA

FECHA

2.



Na metálico
bcc

$$EI = \mathcal{U}(r_0) \quad ¿?$$

$$\mathcal{U} = \frac{8e^2}{r^m} - \alpha_M \frac{e^2}{r}$$

Suponemos potencial repulsivo a primeros vecinos

$\frac{\sqrt{3}\,a}{2} = r_{nn}$, 8 primeros vecinos

$$\frac{d\mathcal{U}}{dr} = -\frac{m8e^2}{r^{m+1}} + \alpha_M \frac{e^2}{r^2} = 0$$

$$+\frac{m8e^2}{r_0^{m+1}} = \alpha_M \frac{e^2}{r_0^2}$$

$$\frac{m8}{r_0^m} = \frac{\alpha_M}{r_0}$$

$$\mathcal{E}_c = \mathcal{U}(r_0) = \frac{8e^2}{r_0^m} - \alpha_M \frac{e^2}{r_0} = \frac{\alpha_M}{r_0 m} e^2 - \alpha_M \frac{e^2}{r_0}$$

$$\mathcal{E}_c = \left(\frac{1}{m} - 1\right) \alpha_M \frac{e^2}{r_0}$$

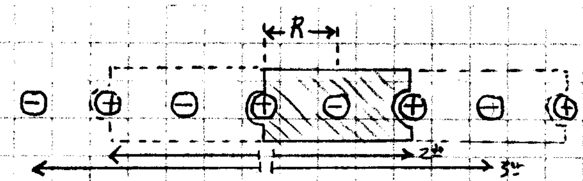
$$\frac{d\mathcal{U}}{dm} = -\frac{8e^2 m}{r^{m+1}}$$

$$\frac{d^2\mathcal{U}}{dm^2} = -8e^2 \left[\frac{1 \cdot r^{m+1} - m \cdot r^m}{(r^{m+1})^2} \right]$$

NOTA

3.

a)



$\begin{cases} N \text{ iones } + \\ N \text{ iones } - \end{cases}$

$\phi^{repulsivo} = \frac{A}{R^n}$ (entre 1eros vecinos) ; Además, como son iones, tenemos interacción de Coulomb.

atractivos repulsivos

$$u^{Coulomb}(R) = -\frac{q^2}{R}\left\{ 1 + \frac{(2)1}{3} - \frac{(2)1}{2} + (1)1 + \frac{(2)1}{5} - \frac{(2)1}{4} + \frac{(2)1}{7} - \frac{(2)1}{6} + \dots \right\}$$

NOTA

$$\sum \frac{1}{\alpha(\vec{R}+\vec{d})} - \frac{1}{\alpha(\vec{R})}$$

iones ⊖ (base) iones ⊕

dist.

ojo! con este → 1R, 3R, 5R, … (1) (2) (2) 2R, 4R, 6R, … (2) (2) (2)

$$-\frac{q^2}{R}2\left\{1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \dots\right\}$$

$$= -\frac{q^2}{R}2\ln(2)$$

\# de 1V (hasta donde llega el pot. $\phi^{repulsivo}$)

$$\frac{U}{N} = u = \frac{A2}{R^n} - \frac{2q^2\ln(2)}{R}$$

\# de pares

$$\boxed{u(R) = \frac{2A}{R^n} - \frac{2\ln(2)}{R}q^2}$$

$$\frac{du}{dR} = -\frac{2An}{R^{n+1}} + \frac{2\ln(2)q^2}{R^2} = 0$$

$$\frac{\cancel{2}An}{R^{n+1}} = \frac{\cancel{2}\ln(2)q^2}{R^2}$$

$$\frac{A}{R_0^n} = \frac{\ln(2)q^2}{nR_0}$$

$$u(R_0) = +\frac{2\ln(2)q^2}{nR_0} - \frac{2\ln(2)q^2}{R_0} = \frac{2\ln(2)q^2}{R_0}\left(\frac{1}{n} - 1\right)$$

$$\boxed{U(R_0) = \frac{2N\ln(2)}{R_0}q^2\left(\frac{1}{n} - 1\right)}$$

b)

