Equations of state (EOS)
An EOS is a relation between P, V and T.

The EOS known to everybody is the ideal gas equation: PV=nRT

Important thermodynamic definitions:

Incompressibility: \[ K_S = -V\left(\frac{\partial P}{\partial V}\right)_S \]

\[ K_T = -V\left(\frac{\partial P}{\partial V}\right)_T \]

Thermal expansivity \( \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \)

Grüneisen parameter \( \left(\frac{\partial P}{\partial T}\right)_V = \gamma \frac{C_V}{V} \)

An important relation is \( \frac{K_S}{K_T} = 1 + \alpha \gamma T \)
Isothermal EOS

i.e. How does the density vary with depth (pressure)?

If we assume $K$ is a constant

$$\Rightarrow P = -K \left( \Delta V/V \right) \text{ for small } \Delta V$$

i.e. Hooke’s Law
But minerals undergo *large* volume strains in the Earth

For *large* $\Delta V$, integrate

$$\frac{dP}{K} = \frac{d\rho}{\rho}$$

with *constant* $K$, we get

$$\frac{\rho}{\rho_0} = \exp\left(\frac{P}{K_0}\right)$$

This is different from observations!
- As density increases, atoms get closer together
- Repulsive forces are non-linear functions of interatomic distances

i.e. the increase of density with depth becomes more difficult with increasing compression.

→ K must increase with increasing P
Murnaghan EOS (empirical)

- Murnaghan (1967) : \( K = K_0 + K'P \)

- In other words \( P = \left( \frac{K_0}{K_0'} \right) \left[ \left( \frac{V}{V_0} \right)^{K_0'} - 1 \right] \)

- Good for compressions up to \( \sim 10\% \)

- Commonly assume \( K' = 4 \)
Birch EOS (empirical)

- Birch (1961) observed for crustal rocks:
  - $V_p = a(m) + b\rho$
    - $m$ is the mean atomic weight
  - Leads to ‘Birch’s Law’…
Figure 4.3. Velocity of the $P$ waves at 10 kbars vs. specific mass for silicates and oxides. The dashed lines show the trend for a constant mean atomic mass (after Birch 1961a).
Schreiber & Anderson, Science 1970
Birch-Murnaghan EOS (finite strain theory)

Eulerian strain: $\varepsilon = \partial u / \partial x - 1/2(\partial u / \partial x)^2$

$V/V_0 = \rho_0 / \rho = (1 - 2\varepsilon)^{-3/2} = (1 + 2f)^{-3/2}$

Helmholtz free energy: $F = af^2 + bf^3 + cf^4 + \ldots$

$P = -(\partial F / \partial V)_T \rightarrow K \rightarrow \rho$

$2^{\text{nd}}$ (linear elasticity), $3^{\text{rd}}, 4^{\text{th}}$ order Birch-Murnaghan EOS
Some remarks:

The assumption is that the strain is Eulerian.

The same theory can be applied to Lagrangian strain which leads to different EOS.
Observations show that Eulerian strain best describes Earth’s lower mantle.

The shear modulus (G) is more difficult because it is not as easily defined thermodynamically, but equations take the same form as for K.
Figure 3. Plot of relative unit cell volumes ($V/V_0$) versus pressure for hydrous $Fo_{89}$ ringwoodite. The data from synchrotron powder diffraction (red symbol) extend the single-crystal data (small symbol) pressure range by a factor of four. The curve is an equation of state of $K_0 = 171.8; K' = 7.1$. The internal precision of the unit cell refinements is smaller than the symbol, however systematic errors, as discussed, may be larger.

Manghnani et al, 2003
Mie-potential EOS (atomic potential representation)
A crystal is a lattice of oscillators (atoms)

\[ F = - \frac{\partial E}{\partial r} = k(r-a_0) \]

The total vibrational energy gives \( T \)

The normal modes give the elastic constants

\( E \) can be expressed as the sum of an attractive and a repulsive potential (Born-Mie potential)

\[ E = -\frac{a}{r^m} + \frac{b}{r^n} \]

where \( n > m \) because repulsive part has a shorter range
Because \( n > m \), we have a non-linear oscillation.

