

# BOSE-EINSTEIN APPROXIMATION IN SELF-CONSISTENT EQUATION OF STATE OF MINERALS

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## Introduction

Knowledge of self-consistent thermodynamic functions of minerals is the main requirement for computer modeling of chemical equilibria and construction of geophysical models in lower crust and mantle of the Earth. This problem is resolved in well known method of potentials in the Debye approximation [e.g. 1-6]. Other approaches to this problem are known also [e.g. 7-10]. Otherwise for calculation of the thermodynamic functions vs.  $T$ ,  $P$  and  $V$  it is necessary to enter different simplifications as it was made in *Anderson and Zou* [11] formulation of the thermodynamic functions for mantle minerals.

The main purpose of this study is the modification of the *Zharkov and Kalinin* [1] formalism. In place of the usual Debye function, we are using the Bose-Einstein functions for the approximation of thermal part of the Helmholtz free energy. The Bose-Einstein functions was proposed by *Kut'in and Pyadushkin* [12] for the Gibbs energy at zero pressure, but these relations may be used in the  $VT$  relations, that is for the Helmholtz free energy. As a result we obtain a set of equation for volume-temperature dependence of a thermodynamic functions. We can apply the derived set of equations for calculation of any thermodynamic functions vs.  $PVT$  if we find a set of fitting parameters in our model optimizing available experimental measurements of the heat capacity and relative enthalpy vs.  $T$ , volume as function of pressure and temperature, thermal expansion coefficient, bulk moduli etc. Finally, we obtain a simple thermal equation of state for mantle minerals which one allows both to evaluate self-consistent thermodynamic functions from experimental measurements and to calculate one vs. any temperature and pressure. This EoS is equally suitable both for petrological constructions and for geophysical models of the deep of the Earth.

## Basic equations

The Helmholtz free energy  $F(V, T)$  may be written as [1, 13]:

$$F(V, T) = U_0 + E_P(V) + F_{th}(V, T) + F_a(V), \quad (1)$$

where  $U_0$  is energy at 0 K and zero pressure,  $E_P(V)$  is a part of energy depend only from volume,  $F_{th}(V, T)$  is a thermal part of the free energy,  $F_a(V)$  is anharmonic part of the free energy.

Energy vs. volume may be expressed using the logarithmic equation of state by *Poirier and Tarantola* [14]:

$$E_P = \frac{1}{2} K_0 V_0 [(\ln x)^2 - \frac{K'-2}{3} (\ln x)^3], \quad (2)$$

where  $K_0$  and  $V_0$  are bulk modulus and volume at zero temperature and pressure,  $K' = dK_0/dP$ ,  $x = V/V_0$ . The pressure  $P(V) = -\partial E_P / \partial V$  and bulk modulus  $K_T(V) = -V(\partial P(V) / \partial V)$  written as:

$$P(V) = K_0 \frac{1}{x} [-\ln x + \frac{K'-2}{2} (\ln x)^2], \quad (3)$$

$$K_T(V) = K_0 \frac{1}{x} [1 + (1 - K') \ln x + \frac{K'-2}{2} (\ln x)^2], \quad (4)$$

The thermal part of free energy expressed using the Bose-Einstein functions [12]:

$$F_{th} = m_B R T \left[ \frac{\Theta_B}{2T} - \ln(1+b) \right] + m_{E1} R T \left[ \frac{\Theta_{E1}}{2T} + \ln\left(1 - \frac{1}{\exp(\Theta_{E1}/T)}\right) \right] + m_{E2} R T \left[ \frac{\Theta_{E2}}{2T} + \ln\left(1 - \frac{1}{\exp(\Theta_{E2}/T)}\right) \right], \quad (5)$$

where  $R$  is gas constant,  $m_B$ ,  $m_{E1}$  and  $m_{E2}$  are degrees of freedom and  $m_B + m_{E1} + m_{E2} \geq 3n$  and  $n$  is number of atoms,  $\Theta_B$ ,  $\Theta_{E1}$  and  $\Theta_{E2}$  are the characteristic temperatures Bose and Einstein parts,  $b = 1/[\exp(g)-1]$ ,  $g = d \ln[1 + \Theta_B/(Td)]$ ,  $d$  is fitting parameters for heat capacity near 0 K. If  $d = 1$  we have linear dependence of heat capacity, for  $d = 4$  this dependence approaches Debye capacity and we have Einstein capacity.

