

4. Equation of state

4. Murnaghan equation of state

4.1 What is 'Murnaghan equation of state'?

The **Murnaghan equation of state** is a one of many equations of state that have been used in Earth and planetary sciences to model the behavior of matter under conditions of high pressure, which is proposed by **Francis D. Murnaghan** in 1944. The Murnaghan equation of state is based on an experimentally established fact that the more a solid is compressed, the more difficult it is to compress further, which is expressed as:

$$P = \left(\frac{K_{T0}}{K'_{T0}} \right) \left[\left(\frac{V}{V_0} \right)^{K'_{T0}} - 1 \right] \quad (4.1.13)$$

, where K_{T0} is **bulk modulus** and K'_{T0} is the derivative of K_{T0} with respect to pressure.

4.2 Derivation of Murnaghan equation of state

To derive Murnaghan's equation of state, we start from an assumption that the isothermal bulk modulus at high pressure K_T is a linear function of P :

$$K_T = K_{T0} + K'_0 * P \quad (4.4.1)$$

From Eq. (4.4.1) with the general definition of K_T Eq. (1.1.29) $K_T = -V \left(\frac{\partial P}{\partial V} \right)_T$,

$$K_T + K'_0 P = -V \left(\frac{\partial P}{\partial V} \right)_T = -\frac{1}{\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T} = -\frac{1}{\left(\frac{\partial \ln V}{\partial P} \right)_T} = -\left(\frac{\partial P}{\partial \ln V} \right)_T \quad (4.4.2)$$

We transform Eq. (4.4.2) to $\left(\frac{\partial \ln V}{\partial P} \right)_T = -\frac{1}{K_T + K'_0 P}$, and substitute $\eta = K_T + K'_0 P$ and $\frac{dP}{d\eta} = \frac{1}{K'_0}$ into

it,

$$\ln V = \int \left(-\frac{1}{K_T + K'_0 P} \right) dP = -\int \frac{1}{\eta} \frac{dP}{d\eta} d\eta = -\frac{1}{K'_0} \ln(K_T + K'_0 P) + C \quad (4.4.3)$$

, where C is integral constant, which can be obtained by Eq. (4.4.3) at $P = 0$,

$$\begin{aligned} \ln V_0 &= -\frac{1}{K'_0} \ln K_{T0} + C \\ C &= \ln V_0 + \frac{\ln K_{T0}}{K'_0} \end{aligned} \quad (4.4.4)$$

Then, Eq. (4.4.3) $\ln V_0 = -\frac{1}{K'_0} \ln K_{T0} + C$ becomes:

$$\begin{aligned} \ln V &= -\frac{1}{K'_0} \ln(K_T + K'_0 P) + \ln V_0 + \frac{\ln K_{T0}}{K'_0} \\ K'_0 \ln \left(\frac{V_0}{V} \right) + \ln K_{T0} &= \ln(K_T + K'_0 P) \end{aligned}$$

$$K_{T0} \left(\frac{V_0}{V} \right)^{K'_0} = K_T + K'_0 P$$

$$P = \frac{K_{T0}}{K'_0} \left[\left(\frac{V_0}{V} \right)^{K'_0} - 1 \right] \quad (4.4.5)$$

, which is the Murnaghan EOS.

4.3 Summary of comparison between different equations of state

We compare the different equations of state for NaCl, MgO and Au in Figs. 1-3. All these equations show no obvious differences at low pressure (V/V_0 below 0.9). Above $V/V_0 = 0.9$, Birch-Murnaghan and Murnaghan's equations of states give similar pressures for the same compression, whereas Vinet equation of state gives lower pressures than Birch-Murnaghan and Murnaghan's equations of states, by 30% for NaCl, MgO and Au. All of these equations of state give much higher pressures than the equations of state from the integration of the isothermal bulk modulus.

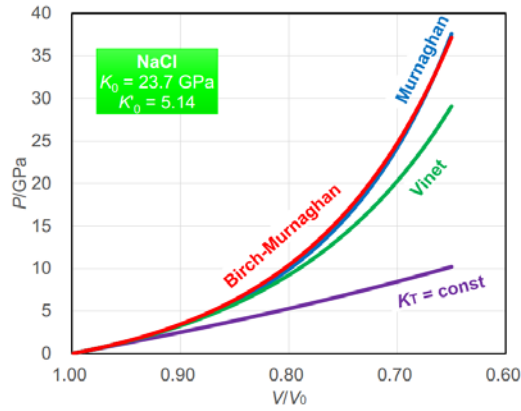


Fig. 1. Compression of NaCl based on various EOS. Very low $K_0 = 23.7$ GPa, K'_0 is larger than 4 (5.14), negative K''_0 . It shows relatively low-pressure values even at high compression.

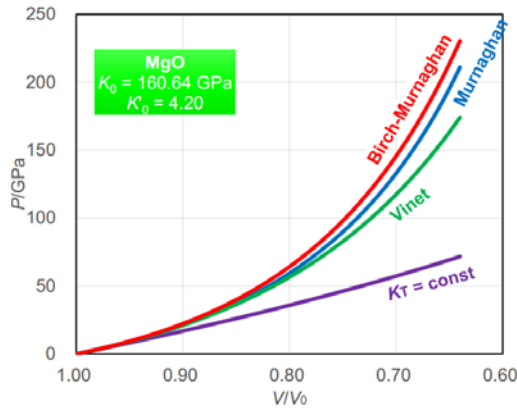


Fig. 2. Compression of MgO based on based on various EOS. Relatively high $K_0 = 160$ GPa, K'_0 is

slightly larger than 4 (4.20). No K_0'' data and $K_0'''=0$, which does not mean that 4th EOS becomes 3rd EOS. It shows relatively high-pressure values by large compression.

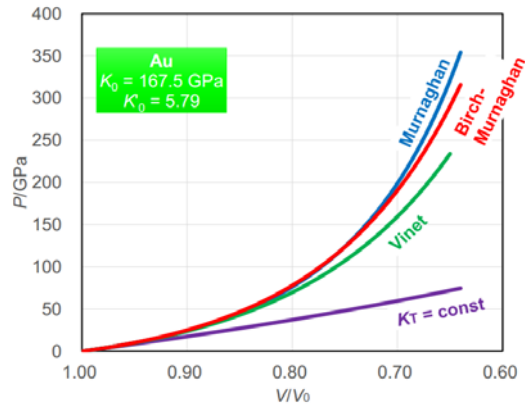


Fig. 3. Compression of Au based on based on various EOS. Relatively high $K_0 = 168 \text{ GPa}$, K_0' is slightly larger than 4 (5.8). No K_0'' data. It shows relatively high-pressure values by large compression.