1. Debye theory and "high" temperatures

It is interesting to try to infer the mineralogical, chemical, and thermal state of the deep Earth by using available experimental data and comparing models with the seismologically defined structure. Such a task would be relatively straightforward if we knew the equation of state of every possible mantle and core constituent (though, of course, our problem would probably be highly non-unique). Unfortunately, a lot of the experimental data is available only at low temperatures and/or pressures (e.g. ultrasonic measurements and static compression data) or pertain to temperature conditions very different from those in the Earth (shock wave data). We therefore need to be able to “correct” the experimental data to Earth conditions or, alternatively, we can “correct” the properties of the Earth to experimental conditions. In either case, we need to be able to predict how density, bulk modulus, etc. can reasonably change as a function of pressure and temperature (or volume and temperature).

As you may know, thermodynamic properties change in quite a complicated way at low temperatures but at “high” temperatures, things get a little more simple. We illustrate the situation with some data on the heat capacity at constant volume for several minerals.

Figure 1 $C_v$ for several minerals as a function of temperature at ambient pressure. Green=MgO, blue=olivine, orange=forsterite, black=corundum, brown =grossular garnet, purple=pyrope garnet, and red is CaO.

At low temperatures, the heat capacity is a rapidly varying function of temperature. At high temperatures, this doesn’t seem to be the case and $C_v$ tends to a constant. The same also appears to be true for thermal expansion (Figure 2) though, now, $\alpha$ is roughly a linear function of temperature at high temperatures.
Figure 2 $\alpha$ for several minerals as a function of temperature at ambient pressure. Green=MgO, blue=olivine, orange=forsterite, black=corundum, brown=grossular garnet, purple=pyrope garnet, and red is CaO.

Once we get above about 750$^\circ$ K (for MgO), we are in the “high temperature” regime where the temperature dependence is relatively slight. The value of temperature above which one is in the high temperature regime is material dependent and can be quantified using simple theories of the behavior of materials. We shall review briefly the Debye theory of specific heat. In most materials of interest in the mantle, the main contribution to the specific heat is due to lattice vibrations. (In metals, we also have to worry about the effects of conduction electrons)

Consider a crystal lattice of $N$ atoms. Each atom is undergoing complicated coupled vibrations but, if the atomic displacements are sufficiently small (i.e. a small fraction of the interatomic spacing) we can approximately describe the motion of the crystal in terms of $3N$ normal modes of vibration which are harmonic and independent. At sufficiently high temperatures, this approximation breaks down and “anharmonic” effects become important. The harmonic approximation is good for calculating specific heats and allows us to define in a quantitative sense what is meant by “high temperature”.

The procedure for calculating specific heats is to compute the average energy of a single mode of vibration then sum over modes to get the total vibrational energy of the crystal, $E$. The heat capacity at constant volume, $C_v$, is then computed using the relation

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v$$

In the harmonic approximation, the frequencies of the modes of vibration are a function only of volume and not temperature which simplifies the calculation considerably.

Consider one mode of oscillation with frequency $\omega_i$. The energy levels of a harmonic oscillator are given by

$$\epsilon_n = (n + \frac{1}{2})\hbar\omega_i$$

where $\hbar$ is Plank’s constant. This result comes from quantum theory by solving Schrodinger’s equation for an harmonic oscillator – this is the only result from quantum theory that we use! The result can also be
classically derived (without a ground state) by considering the energy of normal modes of vibration of a periodic lattice.

The average energy of the $i$'th oscillator in thermal equilibrium at temperature $T$ is given by

$$\bar{\epsilon} = \sum_{n=0}^{\infty} p_n \epsilon_n$$  \hspace{1cm} (2)

where $p_n$ is the probability that the oscillator is in level $\epsilon_n$. $p_n$ is given by the Boltzmann distribution:

$$p_n = \frac{1}{Z} e^{-\epsilon_n/kT}$$  \hspace{1cm} (3)

where $Z = \sum_n e^{-\epsilon_n/kT}$ is the partition function and $k$ is Boltzmann’s constant. This equation states that the population of atoms in a given energy state above the ground state will exponentially depend on the ratio of the energy difference between this state and the ground state. Substitution of (3) into (2) gives

$$\bar{\epsilon} = \frac{1}{2} \hbar \omega_i + \frac{\hbar \omega_i e^{-\hbar \omega_i/kT}}{e^{\hbar \omega_i/kT} - 1}$$  \hspace{1cm} (4)

It may not be completely obvious to you how this result is obtained so we now give a little more detail.

