4. Equation of State

4.6 Thermal equation of state

4.6.1 Thermal equation of state

Thermal equation of state is an equation of state including temperature (T) and pressure (P). Thermal equation of state is essential for geophysics because the planetary interiors are under high temperature conditions. For example, the temperature conditions in the interiors are 1700 K at the top of the asthenosphere, 2000 K at the 660-km discontinuity and 4000-5000 K at the core-mantle boundary. Two paths exists when we consider the change from ambient conditions of (P_0, V_0, T_0) to high P-T conditions (P_3, V_3, T_3). The two paths are first heated then compressed path (HC path) and first compressed then heated path (CH path).

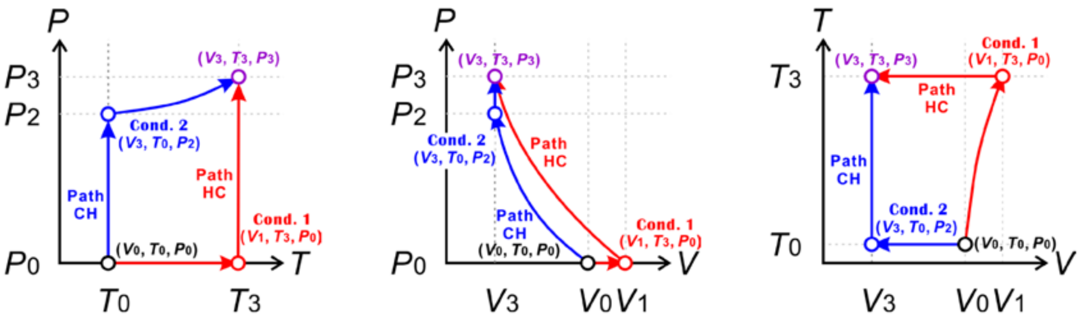


Fig. 1 Paths between two conditions.

4.6.2 HT Birch-Murnaghan EOS

We first consider the example of Birch Murnaghan equation of state (EOS) in higher temperature. Volume changes from V_0 to V_3 by heating from T_0 to T_3 at initial pressure P_0 due to thermal expansion.

$$V_1 = V_0 \int_{T_0}^{T_3} \alpha(T) \tag{4.6.1}$$

α is a thermal expansion coefficient. Assuming the constant coefficient α_0, we have

$$V_1 \cong \{1 + \alpha_0(T_3 - T_0)\}V_0 \tag{4.6.2}$$

By assuming that thermal expansion coefficient is a linear function of T, we have

$$V_1 \cong \{1 + \alpha_0(T_3 - T_0) + \frac{1}{2}\alpha_1(T_3 - T_0)^2\}V_0 \tag{4.6.3}$$

Compression from V_1 to V_3 increases P from P_0 to P_3, expressed by high-temperature 3rd-order Birch-Murnaghan EOS.

$$P_3 - P_0 \cong \frac{1}{2}K_{T,0}(T_3)\left[\left(\frac{V_1}{V_3}\right)^{\frac{7}{3}} - \left(\frac{V_1}{V_3}\right)^{\frac{5}{3}}\right] \times \left\{1 + \frac{3}{4}(K'_{T,0} - 4)\left[\left(\frac{V_1}{V_3}\right)^{\frac{2}{3}} - 1\right]\right\} \tag{4.6.3}$$

$K_{T,0}(T)$ is the isothermal bulk modulus at zero pressure as a function of T.

For simplicity, $K_{T,0}(T)$ is assumed a linear function of T.

$$K_{T,0}(T_3) \cong K_{T=T_0,0}(T_3) + \left(\frac{\partial K_{T,0}}{\partial T}\right)_P (T_3 - T_0) \tag{4.6.3}$$

Because of experimental difficulty, $K'_{T,0} = \left(\frac{\partial K_{T,0}}{\partial P}\right)_T$ is usually assumed independent from P and T.

