4. Equation of state

1. Why "equation of state"?

1.1 Why "equation of state"?

The equation of state (EOS) is the relationship among pressure (P), temperature (T), and volume (V), and we can estimate the density (ρ) of earth and planetary interiors by using the equation of state (EOS). For a given amount of matter related to the equation of state (EOS), if the other two are known, one of the values (P or T or V) can be obtained. The equation of state is important because we can obtain density. Density is one of essential parameters to describe the Earth and planetary interiors. Density is specific mass (m) divided by specific volume (V). Volume (V) of matter in the Earth and planetary interior is different from ambient conditions volume due to high pressure and high temperature (HP-HT). Namely, matters at high pressure have a smaller volume and matters at high temperature have usually larger volume due to thermal expansion (α). Therefore, given pressure and temperature, the volume can be determined using the equation of state (EOS) to estimate the density (ρ) of the earth and planetary interior.

1.2 Isothermal EOS

The pressure (P), refers to how much mechanical energy is stored in given volume. In thermodynamics, pressure (P) defined by volume (V) derivative of Helmholtz free energy (F) at constant temperature (T):

$$P = -(\partial F/\partial V)_T \tag{4.1.1}$$

The Helmholtz free energy is expressed as:

$$F = E - TS \tag{4.1.2}$$

where E is internal energy, and S is entropy. The free energy refers to internal energy available for mechanical works. In the equation (4.1.2), TS means unavailable energy for mechanic and E means stored energy in a matter. From the equation of (4.1.1), pressure (P) means the free energy per unit volume or how much mechanical energy is stored in given volume. In other words, pressure is primarily a function of volume (V) and secondarily a function of temperature (T). In this chapter, the equation of state at a constant temperature T is first described. This state is called the isothermal equation of state, and please note that the bulk modulus in Chap 4 is always "isothermal bulk modulus".

1.3 Pressure increase by infinitesimal compression

The pressure increase due to infinitesimal compression is expressed by the equation relating proportionality constant (K_{T0}), temperature (T), and volume (V). We briefly discuss the pressure increase due to infinitesimal compression. First, consider the uniform compression of a homogeneous object of initial length (L_0). The infinitesimal uniform compression changes the length by $\delta L < 0$. Since the change in length should be proportional to the initial length (L_0):

$$\delta L = cL_0 \tag{4.1.3}$$

where c is constant ($c < 0$), and it is referred to as infinitesimal strain in the usual elasticity. The volume before compression (V_0) is proportional to L_0^3. The volume after compression is $V_0 + \delta V$ and proportional to $(L_0 + \delta L)^3$, also equal to $(L_0 + cL_0)^3$. Therefore, the volume change (δV) is:

$$\delta V \propto (L_0 + \delta L)^3 - L_0^3 = [(1 + c)^3 - 1]L_0^3 \approx 3cV_0 < 0 \tag{4.1.4}$$

Next, we consider the pressure increase due to infinitesimal compression (δP). It should be approximated to be proportional to the volume change relative to the initial volume ($\delta V/V_0$). The

reason for this considering is that if the initial volume is large, the pressure will not increase much when compressed by the same volume. Therefore, infinitesimal compression (δP) is:

$$\delta P = -K_{T0}\frac{\delta V}{V_0} = -K_{T0}\frac{3cV_0}{V_0} = -3cK_{T0} > 0 \tag{4.1.5}$$

where K_{T0} is the proportional constant and related to the isothermal bulk modulus, and δP is pressure increase from zero by infinitesimal compression.

1.4 Compression to zero volume

Neither linear compression nor compression with constant K_T can reproduce realistic compression of matter. First, we consider the compression to zero volume by assuming a linear compression. When $\delta V = -V_0$, pressure increase (δP) is expressed as:

$$\delta P = -K_{T0}\frac{\delta V}{V_0} = -K_{T0}\frac{-V_0}{V_0} = K_{T0} \tag{4.1.6}$$