Consider, first, the partition function, $Z$. Note that the difference between the $n$'th and the $(n+1)$'th energy state is $\Delta E = \hbar \omega_i$ and we let $\beta = 1/kT$ so

$$Z = \sum_n e^{-\epsilon_n/kT} = \sum_n e^{-\beta \epsilon_n} = \sum_n e^{-\beta \Delta E - \beta \Delta E/2} = e^{-\beta \Delta E/2} \sum_n (e^{-\beta \Delta E})^n$$

Now we use the identity $\sum_n x^n = 1/(1 - x)$ to give

$$Z = \frac{e^{-\beta \Delta E/2}}{(1 - e^{-\beta \Delta E})}$$

Now, note that equation (2) can be written

$$\bar{\epsilon} = \sum_n \frac{1}{Z} \epsilon_n e^{-\beta \epsilon_n} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

Differentiating the above equation for $Z$ wrt $\beta$ then gives equation (4).

Note that, at high temperatures, equation (4) gives $\bar{\epsilon} \rightarrow kT$ and we get the classical equipartition of energy result. The total vibrational energy of the crystal is

$$E = \sum_{i=1}^{3N} \epsilon_i$$  \hspace{1cm} (5)

so, in the high temperature limit, $E \approx 3NK$, and differentiating wrt $T$ at constant volume (so the frequencies of oscillation of the crystal don’t change) gives $C_v = 3Nk$. If we consider a ’mole’ of a substance then $N$ is Avogadro’s number and $NK = R$ where $R$ is the gas constant so $C_v = 3R = 24.94 \text{ J K}^{-1} \text{ mole}^{-1}$ – this is the classical Dulong-Petit value. We therefore expect $C_v$ to depend only on the molecular weight of the material at high temperatures. To show how this works, consider a mole of forsterite (the magnesium end member of olivine) $\text{Mg}_2\text{SiO}_4$. This consists of one mole of Si atoms, two moles of Mg atoms and 2 moles of $\text{O}_2$ molecules (or, equivalently, 4 moles of O atoms) – this comes to 140 grams (a mole is sometimes called a ‘gram-molecular-weight’) and would fill a cube of linear dimension 3.4cm. Now, a total of 7 moles of atoms weighs 0.14 kg so 50 moles weighs 1kg so, for forsterite, $C_v = 50 \times 24.94 = 1247 \text{ J kg}^{-1} \text{ K}^{-1}$. A similar calculation for pyrolite gives 47.67 moles/Kg so $C_v$ is 1188 J kg$^{-1}$ K$^{-1}$ and, for Losimag, gives 47.56 moles/Kg so $C_v$ is 1185 J kg$^{-1}$ K$^{-1}$. The bottom line here is that $C_v$ in the mantle is about 1200 J kg$^{-1}$ K$^{-1}$ and is unlikely to depend much on temperature and pressure.

Generally, equation (5) is converted to an integral by introducing the “density of states”, $g(\omega)$, which describes how many modes there are as a function of frequency. Thus
\[ E = \int_{0}^{\infty} \varepsilon(\omega) g(\omega) \, d\omega \]  

(6)

The calculation of the density of states is typically done by considering a cube of material with fixed boundaries (or periodic boundaries) and computing the standing (or travelling) waves of the system. For fixed boundaries, the solutions of the wave equation are standing waves with discrete allowable wavenumbers:

\[ k = \left[ \frac{\pi n_1}{L}, \frac{\pi n_2}{L}, \frac{\pi n_3}{L} \right] \]  

(7)

where \( n_1, n_2, n_3 = 1, 2, 3, 4 \cdots \). These allowable wavenumbers make a cubic point lattice in \( k \)-space with separation \( \pi/L \) (\( L \) is the dimension of the cube). The volume occupied by each allowable wave number is \((\pi/L)^3\) so a density of states in \( k \)-space can be defined as

\[ g(k) \, dk = \frac{V}{\pi^3} d^3k \]  

(8)

where \( V \) is the volume of the cube (i.e. \( L^3 \)).