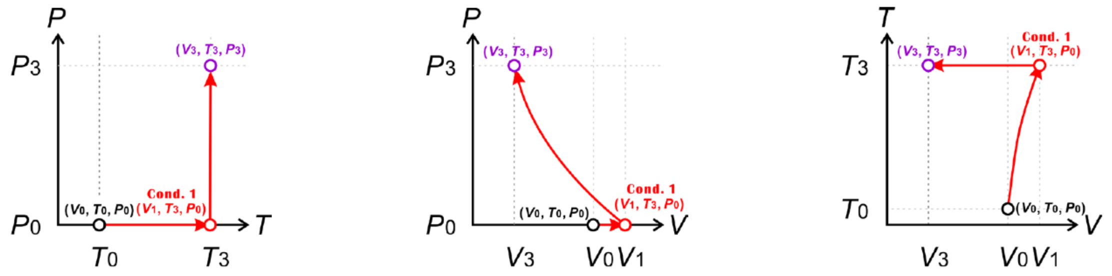


Fig. 2 HC path

4.6.3 Mie-Grüneisen EOS

Next, we consider CH path. V is first decreased from V_0 to V_3 at $T = T_0$ to increase P from P_0 to P_2.

$$P_2 - P_0 = \frac{3}{2} K_{T,0}(T_0) \left[\left(\frac{V_0}{V_3}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V_3}\right)^{\frac{5}{3}} \right] \times \left\{ 1 + \frac{3}{4}(K'_{T,0} - 4) \left[\left(\frac{V_0}{V_3}\right)^{\frac{2}{3}} - 1 \right] \right\} \quad (4.6.6)$$

P increases $\Delta P_{\text{th}} = P_3 - P_2$ by T increase at constant volume $V = V_3$

$$\Delta P_{\text{th}} = P_3 - P_2 = \int_{T_0}^{T_3} \left(\frac{\partial P}{\partial T}\right)_{V=V_3} \mathrm{d}T \quad (4.6.7)$$

$(\partial P/\partial T)_V$ is thermal pressure. This ΔP_{th} is related to E increase by T increase at constant V.

$$\Delta P_{\text{th}} = \gamma_{\text{th}} (\Delta E / V) \quad (4.6.8)$$

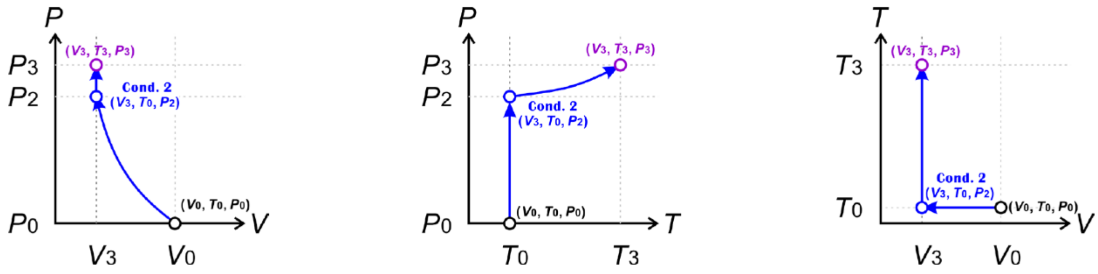
This equation is Mie-Grüneisen equation of state. γ_{th} is the Grüneisen parameter. ΔE_{th} is expressed by isochoric heat capacity C_V.

$$\Delta E_{\text{th}} = \int_{T_0}^{T_3} C_V \mathrm{d}T \quad (4.6.9)$$

This C_V is expressed by the Debye approximation,

$$C_V = 9Nk_B(T/\theta_D)^3 \int_{\theta_D/T_0}^{\theta_D/T_3} \{x^4 \exp x / (\exp x - 1)^2\} \mathrm{d}T \quad (3.7.18')$$

To this point, we consider both HC and CH paths. CH path has some merits. Physical properties under high pressure (HT) and room pressure (RP) conditions for the HC path are more difficult to obtain those under high pressure (HP) and room temperature (RT) conditions for the CH path because minerals at HT conditions (such as gamma iron) are unstable and difficult to measure. The thermal pressure for the CH path is more easily estimated due to the Debye model than high-temperature compression for the CH path.



P
P_3
P_2
P_0
(V_3, T_3, P_3)
Cond. 2
(V_3, T_0, P_2)
(V_0, T_0, P_0)
V_3
V_0
V
P
P_3
P_2
P_0
(V_3, T_3, P_3)
Cond. 2
(V_3, T_0, P_2)
(V_0, T_0, P_0)
T_0
T_3
T
T
T_3
T_0
(V_3, T_3, P_3)
Cond. 2
(V_3, T_0, P_2)
(V_0, T_0, P_0)
V_3
V_0
V

Fig. 3 CH path