From (5) we can obtained the internal energy and the heat capacity at constant volume:

$$E_{th} = m_B R \left( \frac{\Theta_B}{2} + \frac{\Theta_B T d b}{T d + \Theta_B} \right) + m_{E1} R \left[ \frac{\Theta_{E1}}{2} + \frac{1}{\exp(\Theta_{E1}/T) - 1} \right] + m_{E2} R \left[ \frac{\Theta_{E2}}{2} + \frac{1}{\exp(\Theta_{E2}/T) - 1} \right], \quad (6)$$

$$C_{V_{th}} = m_B R \left( \frac{\Theta_B d}{T d + \Theta_B} \right)^2 b(1/d + 1 + b) + m_{E1} R (\Theta_{E1}/T)^2 \frac{\exp(\Theta_{E1}/T)}{[\exp(\Theta_{E1}/T) - 1]^2} + m_{E2} R (\Theta_{E2}/T)^2 \frac{\exp(\Theta_{E2}/T)}{[\exp(\Theta_{E2}/T) - 1]^2}. \quad (7)$$

From (5) we have the thermal pressure  $P_{th} = -(\partial F_{th} / \partial V)_T$ :

$$P_{th} = \tilde{\alpha}_B E_B / V + \tilde{\alpha}_{E2} E_{E1} / V + \tilde{\alpha}_{E2} E_{E2} / V, \quad (8)$$

where  $E_B$ ,  $E_{E1}$  and  $E_{E2}$  are Bose and Einstein parts of the inner energy  $\gamma_B$ ,  $\gamma_{E1}$  and  $\gamma_{E2}$  are the Gruneisen parameters  $\gamma = -(\partial \ln \square / \partial \ln V)_T$ , and from (8) can be found  $K_{Th} = -V(\partial P_{th} / \partial V)_T$ :

$$K_{Th} = P_{thB} (1 + \gamma_B + q_B) - \gamma_B^2 TC_{VB} / V + \\ + P_{thE1} (1 + \gamma_{E1B} + q_{E1}) - \gamma_{E1}^2 TC_{VE1} / V \\ + P_{thE2} (1 + \gamma_{E2B} + q_{E2}) - \gamma_{E2}^2 TC_{VE2} / V, \quad (9)$$

where  $P_{thB}$ ,  $P_{thE1}$  and  $P_{thE2}$ ,  $C_{VB}$ ,  $C_{VE1}$  and  $C_{VE2}$  are Bose and Einstein parts of thermal pressure and heat capacity at constant volume,  $q_B$ ,  $q_{E1}$  и  $q_{E2}$  are logarithmic derivatives  $q = (\partial \ln \gamma / \partial \ln V)_T$ .

At high temperatures the anharmonicity should be taken into account. According [1], the anharmonic part of the free energy is proportional to the square of temperature:

$$F_a(V) = -a(V)T^2, \quad (10)$$

where  $a(V)$  is the anharmonic parameter. From this we have:

$$E_a = aT^2, S_a = 2aT, C_{Va} = 2aT, P_a = \gamma_a E_a / V, \\ \gamma_a = (\partial \ln a / \partial \ln V)_T, K_{Ta} = P_a(1 - \gamma_a). \quad (11)$$

We assume that  $\gamma_a = \text{const}$ .

From the slope at constant volume

$$(\partial P / \partial T)_V = \gamma_B C_{VB} / V + \gamma_{E2} C_{VE1} / V + \\ + \gamma_{E2} C_{VE2} / V + \gamma_a C_{Va} / V \quad (12)$$

we can find thermal expansion coefficient  $\alpha = (\partial P / \partial T)_V / K_T$ , where  $K_T = K_T(V) + K_{Th} + K_{Ta}$ .

The volume dependence of the Gruneisen parameters and characteristic temperatures written in classical form:

$$\gamma = \gamma_0 x^q \text{ и } \Theta = \Theta_0 \exp[\gamma_0(1 - x^q)/q]. \quad (13)$$

Pressure, enthalpy and the Gibbs energy may be found from  $P = P(V) + P_{th} + P_a$ ,  $H = E + PV$ ,  $G = F + PV$ .

We assume that thermodynamic values of the Gruneisen parameter is true for any conditions

$$\gamma = \alpha K_T V / C_V \text{ и } \gamma = \alpha K_S V / C_P, \quad (14)$$

where  $K_S$  is adiabatic bulk modulus and  $C_P$  is heat capacity at constant pressure.

The offered model allows to calculate any thermodynamic functions at given temperature and volume or pressure if we know all fitting parameters:  $U_0$ ,  $V_0$ ,  $K_0$ ,  $K'$ ,  $d$ ,  $m_B$ ,  $m_{E1}$ ,  $m_{E2}$ ,  $\Theta_{B0}$ ,  $\Theta_{E10}$ ,  $\Theta_{E20}$ ,  $a_0$ ,  $\gamma_{B0}$ ,  $\gamma_{E10}$ ,  $\gamma_{E20}$ ,  $\gamma_a$ ,  $q_B$ ,  $q_{E1}$ ,  $q_{E2}$ . The fitting parameters may be obtained by optimization, that is, by solving the set of equations using the weighted least squares method and experimental data on heat capacity at constant pressure, relative enthalpy, volume, thermal expansion coefficient, bulk moduli and other data. The offered set of equations can be simplified by suspecting, that the Gruneisen parameter and parameter  $q$  is identical for all thermal parts, that essentially reduce number of fitting parameters. Now we have a following set of fitting of parameters:  $U_0$ ,  $V_0$ ,  $K_0$ ,  $K'$ ,  $d$ ,  $m_B$ ,  $m_{E1}$ ,  $m_{E2}$ ,  $\Theta_{B0}$ ,  $\Theta_{E10}$ ,  $\Theta_{E20}$ ,  $a$ ,  $\gamma$ ,  $\gamma_a$ ,  $q$ .

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