ELTE III.Fizika BSC
2014/2015 I.félév
Kondenzált anyag fizika
3. GYAKORLAT
(2014. Szeptember 23.)

Kohézió (U), taszítás, Madelung szám (A_M), kompresszó(κ_T)

I. *Kohézió (U), Madelung szám (A_M)*

Párpotenciál

$$V(r)^{ion} = -\left(\frac{Ze^2}{r}\right) + \left(\frac{\lambda}{r^n}\right)$$

Kohézió

$$U(r)^{ion} = -A_M\left(\frac{Ze^2}{r}\right) + \left(\frac{\lambda^*}{r^n}\right)$$

$\boldsymbol{A_M}$ Madelung állandó, A_6, A_{12}, ...

- ***Ionos kötés ($N_a = N_+ + N_- = 2N_{mol}$):***

$$V_{ij}(r) = -\frac{\alpha}{r_{ij}} + \frac{\lambda}{r_{ij}^n} \qquad r_{ij} = p_{ij} R_o$$

$$\mathrm{E} = (\mathrm{N}/2)\ \mathrm{U} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} V(r_i - r_j) = \frac{N}{2}\sum_i V(r_i) =$$

$$i \neq j \qquad (r_{ij} = r_i - r_j \neq 0)$$

$$= \frac{1}{2}\sum_{\langle i,j\rangle} V(r_{i,j}) = \frac{1}{2}\left\{\sum_{\langle i,j\rangle} -\frac{\alpha}{r_{ij}} + \sum_{\langle i,j\rangle}\frac{\lambda}{r_{ij}^n}\right\}$$

$$= \frac{1}{2}\left\{-\frac{\alpha}{R_o}\sum_{\langle i,j\rangle}\frac{1}{p_{ij}} + \frac{\lambda}{R_o^n}\sum_{\langle i,j\rangle}\frac{1}{p_{ij}^n}\right\} = (\mathrm{N}/2)\ \left\{-\frac{\alpha A_M}{R_o} + \frac{\lambda A_n}{R_o^n}\right\}$$

$$A_M = \sum_i^{Z_i}\frac{1}{p_i}(-1)^{n_i}\ ;\ A_n = \sum_i^{Z_i}\frac{1}{p_i^n}$$

$$U^{ion}(R) = -\frac{A}{R} + \frac{\lambda^*}{R^n} \quad ;\ \mathrm{A} = \alpha A_M\ ;\ \alpha = (1/4\pi\varepsilon_o)\ \mathrm{Z}\ e^2\ ;\ \lambda^* = \lambda\ A_n$$

$$\boldsymbol{A_M^{NaCl} = 1.7476..\ \ ;\ A_M^{CsCl} = 1.7626..}$$

- ***A kompresszió modulus és a taszító hatványkitevő (n):***

$$\kappa_T = -1/V\ (\partial V/\partial p)_T\ ;\ \kappa_S = -1/V\ (\partial V/\partial p)_S$$

$$\boxed{dE = TdS - pdV}$$

S = áll. $\Rightarrow$ $dE = -\,pdV$; $\Rightarrow$ $p = -(\partial E/\partial V)_S$

$V\kappa_S = -(\partial V/\partial p)_S$ $\Rightarrow$ $(V\kappa_S)^{-1} = -(\partial p/\partial V)_S = (\partial^2 E/\partial V^2)_S$

$$\kappa_S^{-1} = V\ (\partial^2 E/\partial V^2)_S$$

$$V = 2NR^3 ; \qquad E(R)^{ion} = NU^{ion} = N\left\{-A_M\left(\frac{Ze^2}{R}\right)+\left(\frac{\lambda^*}{R^n}\right)\right\}$$

$$\frac{\partial E}{\partial V} = \frac{\partial E}{\partial R}\frac{\partial R}{\partial V} = \frac{\partial E}{\partial R}\left(\frac{\partial V}{\partial R}\right)^{-1}$$

$$\frac{\partial^2 E}{\partial^2 V} = \frac{\partial}{\partial V}\left(\frac{\partial E}{\partial V}\right) = \frac{\partial}{\partial R}\left[\frac{\partial E}{\partial V}\right]\left(\frac{\partial V}{\partial R}\right)^{-1} = \frac{\partial}{\partial R}\left[\frac{\partial E}{\partial R}\left(\frac{\partial V}{\partial R}\right)^{-1}\right]\left(\frac{\partial V}{\partial R}\right)^{-1} =$$

$$\frac{\partial^2 E}{\partial^2 V} = \left[\frac{\partial^2 E}{\partial R^2}\left(\frac{\partial V}{\partial R}\right)^{-1} + \frac{\partial E}{\partial R}\frac{\partial}{\partial R}\left(\frac{\partial V}{\partial R}\right)^{-1}\right]\left(\frac{\partial V}{\partial R}\right)^{-1} =$$