Now suppose that we make the approximation that the density of states depends only on the magnitude of \( k \) and not its direction. We can then compute the number of modes there are in a spherical shell of radius \( k \) and thickness \( dk \) surrounding the origin. Actually, only 1/8 of this volume is occupied as only positive values of \( k \) are allowed. Thus

\[ g(k) \, dk = \frac{1}{8} \frac{V}{\pi^3} 4\pi k^2 \, dk = \frac{V k^2}{2\pi^2} \, dk \]  

(9)

We convert this to a density of states over frequency using the group velocity \((d\omega/dk)\) so that

\[ g(\omega) = \frac{V k^2}{2\pi^2} \frac{dk}{d\omega} \]  

(10)

Debye starts with the fact that we know some of the normal modes of the crystal: those related to the propagation of sound. These modes sample macroscopic properties of the crystal – they are low frequency, long wavelength modes with wavelength much greater than the interatomic spacing. We consider a perfectly elastic, isotropic, non-dispersive (i.e. velocity independent of frequency) crystal. If \( c \) is the velocity of sound propagation then

\[ k = \frac{\omega}{c} \quad \text{and} \quad \frac{dk}{d\omega} = \frac{1}{c} \]  

(11)

Thus

\[ g(\omega) = \frac{V \omega^2}{2\pi^2} \frac{1}{c^3} \]  

(12)

A small refinement can be had by recognizing that we have longitudinal waves and transverse (polarized) waves so a better approximation is

\[ g(\omega) = \frac{V \omega^2}{2\pi^2} \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) = \frac{V \omega^2}{2\pi^2} \frac{3}{c_l^3} \]  

(13)

where

\[ \frac{3}{c_l^3} = \frac{1}{c_l^3} + \frac{2}{c_t^3} \]

This description of \( g(\omega) \) applies to low frequency lattice vibrations but Debye assumed that it applies to all frequencies and fixed the total number of modes by defining a frequency, \( \omega_D \), (the Debye frequency) such that
\[ \int_0^{\omega_D} g(\omega) \, d\omega = 3N \quad (14) \]

Substituting in the form for \( g(\omega) \) and performing the integral gives

\[ \omega_D^3 = \frac{6\pi^2 N \bar{c}^3}{V} \quad (15) \]

and eliminating \( \bar{c} \) from the expression for \( g \) gives

\[ g(\omega) = \frac{9N\omega^2}{\omega_D^3} \quad (16) \]

for frequencies below the Debye frequency (\( g(\omega) = 0 \) for frequencies above \( \omega_D \)). This parabolic form is often quite a reasonable approximation to \( g(\omega) \) as determined by neutron scattering experiments – an example is shown in figure 3 for periclase (MgO) – I leave it to you to decide if the Debye form (dashed line) is ok!

![Figure 3](image)

**Figure 3**

We can now evaluate equation (6) giving

\[ E = \frac{9}{8} Nk\theta_D + \frac{9NkT}{x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} \, dx \quad (17) \]

where the “Debye temperature”, \( \theta_D = \hbar\omega_D/k \) and

\[ x = \frac{\hbar\omega}{kT} \quad (18) \]

(\( x_D = \theta_D/T \)). Differentiation with respect to \( T \) at constant volume gives \( C_v \):
\[
C_v = 3Nk \left[ \frac{3}{x_D} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \right]
\]  
\hspace{1cm} (19)

This has the experimentally observed \( T^3 \) dependence at low temperatures but we are more interested in the high temperature behavior when \( T > \theta_D \) (i.e., \( x \) small). In this limit we get

\[
C_v = 3Nk \left[ 1 - \frac{1}{20} \left( \frac{\theta_D}{T} \right)^2 + \cdots \right]
\]  
\hspace{1cm} (20)

Clearly \( C_v \) will be close to the classical Dulong-Petit value even when \( T \simeq \theta_D \).

