The Birch–Murnaghan Isothermal Equation of State

(Derivation of third-order form)

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Equations of state (EoS) in general

- Relate thermodynamic state functions (variables that depend only on equilibrium)
  - These include T, P, V, U, H, G, S, ρ
- As opposed to functions of process (path-dependent variables)
  - These include Q, W
- Simplest EoS for is $PV = nRT$ (for an ideal gas)
  - Does not account for intermolecular effects
- Simplest EoS for a solid is $K = -V\left(\frac{\partial P}{\partial V}\right)$
  - Does not account for the increase of incompressibility with pressure

The Murnaghan equation of state

- Created by Francis D. Murnaghan (chair of mathematics at Johns Hopkins) in 1944
  - *Murnaghan, F. D. (1944). "The compressibility of media under extreme pressures." Proceedings of the national academy of sciences of the United States of America 30(9), 244–247.*

The Murnaghan equation of state

- Define isothermal bulk modulus: $$K = -V\left(\frac{\partial P}{\partial V}\right)_T$$
- Assume bulk modulus varies with pressure: $$K = K_0 + K_0' P$$
- Equate and separate P and V: $$\frac{dP}{K_0 + K_0' P} = -\frac{dV}{V}$$
- Integrate: $$P(V) = \frac{K_0}{K'_0}\left[\left(\frac{V}{V_0}\right)^{-K'_0} - 1\right]$$

The Murnaghan equation of state

- Satisfactory fit to experiments if $P < \sim\frac{K_0}{2}$ and $\frac{V_0}{V} > 0.9$
- Does not account for the change in K'_0 with pressure
- Need an equation that considers P, K, K'
  - Also must make K'_0 negligible as pressure goes to infinity

The Birch–Murnaghan equation of state

- Created by Francis Birch (Professor of Geology at Harvard) in 1947
  - *Birch, F. (1947). "Finite Elastic Strain of Cubic Crystals." Physical Review 71(11), 809–824.*

- The "order" of the EoS depends on how many volume derivatives of force you evaluate. Murnaghan EoS is equivalent to the first-order form.
  - The complexity of the algebra increases exponentially with each order.
  - The more precise your experimental data, the higher the order you can reasonably fit.
  - The third-order form overwhelmingly dominates high-pressure geoscience.

The Birch–Murnaghan equation of state

- Finite (Eulerian) strain $f = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{\frac{-2}{3}} - 1\right]$
- Force can be represented by expanding finite strain $F = \sum f^j a_j$
- This assumes homogenous strain and isothermal compression
- We will solve for the three “known” variables in order:
  - $P = -\frac{\partial F}{\partial V}$
  - $K = -V\frac{\partial P}{\partial V}$
  - $K' = \frac{\partial K}{\partial P}$

Solving for P

- $f = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{\frac{-2}{3}} - 1\right]$
- $F = \sum f^j a_j = a_0 + a_1 f + a_2 f^2 + a_3 f^3$
- $P = -\frac{\partial F}{\partial V} = -\frac{\partial F}{\partial f}\frac{\partial f}{\partial V}$
  - $\frac{\partial F}{\partial f} = 0 + a_1 + 2a_2 f + 3a_3 f^2$
  - $P = -a_1\frac{\partial f}{\partial V} - 2a_2 f\frac{\partial f}{\partial V} - 3a_3 f^2\frac{\partial f}{\partial V}$

Evaluate at ambient conditions

- $P = -a_1 \frac{\partial f}{\partial V} - 2a_2 f \frac{\partial f}{\partial V} - 3a_3 f^2 \frac{\partial f}{\partial V}$
- When P = 0: f = 0
- $0 = -a_1 \frac{\partial f}{\partial V} - 0 - 0$
- So, $\boxed{0 = a_1}$

- $P = -2a_2 f \frac{\partial f}{\partial V} - 3a_3 f^2 \frac{\partial f}{\partial V}$

Solving for K

- $K = -V \frac{\partial P}{\partial V}$
  - $P = -2a_2 f \frac{\partial f}{\partial V} - 3a_3 f^2 \frac{\partial f}{\partial V}$
  - $\frac{\partial P}{\partial V} = -2a_2 f \frac{\partial^2 f}{\partial V^2} - 2a_2 \left(\frac{\partial f}{\partial V}\right)^2 - 3a_3 f^2 \frac{\partial^2 f}{\partial V^2} - 6a_3 f \left(\frac{\partial f}{\partial V}\right)^2$
- $K = V \left[2a_2 f \frac{\partial^2 f}{\partial V^2} + 2a_2 \left(\frac{\partial f}{\partial V}\right)^2 + 3a_3 f^2 \frac{\partial^2 f}{\partial V^2} + 6a_3 f \left(\frac{\partial f}{\partial V}\right)^2\right]$