$$R_0 \to R_0(1-\delta) \qquad W = -\Delta U(R)|_{R=R_0}$$

$$\Delta U = U(R_0[1-\delta]) - U(R_0)$$

donde $U(R_0[1-\delta])$ es la expresión general de la energía potencial

$$\Delta U = \frac{2AN}{[R_0(1-\delta)]^n} - \frac{2N\ln(2)q^2}{R_0(1-\delta)} - \frac{2N\ln(2)q^2}{R_0}\left(\frac{1}{n} - 1\right)$$

$$\begin{cases} (1-\delta)^{-1} \approx 1 + \delta + \delta^2 \Rightarrow \\ (1-\delta)^{-n} \approx 1 + n\delta + \frac{n(n+1)}{2}\delta^2 \end{cases}$$

Tenemos que expandir hasta orden 2 porque $U'(R_0) = 0$ (mínimo)

$$\Delta U = \frac{NZA}{R_0^n}\left(1+n\delta+\frac{n(n+1)}{2}\delta^2\right) - \frac{2N\ln(2)}{R_0}q^2\left(\cancel{1}+\delta+\delta^2\right) - \frac{2N\ln(2)}{R_0}q^2\left(\frac{1}{n}-\cancel{1}\right)$$

Si me restrinjo a orden 2 tendré

$$\Delta U^{(2)} = \underbrace{\frac{2NA}{R_0^n}\frac{n(n+1)}{2}\delta^2}_{\frac{2N\ln(2)}{R_0}q^2\frac{(n+1)}{2}\delta^2} - \frac{2N\ln(2)}{R_0}q^2\delta^2$$

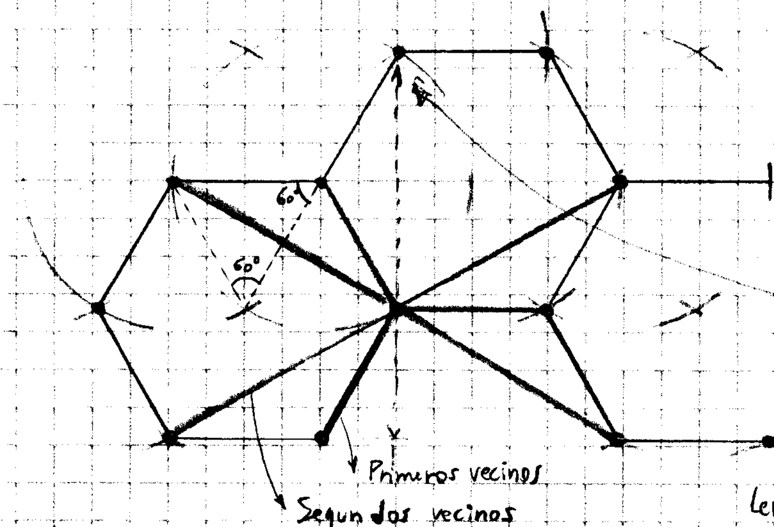
$$\Delta U^{(2)} \xleftarrow{\text{orden}} = \frac{2N\ln(2)}{R_0}q^2\delta^2\left[\frac{n+1}{2}-1\right]$$

$$\Delta U^{(2)} = \frac{2N\ln(2)}{R_0}q^2\delta^2\left(\frac{n+1-2}{2}\right) = \frac{N\ln(2)}{R_0}q^2(n-1)\delta^2$$

$$\boxed{W = -\Delta U^{(2)} = -2\underbrace{\frac{N.\ln(2)}{R_0}q^2(n-1)}_{\equiv C}\frac{\delta^2}{2}}$$

5.

La red panal de abejas no es una red de Bravais; pero igualmente como el potencial $\phi(r)$ es función solamente de las distancias y no de las direcciones de los vecinos en la red, esa restricción no me importa.
La red tiene:



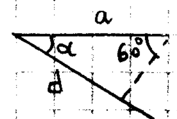
$*$ 3 primeros vecinos a distancia a

$*$ 4 segundos vecinos ~~NO~~ a distancia $\sqrt{3}\,a$

La energía que deviene del potencial de Lenard-Jones es:

$$\mathcal{E} = 2\epsilon\left[\sum_{ij}\left(\frac{\sigma}{p_{ij}a}\right)^{12} - \sum_{ij}\left(\frac{\sigma}{p_{ij}a}\right)^{6}\right]$$