The Debye temperature can be estimated for a variety of minerals by varying \( \theta_D \) until the observed specific heat dependence best fits the predictions of equation 19. The table below (from chapter 5 of Anderson’s book) shows that Debye temperatures are typically on the order of \( 500 - 1000 \) K and are exceeded at very shallow depths within the Earth. The Earth is therefore in the “high temperature” regime.

<table>
<thead>
<tr>
<th>mineral</th>
<th>( \theta ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>940</td>
</tr>
<tr>
<td>CaO</td>
<td>680</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>1040</td>
</tr>
<tr>
<td>Mg(_2)SiO(_4)</td>
<td>760</td>
</tr>
<tr>
<td>MgSiO(_3)</td>
<td>710</td>
</tr>
<tr>
<td>MgAl(_2)O(_4)</td>
<td>860</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>570</td>
</tr>
<tr>
<td>Garnet</td>
<td>750</td>
</tr>
</tbody>
</table>

In reality, \( C_v \) does show a temperature dependence at temperatures several times the Debye temperature due to “anharmonic” effects. In Debye theory, \( \theta_D \) is independent of temperature at fixed volume. If the expression for \( C_v \) is fit to experimental data at different temperatures (and fixed volume), it is found that the inferred \( \theta_D \) varies slightly as a function of \( T \). Again, this variation is due to the neglect of the dispersion of lattice waves and anharmonic effects.

2. Mie-Gruneisen equation of state

When fitting properties of the Earth’s deep interior with those of candidate mineral phases, it is convenient to have an “equation of state” describing the mineral from which useful properties can be extracted. An alternative method is to have polynomial fits to things like the temperature dependence of bulk modulus, \( K_T \), or the pressure dependence of the thermal expansion coefficient. The problem with this approach is that there are often thermodynamic relations between properties which our polynomial fits may not honor. A more desirable approach is to choose to parameterize some fundamental thermodynamic potential from which all properties may be derived in an internally consistent way.

When looking at the volume dependence of properties along isotherms, the Helmholtz free energy, \( F \), is the natural function to use. If we know \( F(V,T) \) for a material then it is straightforward to derive useful thermodynamic properties:

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

\[
S = -\left( \frac{\partial F}{\partial T} \right)_V
\]

\[
K_T = V \left( \frac{\partial^2 F}{\partial V^2} \right)_T = -V \left( \frac{\partial P}{\partial V} \right)_T
\]
\[ C_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V \]

\[ \alpha K_T = - \left( \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial V} \right)_T \right)_V = \left( \frac{\partial P}{\partial T} \right)_V \quad \text{(gives } \alpha) \]

\[ \gamma = \frac{\alpha K_T V}{C_V} \]

\[ K_S = K_T (1 + \alpha T \gamma) \]

\[ C_P = C_V (1 + \alpha T \gamma) \]

e等。请注意，Gibbs自由能，\( G \)，在相平衡中很有用，可以通过已知\( F \)来容易计算。

我们概念性地将\( F \)分为两部分：由于晶格的静态部分，它仅是体积的函数（即在绝对零度）；以及来自晶格振动的热部分。这一振动部分在谐波近似中给出

\[ F = -kT \ln Z \]  \( \text{(21)} \)

其中，\( Z \)是描述上述的partition function。对于具有\( 3N \)个独立谐波模式的晶体，我们有

\[ F = \phi_0 + \frac{1}{2} \sum_i \hbar \omega_i + kT \sum_i \ln (1 - e^{-\hbar \omega_i / kT}) \]  \( \text{(22)} \)

此处，\( \phi_0(V) \)是静态晶格的势能。我们可以像之前那样处理\( E \)去求解，将模式的和替换为频率的积分与密度的等式。在Debye近似中，这给出

\[ F = \phi_0 + \frac{9}{8} N kT \theta_D + \frac{9NkT}{xD^3} \int_0^{x_D} \ln(1 - e^{-x}) x^2 dx \]  \( \text{(23)} \)