Evaluate at ambient conditions

- $K = V\left[2a_2 f \frac{\partial^2 f}{\partial V^2} + 2a_2\left(\frac{\partial f}{\partial V}\right)^2 + 3a_3 f^2 \frac{\partial^2 f}{\partial V^2} + 6a_3 f\left(\frac{\partial f}{\partial V}\right)^2\right]$
- At P =0: f=0, K = K_0, V = V_0
- $K_0 = V_0\left[0 + 2a_2\left(\frac{\partial f}{\partial V}\right)^2 + 0 + 0\right]$
  - $f = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{\frac{-2}{3}} - 1\right]$
  - $\frac{\partial f}{\partial V} = \frac{1}{2}\left[\frac{-2}{3}\frac{1}{V_0}\left(\frac{V}{V_0}\right)^{\frac{-5}{3}}\right] = \frac{-1}{3V_0}\left(\frac{V}{V_0}\right)^{\frac{-5}{3}}$
  - If V = V_0 :$\frac{\partial f}{\partial V} = \frac{-1}{3V_0}$
- $K_0 = V_0\left[0 + 2a_2\left(\frac{-1}{3V_0}\right)^2 + 0 + 0\right] = \frac{2a_2}{9V_0}$, so $\boxed{a_2 = K_0 V_0 \frac{9}{2}}$

Solving for K'

- $K' = \frac{\partial K}{\partial P} = \frac{\partial K}{\partial V}\frac{\partial V}{\partial P} = \frac{\partial K}{\partial V}\left(-\frac{V}{K}\right)$ (because $K = -V\frac{\partial P}{\partial V}$)
  - $K = V\left[\left(2a_2 f\frac{\partial^2 f}{\partial V^2}\right) + \left(2a_2\left(\frac{\partial f}{\partial V}\right)^2\right) + \left(3a_3 f^2\frac{\partial^2 f}{\partial V^2}\right) + \left(6a_3 f\left(\frac{\partial f}{\partial V}\right)^2\right)\right]$
  - $\frac{\partial K}{\partial V} = \left[\left(2a_2 f\frac{\partial^2 f}{\partial V^2}\right) + \left(2a_2\left(\frac{\partial f}{\partial V}\right)^2\right) + \left(3a_3 f^2\frac{\partial^2 f}{\partial V^2}\right) + \left(6a_3 f\left(\frac{\partial f}{\partial V}\right)^2\right)\right] + V\left[\left(2a_2 f\frac{\partial^3 f}{\partial V^3} + 2a_2\frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2}\right) + \left(2a_2\frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 2a_2\frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2}\right) + \left(6a_3 f\frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 3a_3 f^2\frac{\partial^3 f}{\partial V^3}\right) + \left(6a_3\left(\frac{\partial f}{\partial V}\right)^3 + 12a_3 f\frac{\partial f}{\partial V}\left(\frac{\partial f}{\partial V}\right)^2\right)\right]$
  - Parentheses show which terms come from the same derivation step
- $K' = \left(-\frac{V}{K}\right)\left[2a_2 f\frac{\partial^2 f}{\partial V^2} + 2a_2\left(\frac{\partial f}{\partial V}\right)^2 + 3a_3 f^2\frac{\partial^2 f}{\partial V^2} + 6a_3 f\left(\frac{\partial f}{\partial V}\right)^2 + V\left[2a_2 f\frac{\partial^3 f}{\partial V^3} + 2a_2\frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 2a_2\frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 2a_2\frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 6a_3 f\frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 3a_3 f^2\frac{\partial^3 f}{\partial V^3} + 6a_3\left(\frac{\partial f}{\partial V}\right)^3 + 12a_3 f\frac{\partial f}{\partial V}\left(\frac{\partial f}{\partial V}\right)^2\right]\right]$

Evaluate at ambient conditions

- $K' = \left(-\frac{V}{K}\right)\left[2a_2 f \frac{\partial^2 f}{\partial V^2} + 2a_2\left(\frac{\partial f}{\partial V}\right)^2 + 3a_3 f^2 \frac{\partial^2 f}{\partial V^2} + 6a_3 f\left(\frac{\partial f}{\partial V}\right)^2 + V\left[2a_2 f \frac{\partial^3 f}{\partial V^3} + 2a_2 \frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 2a_2 \frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 2a_2 \frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 6a_3 f \frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 3a_3 f^2 \frac{\partial^3 f}{\partial V^3} + 6a_3\left(\frac{\partial f}{\partial V}\right)^3 + 12a_3 \frac{\partial f}{\partial V}\left(\frac{\partial f}{\partial V}\right)^2\right]\right]$
- At P =0: f=0, K = K_0, V = V_0, K' = K'_0
  - $\frac{\partial f}{\partial V} = \frac{-1}{3V_0}\left(\frac{V}{V_0}\right)^{\frac{-5}{3}}$
  - $\frac{\partial^2 f}{\partial V^2} = \frac{5}{9V_0}\left(\frac{V}{V_0}\right)^{\frac{-8}{3}}$
  - If V=V_0: $\frac{\partial^2 f}{\partial V^2} = \frac{5}{9{V_0}^2}$

Evaluate at ambient conditions (cont.)

