Mineral Physics I
Chapter 4. Equation of state

TOMOO KATSURA

BAYERISCHES GEOINSTITUT, UNIVERSITY OF BAYREUTH, GERMANY

Mineral Physics I
Chapter 4. Equation of State
Section 1. Why “equation of state”?

TOMOO KATSURA

BAYERISCHES GEOINSTITUT, UNIVERSITY OF BAYREUTH, GERMANY

Why “equation of state”?

q Equation of state (EOS): relations among P, T, and V

Ø With a given amount of matter, one valuable is obtained if the other two are known.

q Density (ρ): one of essential parameters to describe the Earth and planetary interiors

Ø $\rho = m/V$

ü m: specific mass, V: specific volume

Ø V of matter in the Earth and planetary interior: different from ambient V due to HP-HT

ü Matters at HP: smaller V

ü Matters at HT: usually larger V due to thermal expansion (α)

Ø P, T à V using EOS à ρ

Isothermal EOS

- P: defined by V derivative of Helmholtz free energy, F, at constant T:
  - $P = -(\partial F/\partial V)_T$ (4.1.1)
    - $F = E - TS$ (4.1.2)
      - E: internal energy, S: entropy
      - (Free energy): (stored energy in a matter) – (unavailable energy for mechanics)
    - $P = -(\partial F/\partial V)_T$ à P is the free energy per unit volume
      - Or, how much mechanical energy is stored in a given volume
- P is primarily a function of V, and secondarily a function of T.
  - First discuss equations of state at constant T
    - Isothermal equation of state
      - The bulk modulus in Chap 4 is always “isothermal bulk modulus”

Pressure increase by infinitesimal compression -1

- A uniform compression of a homogeneous body with an initial length of L_0
  - The length of the body is changed by $\delta L < 0$ due to infinitesimal uniform compression
  - The length change should be proportional to L_0:
    - $\delta L = cL_0$ (4.1.3)
      - Constant $c < 0$: (infinitesimal) strain
  - The volume of the body before compression:
    - $V_0 \propto L_0^3$
  - The volume after compression:
    - $V_0 + \delta V \propto (L_0 + \delta L)^3 = (L_0 + cL_0)^3$
  - The volume change:
    - $\delta V \propto (L_0 + cL_0)^3 - L_0^3 = [(1 + c)^3 - 1]L_0^3 \approx 3cV_0 < 0$ (4.1.4)

Pressure increase by infinitesimal compression -2

- Pressure increase by infinitesimal compression, δP
  - Should be approximated to be proportional to the volume change relative to the initial volume, $\delta V / V_0$
    - If the initial volume is larger, the pressure does not increase significantly even compressed in the same volume.
  - $\delta P = -K_{T0} \frac{\delta V}{V_0} = -K_{T0} \frac{3cV_0}{V_0} = -3cK_{T0} > 0$ (4.1.5)
    - δP: pressure increase by infinitesimal compression
    - The proportional constant K_{T0}: the isothermal bulk modulus

Compression to zero volume

q Linear compression to zero volume

ü $\delta V = -V_0$

ü $\delta P = -K_{T0}\frac{\delta V}{V_0} = -K_{T0}\frac{-V_0}{V_0} = K_{T0}$ (4.1.6)

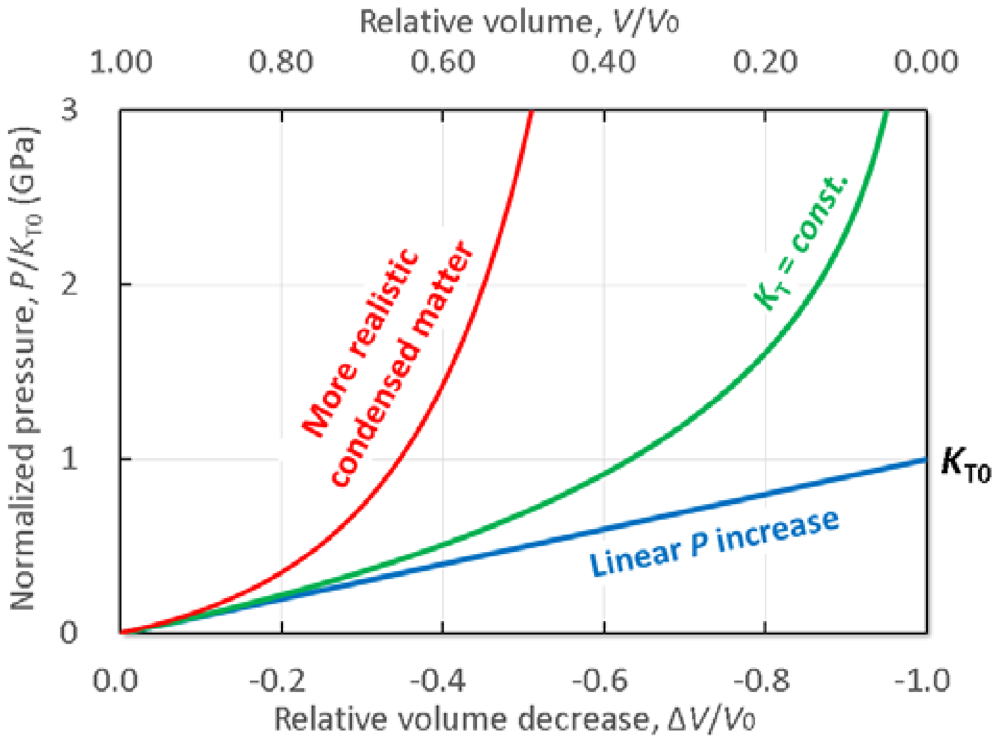
ü The pressure increase = the isothermal bulk modulus

§ Of course, incorrect!

