Mineral Physics I
Chapter 4. Equation of State
Section 3. Vinet equation of state

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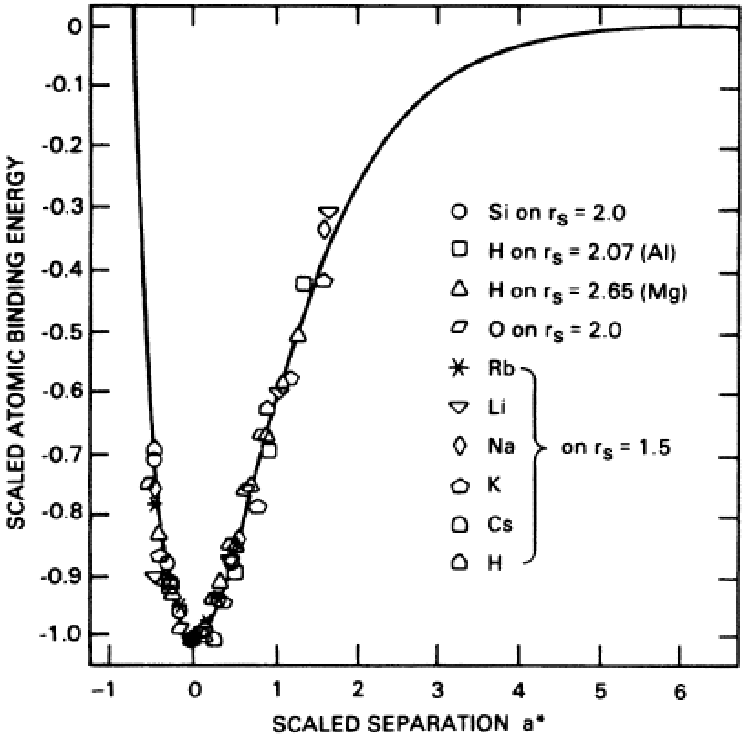
Derivation of Vinet EOS

- Vinet's EOS:

  - $P = 3K_{T0}\left(\frac{V}{V_0}\right)^{-\frac{2}{3}}\left[1-\left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\exp\left\{\frac{3}{2}(K'_{T0}-1)\left[1-\left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\right\}$ (4.1.9)

1. Assume a form of the Helmholtz free energy (F) as a function of V.
2. Obtain a formula of P as a function of V with K_{T0} and K'_{T0} by differentiating F by V.
3. Obtain the K_T by multiplying the V derivative of P by V.
4. Obtain K_{T0} by substituting $V = V_0$ into the formula in Step 3.
5. Obtain $K_T{}'$ from K_T.
6. Obtain K'_{T0} by substituting $V = V_0$ into the formula in Step 5.
7. Substitute K_{T0} and K'_{T0} from the formulas in Steps 4 and 6 into the formula of P in Step 2 .

Relations of binding energy to atomic separation



Atomic binding energy – atomic separation relation by ab initio calculation

FIG. 2. Atomic-binding-energy curves for chemisorption on jellium surfaces scaled as described in the text. The jellium bulk densities are denoted by the corresponding r_s values listed in the figure. The O results are from Ref. 12, the H results on $r_s = 2.07$ (Al) and 2.65 (Mg) are from Ref. 11, the Si results are from Ref. 10, the H results on $r_s = 1.5$ are from Ref. 8, and the alkali results are from Ref. 9.

- Rose [1983] & Vinet et al. [1983]
  - The atomic binding energy can be approximated by:
  - $E(a) = E_0(1 + a)\exp(-a)$ (4.3.1)

    $a = \dfrac{r - r_0}{l}$ (4.3.2)

    - r_0 and r: the interatomic distances at zero and high P
    - l: the scaling length

Derivation of Vinet EOS -1

q Assume that F has a formula similar to (4.3.1), $F(a) = F_0(1 + a)\exp(-a)$ with (4.3.2) $a = \frac{r - r_0}{l}$

Ø $$F(r) = F_0\left(1 + \frac{r - r_0}{l}\right)\exp\left(-\frac{r - r_0}{l}\right) \qquad (4.3.3)$$