- $K' = \left(-\frac{V}{K}\right)\left[2a_2 f \frac{\partial^2 f}{\partial V^2} + 2a_2\left(\frac{\partial f}{\partial V}\right)^2 + 3a_3 f^2 \frac{\partial^2 f}{\partial V^2} + 6a_3 f\left(\frac{\partial f}{\partial V}\right)^2 + V\left[2a_2 f \frac{\partial^3 f}{\partial V^3} + 2a_2 \frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 2a_2 \frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 2a_2 \frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 6a_3 f \frac{\partial f}{\partial V}\frac{\partial^2 f}{\partial V^2} + 3a_3 f^2 \frac{\partial^3 f}{\partial V^3} + 6a_3\left(\frac{\partial f}{\partial V}\right)^3 + 12a_3 f \frac{\partial f}{\partial V}\left(\frac{\partial f}{\partial V}\right)^2\right]\right]$
- $K'_0 = \left(-\frac{V_0}{K_0}\right)\left[0 + 2a_2\left(\frac{-1}{3V_0}\right)^2 + 0 + 0 + V_0\left[0 + 2a_2\left(\frac{-1}{3V_0}\right)\frac{5}{9{V_0}^2} + 2a_2\left(\frac{-1}{3V_0}\right)\frac{5}{9{V_0}^2} + 2a_2\left(\frac{-1}{3V_0}\right)\frac{5}{9{V_0}^2} + 0 + 0 + 6a_3\left(\frac{-1}{3V_0}\right)^3 + 0\right]\right]$
    - $K'_0 = \left(-\frac{V_0}{K_0}\right)\left[2\left(K_0 V_0 \frac{9}{2}\right)\frac{1}{9{V_0}^2} + V_0 6\left(K_0 V_0 \frac{9}{2}\right)\frac{-5}{27{V_0}^3} + V_0 6a_3 \frac{-1}{27{V_0}^3}\right]$

Evaluate at ambient conditions (cont.)

- $K'_0 = \left(-\frac{V_0}{K_0}\right)\left[2\left(K_0 V_0 \frac{9}{2}\right)\frac{1}{9{V_0}^2} + V_0 6\left(K_0 V_0 \frac{9}{2}\right)\frac{-5}{27{V_0}^3} + V_0 6 a_3 \frac{-1}{27{V_0}^3}\right]$
- $K'_0 = \left(-\frac{V_0}{K_0}\right)\left[(K_0)\frac{1}{V_0} + (K_0)\frac{-5}{V_0} + a_3 \frac{-2}{9{V_0}^2}\right]$
- $K'_0 = \left[-1 + 5 - \frac{2}{9K_0 V_0} a_3\right]$
- So $\boxed{a_3 = (K'_0 - 4)\frac{9K_0 V_0}{2}}$

Solving for P (again)

- $P = -a_1 \frac{\partial f}{\partial V} - 2a_2 f \frac{\partial f}{\partial V} - 3a_3 f^2 \frac{\partial f}{\partial V}$
- Now we know:
  - $a_1 = 0$
  - $a_2 = K_0 V_0 \frac{9}{2}$
  - $a_3 = (K'_0 - 4) \frac{9K_0V_0}{2}$
- And
  - $\frac{\partial f}{\partial V} = \frac{-1}{3V_0} \left(\frac{V}{V_0}\right)^{\frac{-5}{3}}$
- $P = -9K_0V_0 f \frac{-1}{3V_0} \left(\frac{V}{V_0}\right)^{\frac{-5}{3}} - (K'_0 - 4) \frac{27K_0V_0}{2} f^2 \frac{-1}{3V_0} \left(\frac{V}{V_0}\right)^{\frac{-5}{3}}$
  - $P = 3K_0 f \left(\frac{V}{V_0}\right)^{\frac{-5}{3}} + (K'_0 - 4) \frac{9K_0}{2} f^2 \left(\frac{V}{V_0}\right)^{\frac{-5}{3}} = 3K_0 f \left(\frac{V}{V_0}\right)^{\frac{-5}{3}} \left[1 + (K'_0 - 4) \frac{3}{2} f\right]$

And finally…

- $P = 3K_0 f \left(\frac{V}{V_0}\right)^{\frac{-5}{3}} \left[1 + (K'_0 - 4)\frac{3}{2} f\right]$
  - $f = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{\frac{-2}{3}} - 1\right]$
- $P = 3K_0 \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{\frac{-2}{3}} - 1\right]\left(\frac{V}{V_0}\right)^{\frac{-5}{3}}\left[1 + (K'_0 - 4)\frac{3}{2}\frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{\frac{-2}{3}} - 1\right]\right]$
- $P = \frac{3}{2} K_0 \left[\left(\frac{V}{V_0}\right)^{\frac{-7}{3}} - \left(\frac{V}{V_0}\right)^{\frac{-5}{3}}\right]\left\{1 + \frac{3}{4}(K'_0 - 4)\left[\left(\frac{V}{V_0}\right)^{\frac{-2}{3}} - 1\right]\right\}$