$$\frac{\partial^2 E}{\partial^2 V} = \left[\frac{\partial^2 E}{\partial R^2}\left(\frac{\partial V}{\partial R}\right)^{-2} + \frac{\partial E}{\partial R}\frac{\partial}{\partial R}\left(\frac{\partial V}{\partial R}\right)^{-1}\left(\frac{\partial V}{\partial R}\right)^{-1}\right] =$$

$$\frac{\partial^2 E}{\partial^2 V} = \left[\frac{\partial^2 E}{\partial R^2}\left(\frac{\partial V}{\partial R}\right)^{-2} - \frac{\partial E}{\partial R}\left(\frac{\partial^2 V}{\partial^2 R}\right)\left(\frac{\partial V}{\partial R}\right)^{-1}\right]$$

$$R{=}R_o \text{ helyen}: \quad \left(\frac{\partial E}{\partial R}\right)_{R=Ro} = 0 = -A_M\frac{Ze^2}{R_o^{\ 2}} + n\frac{\lambda^*}{R_o^{\ n+1}}$$

$$\frac{\partial^2 E}{\partial^2 V} = \left[\frac{\partial^2 E}{\partial R^2}\left(\frac{\partial V}{\partial R}\right)^{-2}\right] = \left(\frac{\partial^2 E}{\partial R^2}\right)_{R=Ro}\left(6NR^2\right)^{-2}_{R=Ro}$$

$$\frac{1}{N}\left(\frac{\partial^2 E}{\partial R^2}\right)_{R=Ro} = -2A_M\frac{Ze^2}{R_o^{\ 3}} + n(n+1)\frac{\lambda^*}{R_o^{\ n+2}}$$

$$\frac{1}{N}\left(\frac{\partial^2 E}{\partial R^2}\right)_{R=Ro} = -2A_M\frac{Ze^2}{R_o^{\ 3}}\left(1-\frac{n(n+1)}{2n}\right) = A_M\frac{Ze^2}{R_o^{\ 3}}(n-1)$$

$$\kappa_S^{-1} = V(\partial^2 E/\partial V^2)_S = \left(2NR_o^3\right)N\left[A_M\frac{Ze^2}{R_o^{\ 3}}(n-1)\right]\frac{1}{\left(6NR_o^{\ 2}\right)^2}$$

$$\kappa_S^{-1} = \left[\frac{A_M}{18}\frac{Ze^2}{R_o^{\ 4}}\right](n-1)$$

NaCl –re : $\boldsymbol{R_o}$ =0.281 nm; $\boldsymbol{\kappa}$ = $3.3\,^{x}10^{-11}$ Pa^{-1} **;** $\boldsymbol{A_M^{NaCl}}$ =1.7476

n = 9.4

- ***Nem ionos potenciálok***
  -Van der Waals kötés, Lenard-Jones potenciál (dipól)
  ($N_{pár} = ½N_{atom}$):

$$V^{L.J.}(r) = -V_o\left\{2\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right\};$$

$$U^{V.W.}(R) = -V_o\left\{2\frac{\sigma^6}{R_o^6}\sum_{i,j}\left(\frac{1}{p_{ij}}\right)^6 - \frac{\sigma^{12}}{R_o^{12}}\sum_{i,j}\left(\frac{1}{p_{ij}}\right)^{12}\right\}$$

$$E = (N/2)\; U(R) = (N/2)\left[-V_o\left\{2\frac{\sigma^6 A_6}{R_o^6} - \frac{\sigma^{12} A_{12}}{R_o^{12}}\right\}\right]$$

, ahol $A_6 = \left\{\sum_{i,j}\left(\frac{1}{p_{ij}}\right)^6;\ \text{és}\ A_{12} = \sum_{i,j}\left(\frac{1}{p_{ij}}\right)^{12}\right\}$

$$U^{V.W.}(r) = -\frac{\alpha}{r^6} + \frac{\beta}{r^{12}}$$

$$\boldsymbol{A_6^{FCC} = 14.2235\ ;\ A_{12}^{FCC} = 12.13..\ (\approx Z!)}$$

- ***Vegyes potenciálok /párpotenciál/***

a) Exponenciális (Morse):

$$V(r)^{Morse} = V_0\left(\exp\left(2\alpha\left(1-\frac{r}{\sigma}\right)\right) - 2\exp\left(\alpha\left(1-\frac{r}{\sigma}\right)\right)\right)$$

$$V^{vonz}(r_o) = 2\,V^{tasz}(r_o)$$

$$r_o = \sigma$$

$$V_{min} = -V_o = V(r_o)$$

b) Módosított taszítású ionos potenciál

Párpotenciál
(hatványtaszító)

Párpotenciál
(exp. taszító)

V_{min}, r_o
(azonos)

$$V(r)^{ion} = -\left(\frac{Ze^2}{r}\right) + \left(\frac{\lambda}{r^n}\right)$$

$$V(r)^{ion} = -\left(\frac{Ze^2}{r}\right) + C\exp\left(-\frac{r}{\rho}\right)$$

$$\rho = r_o/n$$