注意，ground state energy可以包含进\( \phi_0 \)而不会失去一般性。在继续之前，回到等式22并以与体积固定的温度为固定值去求压强:

\[ P = -\frac{d\phi_0}{dV} - \frac{1}{2} \sum_i \hbar \left( \frac{\partial \omega_i}{\partial V} \right)_T - \sum_i \frac{\hbar e^{-\hbar \omega_i / kT}}{(1 - e^{-\hbar \omega_i / kT})} \left( \frac{\partial \omega_i}{\partial V} \right)_T \]

\[ = -\frac{d\phi_0}{dV} - \sum_i \left( \frac{\hbar \omega_i}{2} + \frac{\hbar \omega_i}{e^{\hbar \omega_i / kT} - 1} \right) \left( \frac{\partial \ln \omega_i}{\partial V} \right)_T \]

\[ = \frac{d\phi_0}{dV} + \frac{1}{V} \sum_i \varepsilon_i \gamma_i \quad \text{where} \quad \gamma_i = -\left( \frac{\partial \ln \omega_i}{\partial \ln V} \right)_T \]  \( \text{(24)} \)

如果假设所有\( \omega_i \)的体积依赖是相同的，我们有\( \gamma_i = \gamma \)并

\[ P = -\frac{d\phi_0}{dV} + \frac{\gamma E}{V} \]  \( \text{(25)} \)

这被称为“Mie-Grüneisen”方程的状态。在这种近似下，\( \gamma \)是独立于温度的。
A more general approach to the Mie-Grüneisen EOS which doesn’t rely on the harmonic approximation is to consider the Helmholtz free energy as a sum of a static part (dependent on volume) and a thermal (or vibrational) part i.e.

\[ F(V, T) = \phi_0(V) + F_T(V, T) \]  

(26)

where \( F_T = 0 \) when \( T = 0 \). Then

\[ P(V, T) = -\frac{d\phi_0}{dV} + \frac{\hat{\gamma}E}{V} = P(V, 0) + \frac{\hat{\gamma}E}{V} \]  

(27)

where \( \hat{\gamma} \) is now defined as

\[ \hat{\gamma} = -\frac{V}{E} \left( \frac{\partial F_T}{\partial V} \right)_T \]  

(28)

and \( \hat{\gamma}E/V \) is called the “thermal pressure”. \( \hat{\gamma} \) is related to the thermodynamic Grüneisen ratio which we can show by using the thermodynamic identity:

\[ \left( \frac{\partial P}{\partial T} \right)_V = \alpha K_T \]  

(29)

where \( \alpha \) is the coefficient of thermal expansion and \( K_T \) is the isothermal bulk modulus. Applying this to equation 27 gives

\[ \alpha K_T = \rho E \left( \frac{\partial \hat{\gamma}}{\partial V} \right)_V + \rho C_v \hat{\gamma} \]  

(30)

where density \( \rho = 1/V \). Thus

\[ \gamma = \frac{\alpha K_S}{\rho C_p} = \frac{\alpha K_T}{\rho C_v} = \hat{\gamma} + \frac{E}{C_v} \left( \frac{\partial \hat{\gamma}}{\partial T} \right)_V \]  

(31)

Thus if \( (\partial \hat{\gamma}/\partial T)_V = 0 \) we have \( \gamma = \hat{\gamma} \). It isn’t totally unreasonable that this condition should apply since \( (\partial \hat{\gamma}/\partial T)_V \) is related to the temperature dependence of the mode frequencies at fixed volume which we expect to be small. In what follows, we shall assume we can take \( \gamma = \hat{\gamma} \).

For the Mie-Grüneisen equation to be useful, we have to make some assumptions about the behavior of \( \gamma \). A common assumption is that \( \gamma \) is a function of volume given by the form

\[ \gamma = \gamma_0 \left( \frac{V}{V_0} \right)^q \]  

where \( q \) is between 1 and 3 (we shall discuss alternative formulations for \( \gamma(V) \) below). \( E \) in equation (25) is often taken to have the Debye form (equation 17) so the whole of the thermal part of the Mie-Grüneisen equation of state is specified by three numbers: \( \gamma_0, q, \) and \( \Theta_D \). What remains to be done is to characterize the static part of the EOS.