ü F_0: constant

q Express Eq. (4.3.3) by volumes at zero and high *P*, V_0 and V, as:

Ø $$F(V) = F_0\left(1 + \frac{V^{1/3} - V_0^{1/3}}{l}\right)\exp\left(-\frac{V^{1/3} - V_0^{1/3}}{l}\right) \qquad (4.3.4)$$

ü $V = r^3$, $V_0 = r_0^3$

q From Eq. (4.1.1), P is:

Ø $$P = -\frac{\partial F(V)}{\partial V} = -F_0\left[\left(1 + \frac{V^{1/3} - V_0^{1/3}}{l}\right)' \exp\left(-\frac{V^{1/3} - V_0^{1/3}}{l}\right) + \left(1 + \frac{V^{1/3} - V_0^{1/3}}{l}\right)\left\{\exp\left(\frac{V_0^{\frac{1}{3}} - V^{\frac{1}{3}}}{l}\right)\right\}'\right]$$

$$= -F_0\left[\frac{1}{3l}V^{-\frac{2}{3}}\exp\left(-\frac{V^{1/3} - V_0^{1/3}}{l}\right) + \left(1 + \frac{V^{1/3} - V_0^{1/3}}{l}\right)\left(-\frac{1}{3l}V^{-\frac{2}{3}}\right)\exp\left(\frac{V_0^{\frac{1}{3}} - V^{\frac{1}{3}}}{l}\right)\right]$$

$$= -\frac{F_0}{3l^2}V^{-\frac{2}{3}}\left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right)\exp\left(\frac{V_0^{\frac{1}{3}} - V^{\frac{1}{3}}}{l}\right) \qquad (4.3.5)$$

Derivation of Vinet EOS - 2

- (4.3.5) $P = \frac{F_0}{3l^2} V^{-\frac{2}{3}} \left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right) \exp\left(\frac{V_0^{\frac{1}{3}} - V^{\frac{1}{3}}}{l}\right)$: Vinet's EOS
  - need to express it using neither F_0 nor l but using the macroscopic parameters, K_{T0} and K_{T0}'
- K_{T0} is obtained as:
  - $\left(\frac{\partial P}{\partial V}\right)_T = \frac{\partial}{\partial V}\left[\frac{F_0}{3l^2} V^{-\frac{2}{3}} \left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right) \exp\left[\left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right)/l\right]\right]$

$$= \frac{F_0}{3l^2}\left[-\frac{2}{3}V^{-\frac{5}{3}}\left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right) + V^{-\frac{2}{3}}\left(-\frac{1}{3}V^{-\frac{2}{3}}\right) + V^{-\frac{2}{3}}\left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right)\left(-\frac{1}{3l}V^{-\frac{2}{3}}\right)\right]\exp\left[\left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right)/l\right]$$

$$= \frac{F_0}{9l^3}\left[-2lV_0^{\frac{1}{3}}V^{-\frac{5}{3}} + \left(l - V_0^{\frac{1}{3}}\right)V^{-\frac{4}{3}} + V^{-1}\right]\exp\left[\left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right)/l\right] \quad (4.3.6)$$

  - $K_T = -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{F_0}{9l^3}\left[2lV_0^{\frac{1}{3}}V^{-\frac{2}{3}} - \left(l - V_0^{\frac{1}{3}}\right)V^{-\frac{1}{3}} - 1\right]\exp\left[\left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right)/l\right]$ (4.3.7)
  - $K_{T0} = \frac{F_0}{9l^3}\left[2lV_0^{\frac{1}{3}}V_0^{-\frac{2}{3}} - \left(l - V_0^{\frac{1}{3}}\right)V_0^{-\frac{1}{3}} - 1\right]\exp\left[\left(V_0^{\frac{1}{3}} - V_0^{\frac{1}{3}}\right)/l\right] = \frac{F_0}{9l^2}V_0^{-\frac{1}{3}} \quad (V = V_0)$ (4.3.8)

Derivation of Vinet EOS - 3

q From (4.3.7), K'_T and K'_{T0} are obtained as:

Ø $$K'_T = \left(\frac{\partial K_T}{\partial P}\right)_T = \left(\frac{\partial K_T}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial K_T}{\partial V}\right)_T \Big/ \left(\frac{\partial P}{\partial V}\right)_T \qquad (4.3.9)$$

Ø $$\left(\frac{\partial K}{\partial V}\right)_T = \frac{F_0}{27l^4}\left[V^{-\frac{2}{3}} + \left(l - V_0^{\frac{1}{3}}\right)V^{-1} + \left(l^2 - 3V_0^{\frac{1}{3}}l\right)V^{-\frac{4}{3}} - 4V_0^{\frac{1}{3}}l^2V^{-\frac{5}{3}}\right]\exp\left(\frac{V_0^{\frac{1}{3}} - V^{\frac{1}{3}}}{l}\right) \qquad (4.3.10)$$

Ø $$K'_T = \frac{1}{3l}\,\frac{V^{-\frac{2}{3}} + \left(l - V_0^{\frac{1}{3}}\right)V^{-1} + \left(l^2 - 3V_0^{\frac{1}{3}}l\right)V^{-\frac{4}{3}} - 4V_0^{\frac{1}{3}}l^2V^{-\frac{5}{3}}}{-2lV_0^{\frac{1}{3}}V^{-\frac{5}{3}} + \left(l - V_0^{\frac{1}{3}}\right)V^{-\frac{4}{3}} + V^{-1}} \qquad (4.3.11)$$

ü (4.3.6): $$\left(\frac{\partial P}{\partial V}\right)_T = \frac{F_0}{9l^3}\left[-2lV_0^{\frac{1}{3}}V^{-\frac{5}{3}} + \left(l - V_0^{\frac{1}{3}}\right)V^{-\frac{4}{3}} + V^{-1}\right]\exp\left(\frac{V_0^{\frac{1}{3}} - V^{\frac{1}{3}}}{l}\right)$$

Ø $$K'_{T_0} = \left(\frac{\partial K}{\partial P}\right)_{T,P=0} = \frac{1}{3l}\,\frac{V_0^{-\frac{2}{3}} + \left(l - V_0^{\frac{1}{3}}\right)V_0^{-1} + \left(l^2 - 3V_0^{\frac{1}{3}}l\right)V_0^{-\frac{4}{3}} - 4V_0^{\frac{1}{3}}l^2V_0^{-\frac{5}{3}}}{-2lV_0^{\frac{1}{3}}V_0^{-\frac{5}{3}} + \left(l - V_0^{\frac{1}{3}}\right)V_0^{-\frac{4}{3}} + V_0^{-1}} = 1 + \frac{2}{3l}V_0^{\frac{1}{3}} \quad (V = V_0) \qquad (4.3.12)$$

Derivation of Vinet EOS - 4

q Eq. (4.3.5):

$$\text{Ø}P = \frac{F_0}{3l^2} V^{-\frac{2}{3}} \left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right) \exp\left[\left(V_0^{\frac{1}{3}} - V^{\frac{1}{3}}\right)/l\right] = 3\frac{F_0}{9l^2 V_0^{\frac{1}{3}}} \left(\frac{V}{V_0}\right)^{-\frac{2}{3}} \left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right] \exp\left\{\frac{3}{2}\frac{2V_0^{\frac{1}{3}}}{3l}\left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\right\}$$

q Vinet's EOS:

$$\text{Ø}P = 3K_{T0} \left(\frac{V}{V_0}\right)^{-\frac{2}{3}} \left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right] \exp\left\{\frac{3}{2}(K'_{T0} - 1)\left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\right\} \quad (4.1.9)$$

ü From (4.3.8): $\frac{F_0}{9l^2} V_0^{-\frac{1}{3}} = K_{T0}$

ü From (4.3.9): $K'_{T_0} = 1 + \frac{2}{3l} V_0^{\frac{1}{3}} \Rightarrow \frac{2V_0^{\frac{1}{3}}}{3l} = K'_{T_0} - 1$

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