With increasing pressure, the interatomic spacing decreases and the restoring force increases more rapidly. Compression becomes more difficult, i.e. the bulk modulus increases with pressure.

At \( T = 0 \), we are at the bottom of \( E \). At low temperature, we are near the bottom, and the vibrations are nearly harmonic. At high \( T \), the vibrations are asymmetric and on average \( r \) is bigger than \( a_0 \) \( \rightarrow \) the volume of the atom increases. This is thermal expansion.
Consider a crystal with N atoms

E is the potential energy between two atoms.

At \( r = a_0 \), \( P = 0 \) and \( \frac{\partial E}{\partial r} = 0 \)

The density \( \rho \) at \( P > 0 \) is \( \frac{\rho}{\rho_0} = (a_0/r)^3 \)

The internal energy \( U = 3fNE \)

The volume \( V = gN r^3 \)

(\( g \) and \( f \) are constants related to the packing style of the crystals)
\[ P = -\frac{dU}{dV} = \left(\frac{dU}{dr}\right)\left(\frac{dr}{dV}\right) = \frac{f}{g(1/r^2)}E' \]

\[ K = -V\left(\frac{dP}{dV}\right) \]

\[ K' = \frac{dK}{dP} \ldots \]

The EOS is given by the choice of E.

For the Born-Mie potential with \( m=2 \) and \( n=4 \), we get the same results as with 2\(^{nd}\) order Birch-Murnaghan EOS.
Vinet EOS
(atomic potential representation)

\[ P = 3K_0(1 - \frac{f_v}{f_v^2}) \exp \left[ \frac{3}{2}(K' - 1)(1 - f_v) \right] \]

where \( f_v = \left( \frac{V}{V_0} \right)^{1/3} \)

• For simple solids under high compression (~40%). E.g. NaCl, hydrogen, MgSiO_3

• Not suitable for solids with significant structural flexibility, such as bond-bending (e.g. feldspars)
The shear modulus

The thermodynamics of the shear modulus is difficult, but to a good approximation

\[ G = aK + bP \]

along an adiabat, \( a \) and \( b \) are constants.
Bulk sound (linear for small compression)

Figure 4.4. Bulk sound velocity versus specific mass for metals, from shock data (solid curves). The corresponding atomic masses are indicated. The curves (dashed) for the mantle and core materials, from seismic data, are also shown (after Birch 1963).
Bulk sound (exponential for high compression, closed packed)

Figure 4.8. Seismic equation of state for selected rocks and minerals (after D. L. Anderson 1967).
Thermal EOS \[ V(P,T) \]

a) ‘ad hoc’
Repeat B-M at successively higher T.

\[ \alpha(T) = a + bT + c/T^2 \quad a,b,c \text{ from experimental data (calorimetry)} \]

\[ \rho(T) = \rho_0(T_0).\exp(-\int \alpha(T)\,dT) \]

\[ K(T) = K(T_0) + (\partial K/\partial T)_P.(T-T_0) \text{ or} \]

\[ K_S(T_p, P = 0) = K_{S_0}\exp \left[ \frac{\rho(T_p, P = 0)}{\rho_0} \right]^{\delta_{S_0}} \]

\[ \delta_S = -1/(\alpha K_s)\dot{K}_{S_0} \]
$K(T, P=0)$ exponential Anderson-Grüneisen
\( G(T, P=0) \) linear
b) Thermodynamic approach (Mie-Gruneisen or “Debye model”)

\[ P(V,T) = P(V,T_0) + P_{th}(V,T) \]

“Thermal pressure”
A practical approach with BM3

Thermal pressure

Adiabatic compression

Isothermal compression

Heating

$T_0, P_0$

$T$, $T_f$

$T+dT$