Finally, if the temperature is sufficiently high, anharmonic effects can be important. A good discussion of anharmonic effects can be found in D.C. Wallace (1972, Chapter 4). At high temperatures, the dominant effect is to introduce another term into the Helmholtz free energy which is proportional to \( T^2 \):

\[ F = \phi_0 + F_H + F_A \]  

(32)

where \( F_A = AT^2 \) and \( F_H \) is the harmonic contribution. Following through the algebra, we find that \( C_v \) is proportional to \( T \) at high temperatures though the sign of \( A \) depends upon the crystal structure, i.e.

\[ C_v = 3R \left[ 1 - \frac{2}{3R}AT + O(T^{-2}) \right] \]  

(33)
A can be computed for some simple crystal structures using lattice dynamics but this is beyond the scope of this course. The limited data available suggest that anharmonic effects are slight until temperatures several time the Debye temperature are reached. We hope that actual temperatures in the Earth are lower than this.

Before considering the characterization of the volume dependence of the static part of $F$, we briefly look at the pressure (or volume) dependence of the common thermodynamic properties.

3. Pressure variation of thermodynamic properties

We give some simple results for the behavior of homogeneous materials under compression. It is often convenient to consider variations with respect to density or volume rather than with respect to pressure. E.g., we have the thermodynamic identity

$$
\left( \frac{\partial \alpha}{\partial P} \right)_T = - \frac{\alpha \delta_T}{K_T}
$$

where

$$
\delta_T = - \frac{1}{\alpha K_T} \left( \frac{\partial K_T}{\partial T} \right)_P
$$

Using the fact that $K_T = \rho(\partial P/\partial \rho)$ we get

$$
\left( \frac{\partial \alpha}{\partial \rho} \right)_T = - \frac{\alpha \delta_T}{\rho}
$$

so that if $\delta_T$ is roughly independent of pressure along an isotherm (as is experimentally observed) then

$$
\alpha = \alpha_0 \left( \frac{\rho}{\rho_0} \right)^{-\delta_T}
$$

Note that $\delta_T$ is typically 4–6 so that $\alpha$ is a rapidly decreasing function of density or pressure. Because $\alpha$ is so small in the deep Earth, we find that $\alpha T \gamma \ll 1$ which means that

$$
\frac{K_S}{K_T} = \frac{C_p}{C_v} = 1 + \alpha T \gamma \approx 1
$$

Other results for the volume dependence of important thermodynamic quantities are:

$$
\left( \frac{\partial \alpha}{\partial \rho} \right)_S = - \frac{\alpha}{\rho} \left[ \delta_S + \gamma + \alpha T \gamma \left( \delta_S + \frac{1}{\alpha \gamma} \left( \frac{\partial \gamma}{\partial T} \right)_P \right) \right]
$$

$$
\left( \frac{\partial C_p}{\partial \rho} \right)_T = - \frac{\alpha T \gamma C_p}{1 + \alpha T \gamma} \left[ \frac{1}{\alpha^2} \left( \frac{\partial \alpha}{\partial T} \right)_P + \left( \frac{\partial K_T}{\partial T} \right)_P \right]
$$

$$
\left( \frac{\partial C_p}{\partial \rho} \right)_S = - \alpha T \gamma \frac{C_p}{\rho} \left[ \delta_S + \frac{1}{\alpha \gamma} \left( \frac{\partial \gamma}{\partial T} \right)_P \right]
$$

$$
\left( \frac{\partial C_v}{\partial \rho} \right)_T = - \alpha T \gamma \frac{C_v}{\rho} \left[ \frac{1}{\alpha^2} \left( \frac{\partial \alpha}{\partial T} \right)_P - 2 \delta_T + \left( \frac{\partial K_T}{\partial P} \right)_T \right]
$$

$$
\left( \frac{\partial C_v}{\partial \rho} \right)_S = - \alpha T \gamma \frac{C_v}{\rho} \left[ \frac{1}{\alpha \gamma} \left( \frac{\partial \gamma}{\partial T} \right)_P \right]
$$

$$
\left( \frac{\partial \gamma}{\partial \rho} \right)_S = - \frac{\gamma}{\rho} \left[ 1 + \gamma + \delta_S - \left( \frac{\partial K_g}{\partial P} \right)_S \right]
$$

