

ELTE III.Fizika BSC
2014/2015 I.félév
Kondenzált anyag fizika
3. GYAKORLAT
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Kohézió (U), taszítás, Madelung szám (A_M), kompresszó(κ_T)

I. Kohézió (U), Madelung szám (A_M)

Párpotenciál

Kohézió

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

A_M Madelung állandó, A_6, A_{12}, \dots

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

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

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

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

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

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

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

$$U^{ion}(R) = -\frac{A}{R} + \frac{\lambda^*}{R^n}; \quad A = \alpha A_M; \quad \alpha = (1/4\pi\epsilon_0) Z e^2; \quad \lambda^* = \lambda A_n$$

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

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

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

$$dE = TdS - pdV$$

S = áll. \Rightarrow

$$dE = -pdV; \quad \Rightarrow \quad p = -(\partial E/\partial V)_S$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\text{NaCl-re: } R_o = 0.281 \text{ nm; } \kappa = 3.3 \times 10^{11} \text{ Pa}^{-1}; A_M^{NaCl} = 1.7476$$

$$n = 9.4$$

- **Nem ionos potenciálok**
-Van der Waals kötés, Lenard-Jones potenciál (dipól)
($N_{pár} = 1/2 N_{atom}$):

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

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

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

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

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

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

- **Vegyes potenciálok /párpotenciál/**

a) Exponenciális (Morse):

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

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

$$r_o = \sigma$$

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

b) Módosított taszítású ionos potenciál

Párpotenciál
(hatványtaszító)

Párpotenciál
(exp. taszító)

V_{min}, r_o
(azonos)

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

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

$$\rho = r_o/n$$