Ø The idea that δP is proportional to $\delta V/V_0$ need to be corrected

ü δP along the compression path is proportional to δV relative to the V at the time

ü $\mathrm{d}P = -K_T\frac{\mathrm{d}V}{V}$ (4.1.7)



Blue: linear compression

Green: compression with constant K_T

Red: more realistic compression

Integration of pressure increase

q Integration of (4.1.7) $\mathrm{d}P = -K_T \frac{\mathrm{d}V}{V}$

q If the isothermal bulk modulus is constant, $K_T = K_{T0}$

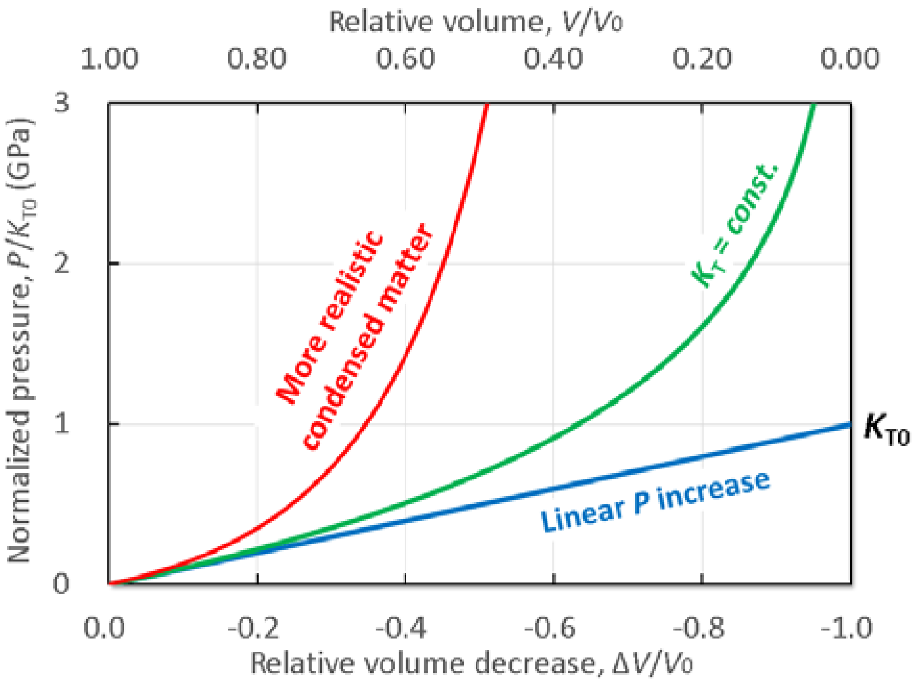
Ø $P = K_{T0} \ln\left(\frac{V_0}{V}\right)$ (4.1.8)

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

q However, neither linear compression nor constant-K_T compression reproduces the compression of real matters.

Ø Matters become more incompressive with *P*

Ø We need more realistic EOS



Blue: linear compression

Green: compression with constant K_T

Red: more realistic compression

Frequently used isothermal EOS's in geophysics

- **2nd-order Birch-Murnaghan equation of state** (BM2-EOS):
  - $P = (3/2)K_{T0}\left[(V_0/V)^{7/3} - (V_0/V)^{5/3}\right]$ (4.1.10)
- **3rd-order Birch-Murnaghan equation of state** (BM3-EOS):
  - $P = (3/2)K_{T0}\left[(V_0/V)^{7/3} - (V_0/V)^{5/3}\right] \times \left\{1 + (3/4)\left(K'_{T_0} - 4\right)\left[(V_0/V)^{2/3} - 1\right]\right\}$ (4.1.11)
    - Higher order than 2nd-order Birch-Murnaghan EOS
    - Most frequently used
    - identical to 2nd-order Birch (BM2-EOS) when $K'_{T_0} = 4$
- **Vinet equation of state**
  - $P = 3K_{T0}(V/V_0)^{-2/3}\left[1 - (V/V_0)^{1/3}\right]\exp\left\{(3/2)(K'_{T0} - 1)\left[1 - (V/V_0)^{1/3}\right]\right\}$ (4.1.12)
- **Murnaghan's integrated equation of state**
  - $P = \left(K_{T_0}/K'_{T0}\right)\left[(V_0/V)^{K'_{T0}} - 1\right]$ (4.1.13)

Mineral Physics I

Chapter 4. Equation of state

Section 1. Why “equation of state”?

End