$$
\left( \frac{\partial \gamma}{\partial \rho} \right)_T = - \frac{\gamma}{\rho} \left[ 1 + \delta_T - \left( \frac{\partial K_T}{\partial P} \right)_T + \frac{K_T}{C_v} \left( \frac{\partial C_v}{\partial P} \right)_T \right]
$$

and we also have
$$\delta_T = \delta_s + \gamma + \alpha T \gamma \left[ \frac{1}{\alpha^2} \left( \frac{\partial \alpha}{\partial T} \right)_p + \delta_s - \delta_T + \frac{1}{\alpha \gamma} \left( \frac{\partial \gamma}{\partial T} \right)_p \right]$$ (45)

I have written all these equations to emphasize dimensionless quantities such as $\delta_s$, etc. as these are all a few units in magnitude at high temperatures. Since $\alpha T \gamma \ll 1$, the volume derivatives of the heat capacities can be neglected and we can take $C_v \simeq C_p = \text{constant}$.

Birch in his classic 1952 paper was the first to show that quantities like $\gamma$, $\delta_s$, $1/\alpha^2 (\partial \alpha/\partial T)_p$, etc. are of the order of a few units at high temperatures and pressures and are similar in magnitude from material to material. (He called this a kind of “law of corresponding states” for the thermodynamic behavior of minerals). He used this empirical fact to make quite far-reaching conclusions about the chemical and thermal structure of the Earth. Since that time, more and better experimental data have confirmed Birch’s idea though a theoretical understanding of the phenomenon is by no means complete.

The experimental evidence comes from many sources and we use one experimental technique as an example. Bohler and Ramakrishnan, 1980 (JGR 85,6996) review the results of an experimental procedure to determine $(\partial T/\partial P)_S$ at high pressures along an isotherm. They do this by compressing the material with a piston apparatus to high pressures. They then apply a very rapid pressure pulse to the system and measure the associated temperature rise. If we write

$$x = \left( \frac{\partial T}{\partial P} \right)_S = \frac{\alpha T}{\rho C_p}$$ (46)

we find that the experimental results can be accurately expressed as a power law:

$$x = x_0 \left( \frac{\rho_0}{\rho} \right)^n$$ (47)

along an isotherm. $n$ typically lies between 4 and 8. If we indulge in a little algebra, we find that

$$\left( \frac{\partial \ln x}{\partial \ln \rho} \right)_T = - \left[ 1 + \delta_T + \frac{\rho}{C_p} \left( \frac{\partial C_p}{\partial \rho} \right)_T \right]$$ (48)

When $\alpha T \gamma$ is small, the last term is negligible and if $\delta_T$ is a constant (i.e. $\delta_T$ is independent of pressure), we find that

$$n = 1 + \delta_T$$ (49)

Boehler’s experiment therefore indicates that $\delta_T$ is independent of pressure and has a value of 3–7. The value of $\delta_T$ so measured agrees with independent determinations of $\delta_T$ at low pressures.

The determination of the bulk modulus and its pressure derivatives is usually done by static compression experiments or by ultrasonic experiments. In most experiments, the compressibility of mantle materials is so small that it is extremely difficult to measure the pressure derivatives of the bulk modulus accurately. (The alkali halides are an exception as they are highly compressible.) A large number of equations of state (relationships between $P, V$ and $T$) have been developed to describe compression effects. Almost all of these are empirical in nature requiring fits of some parameters to the data. They can therefore be used for interpolation between data points but using them for extrapolation beyond the range of compressions of the raw data is risky (but a popular pastime nevertheless). Fitting different equations of state to the same data can also give different values of parameters in common to the equations. For example, $(\partial K_S/\partial P)_T$ or $(\partial K_T/\partial P)_T$ (at constant $T$ since this is the usual experimental configuration) evaluated at zero compression ($P = 0$) is a common feature of many EOS. Its value as determined by a given set of data depends upon the EOS being fitted. This is even more true of higher order derivatives (e.g. $(\partial^2 K_T/\partial P^2)_T$) and, if a value is quoted, you should be aware that a different EOS would probably give a different value.