Cálculo 2vecino



$\alpha = 30°$

$$\cos\alpha = \frac{d}{a}$$

$$a.\frac{\sqrt{3}}{2} = d$$

como sólo considero que la interacción alcanza hasta segundos vecinos cada sumatoria tendrá sólo dos términos; pues parado en un átomo sólo sumo en sus primeros vecinos y en sus segundos.
La energía por átomo será: ✓

$$\mathcal{E} = 2\epsilon\left[3\left(\frac{\sigma}{a}\right)^{12} + 4\left(\frac{\sigma}{\sqrt{3}a}\right)^{12} - 3\left(\frac{\sigma}{a}\right)^{6} - 4\left(\frac{\sigma}{\sqrt{3}a}\right)^{6}\right]$$

$$\mathcal{E} = 2\epsilon\left\{\left(\frac{\sigma}{a}\right)^{12}\left[3 + 4\left(\frac{1}{\sqrt{3}}\right)^{12}\right] - \left(\frac{\sigma}{a}\right)^{6}\left[3 + 4\left(\frac{1}{\sqrt{3}}\right)^{6}\right]\right\}$$

$$\mathcal{E} = 2\epsilon\left\{\frac{\sigma^{12}}{a^{12}}[3{,}0055] - \frac{\sigma^{6}}{a^{6}}[3{,}1481]\right\} \qquad (1)$$

La distancia de equilibrio es la que minimiza la energía

$$\frac{\partial\mathcal{E}}{\partial a} = 0 \rightarrow \qquad 2\epsilon\left[\sigma^{12}[3{,}0055]\,a^{-13}(-12) - \sigma^{6}[3{,}1481]\,a^{-7}(-6)\right] = 0$$

$$\cancel{-}\frac{\sigma^{\cancel{12}\,6}[3{,}0055]\,\cancel{12}\,2}{a^{\cancel{13}\,6}} = \cancel{-}\frac{\cancel{\sigma^6}[3{,}1481]\,\cancel{6}}{\cancel{a^7}}$$

$$\left(\frac{3{,}0055}{3{,}1481}\right)\sigma^6\,2 = a^6$$

$$\sigma\left(\frac{2.\,3{,}0055}{3{,}1481}\right)^{1/6} = a_0$$

$$\sigma.\,1{,}1138 = a_0$$

OK, arrastró el error.

$$\boxed{a_0 \approx 4{,}065\ \text{Å}} \qquad (2)$$

Usando (2) y metiendo en la expresión (1) se tiene:

$$\mathcal{E} = 2\epsilon\left[0,8254 - 1,6498\right] = -1,6488\,\epsilon \cong \boxed{-3,71 . 10^{-14} \text{ ergios}} \quad \checkmark$$

6.

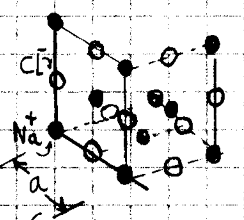
$$\mathcal{U}^{\text{coulomb}} = -\frac{e^2}{r}\left\{\underbrace{\frac{1}{\alpha(\vec{d})} + \sum_{\vec{R}\neq 0}\frac{1}{\alpha(\vec{R}+\vec{d})} - \frac{1}{\alpha(\vec{R})}}_{\alpha_M}\right\}$$

$Na^+ \; Cl^-$

$$\mathcal{U}^{\text{Core}} = \sum_{ij}\frac{\gamma}{r_{ij}^n} = \frac{6\gamma}{r^n}$$

1$^{\text{eros}}$ vecinos

con $r \equiv$ distancia entre primeros vecinos



6 primeros vecinos a distancia d

$$\boxed{\mathcal{U}(r) = \frac{6\gamma}{r^n} - \alpha_M\frac{e^2}{r}}$$

Energía por par iónicos en función de la distancia r a 1$^{\text{o}}$ vecinos.