The pressure increase should be equal to the isothermal volume modulus. Considering the situation (4.1.6), in a linear compression (see blue line in Fig. 1.), the pressure is zero without a compression, which increase to K_{T0} at zero volume. Of course, this situation is incorrect against the compression results obtained in our experiment. In a more realistic condensed matter, we can see that the compression is over the red curve in Fig.1. The pressure rapidly increases with increasing a compression. Therefore, the idea that pressure increase (δP) is proportional to the relative volume ($\delta V/V_0$) need to be corrected. The pressure increase (δP) is always having to consider along the compression path. This should be proportional to δV to the V at each time. Therefore, the relationship between pressure and volume can be expressed by the following differential equation:

$$dP = -K_T\frac{dV}{V} \tag{4.1.7}$$

Then, integrating the differential equation (4.1.7), we find that K_T is always K_{T0} if the isothermal volume fraction is constant, and P is:

$$P = K_{T0}\, ln\left(\frac{V_0}{V}\right) \tag{4.1.8}$$

or V/V_0 is:

$$\frac{V}{V_0} = \exp\left(-\frac{P}{K_{T,0}}\right) \tag{4.1.9}$$

This situation (compression with constant K_T) is expressed as green curve in Fig. 1. However, neither linear compression nor constant K_T compression reproduces the compression of real matters. As pressure increases, matter becomes more incompressible, requiring more realistic equation states.
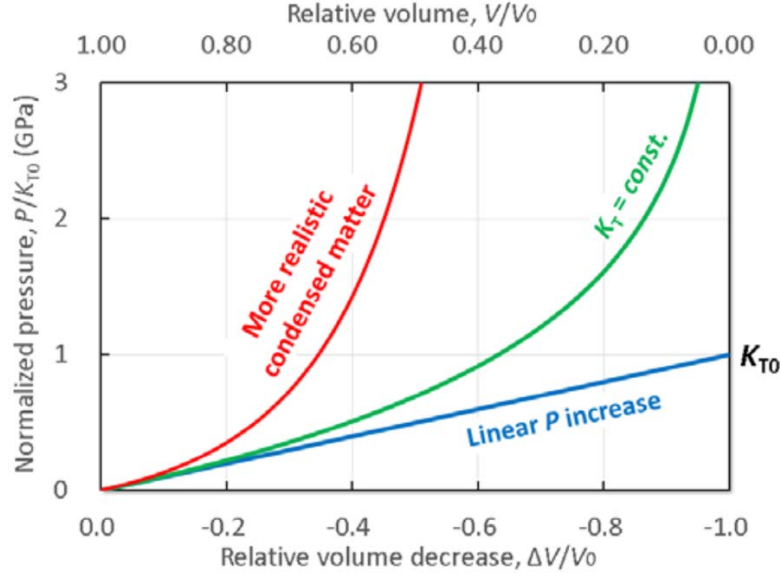
Fig. 1. The relationship between pressure and volume. The lower horizontal axis is relative volume decrease, with zero compression on the left side and zero volume with compression on right side. The upper horizontal axis is relative volume, with unity relative volume on the left side and the zero relative volume on right side. The vertical axis shows normalized pressure.

1.5 Frequently used isothermal EOS's in geophysics

We summarize the frequently used isothermal equation of state in geophysics. Following equation will introduce in next section. First one is 2nd-order Birch-Murnaghan equation of state (BM2-EOS):

$$P = \left(\frac{3}{2}\right) K_{T0} \left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}} \right] \tag{4.1.10}$$

Next is 3rd-order Birch-Murnaghan equation of state (BM3-EOS):

$$P = \left(\frac{3}{2}\right) K_{T0} \left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}} \right] \times \left\{ 1 + \left(\frac{3}{4}\right)(K'_{T0} - 4) \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right] \right\} \tag{4.1.11}$$

This equation is higher order than 2nd-order Birch-Murnaghan equation of state and most frequently used. When $K'_{T0} = 4$, this equation is identical to 2nd-order Birch-Murnaghan equation of state. 3rd one is Vinet equation of state:

$$P = 3 K_{T0} \left(\frac{V}{V_0}\right)^{-\frac{2}{3}} \left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}} \right] \exp \left\{ \left(\frac{3}{2}\right)(K'_{T0} - 1) \left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}} \right] \right\} \tag{4.1.12}$$

Last one is Murnaghan's integrated equation of state:

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

3