$$\frac{d\mathcal{U}(r)}{dr} = -n6\gamma r^{-n-1} + \alpha_M\frac{e^2}{r^2} = 0$$

$$\frac{n6\gamma}{r_0^{n+\cancel{1}}} = \alpha_M\frac{e^2}{r_0^{\cancel{2}}}$$

$$\frac{n6\gamma}{\alpha_M e^2} = r_0^{n-1} \quad \leftarrow \text{dist. de equilibrio}$$

El módulo de Bulk es

$$B = v\frac{\partial}{\partial v}\left(\frac{\partial \mathcal{U}}{\partial v}\right)$$

$v = \frac{V}{N}$ ← (volumen por ion)

$v = \frac{a^3}{8}$ ← volumen de la celda primitiva
← # de iones que hay en la celda prim.
4 de Na^+
4 de Cl^-

Vale siempre (con r no nec. igual a r_0)

$$r = \frac{a}{2}$$

$$\frac{\partial \mathcal{U}}{\partial v} = \frac{\partial \mathcal{U}}{\partial r}\cdot\frac{\partial r}{\partial v}$$

$$v = \frac{\cancel{8}r^3}{\cancel{8}} = r^3$$

$$r = v^{1/3}$$

$$\mathcal{U}(v) = \frac{6\gamma}{v^{n/3}} - \alpha_M\frac{e^2}{v^{1/3}}$$

$$\frac{\partial\mathcal{U}(v)}{\partial v} = \left(-\frac{n}{3}\right)\frac{6\gamma}{v^{n/3+1}} + \frac{1}{3}\alpha_M\frac{e^2}{v^{4/3}}$$

$$\frac{\partial^2\mathcal{U}(v)}{\partial v^2} = \left(-\frac{n}{3}\right)\left(-\frac{n}{3}-1\right)\frac{6\gamma}{v^{n/3+2}} + \left(-\frac{4}{3}\right)\left(\frac{1}{3}\right)\alpha_M\frac{e^2}{v^{4/3+1}}$$

$$B = -\frac{n}{3}\left(-\frac{n}{3}-1\right)\frac{6\gamma}{v^{n/3+1}} - \frac{4}{9}\alpha_M\frac{e^2}{v^{4/3}}$$

$$B = \frac{n}{3}\left(1+\frac{n}{3}\right)\frac{6\gamma}{v^{n/3}\cdot v} - \frac{4}{9}\alpha_M\frac{e^2}{v^{4/3}}$$

$$B = \frac{n}{3}\left(1+\frac{n}{3}\right)\frac{6\gamma}{r^n r^3} - \frac{4}{9}\alpha_M\frac{e^2}{r^4}$$

dos ecuaciones con 2 incógnitas (n, γ)

$B(r_0)$, r_0 son datos

$$\begin{cases} B(r_0) = \frac{n}{3}\left(1+\frac{n}{3}\right)6\gamma\frac{1}{r_0^{n+3}} - \frac{4}{9}\alpha_M\frac{e^2}{r_0^4} \\ r_0^{n-1} = \frac{n6\gamma}{\alpha_M e^2} \quad \rightarrow \quad n6\gamma = r_0^{n-1}\alpha_M e^2 \end{cases}$$

$$B(r_0) = \frac{1}{3}\left(1+\frac{n}{3}\right) r_0^{n-1} \frac{\alpha_M e^2}{\cancel{r_0^n} \cdot r_0^3} - \frac{1}{9}\alpha_M \frac{e^2}{r_0^4}$$

$$= \left(1+\frac{n}{3}\right)\frac{\alpha_M e^2}{3 r_0^4} - \frac{1}{9}\frac{\alpha_M e^2}{r_0^4}$$

$$B = \frac{\alpha_M e^2}{r_0^4}\left[-\frac{1}{9}+\frac{1}{3}+\frac{n}{9}\right] = \frac{\alpha_M e^2}{r_0^4}\cdot\left(\frac{-1+3+n}{9}\right)$$

$$B = \frac{\alpha_M e^2}{r_0^4}\cdot\left(\frac{n-1}{9}\right)$$

$$\boxed{\gamma = \frac{r_0^{n-1}}{n6}\alpha_M e^2} \quad \leftarrow \quad \boxed{9\frac{B(r_0)\, r_0^4}{\alpha_M e^2} + 1 = n}$$

Acá habría que tomar parte entera