A rather simple EOS is the Murnaghan EOS which is based on the observational fact that the bulk modulus, $K$, is roughly a linear function of pressure, $P$. This EOS therefore looks like
\[ K = K_0 + \frac{dK_0}{dP} P \]  
(50)

which can be integrated to give \( \rho(P) \). This equation can be used for both adiabatic and isothermal conditions by substitution of the appropriate modulus. Since \( K = \rho(\partial P/\partial \rho) \), we have

\[ \rho = \rho_0 \left( 1 + \frac{dK_0}{dP} \frac{P}{K_0} \right)^{1/dK_0/dP} \]  
(51)

The applicability of the Murnaghan EOS to the Earth can be assessed by looking at plots of \( K(P) \):

\[ K_S \] seems to be a reasonably linear function of \( P \) in both the lower mantle and outer core. Note the similarity of gradient despite the fact that the lower mantle is a crystalline solid and the outer core is a liquid metal. In this context, the EOS might be used to extrapolate the properties of these regions to zero pressure for comparison with experimentally determined properties. The Murnaghan EOS is not good enough for this purpose as the slight curvature of \( K_S(P) \) causes spurious values of \( K_0 \) and \( dK_0/dP \) to be found.

A “better” EOS for this purpose is one based on the theory of finite strain. The finite strain EOS has the appearance of being theoretically based but, again, it is really just an empirical description of what is going on. In this case, a measure of “goodness” of an EOS really reduces to choosing one which models the data with a small number of unknowns. We consider the finite strain EOS in some detail as it is the one most commonly used in the literature. Poirier, in his book, describes some alternatives (the Vinet EOS, and the logarithmic EOS) though we have not found them to be particularly superior to the finite strain EOS.
4. Finite strain theory

Finite strain theory is based on the assumption that the strain energy of the lattice can be expanded in the form:

\[ \phi = \phi_2 + \phi_3 + \phi_4 + \cdots \]

where \( \phi_2 \) depends upon second order products of the strain components, \( \phi_3 \) upon third order products, and so on. The neglect of \( \phi_1 \) is valid for isotropic materials or cubic lattices since it can be eliminated by a suitable choice of coordinate system. The strain energy is then identified with the Helmholtz free energy, \( F \), and if the compression is hydrostatic, an EOS relating \( P \) to \( \rho \) at constant temperature can be found using the relationship

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

If isentropic conditions are required, \( \phi \) is identified with the internal energy, \( E \) and the relationship

\[ P = -\left( \frac{\partial E}{\partial V} \right)_s \]

is used.

The theory of finite strain for general crystals is algebraically heavy so, for simplicity, we consider an isotropic medium undergoing hydrostatic compression (isotropic strain). The main required ingredient is a definition of “strain”. We require that the definition of finite strain leaves the constitutive relations unchanged under changes of frame of reference. This can be guaranteed by using a measure of strain that is “frame-indifferent”. This still leaves us with an infinite number of strain measures to choose from.

Strain tensors generally separate into two classes: those in which the deformation is referred to the initial state (“material”) and those in which deformation is referred to the final state (“spatial”). Material strain tensors are frame-indifferent but spatial tensors generally are not. Under isotropic strain, the frame sensitivity of spatial tensors is unimportant so we can choose just about anything we like.

Consider a point in the material initially at position \( X \) and ending up at position \( x \) so that

\[ x_i = X_i + u_i \]

In finite strain theory, two strain tensors are commonly used (Malvern section 4.5): the Lagrangian

\[ \eta_{ij} = \frac{1}{2} \left[ \frac{\partial u_i}{\partial X_j} + \frac{\partial u_j}{\partial X_i} + \frac{\partial u_k}{\partial X_i} \frac{\partial u_k}{\partial X_j} \right] \]

and the Eulerian

\[ \epsilon_{ij} = \frac{1}{2} \left[ \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{\partial u_k}{\partial x_i} \frac{\partial u_k}{\partial x_j} \right] \]

The expansion of the Helmholtz free energy or internal energy using the Eulerian strain measure has been found to give superior results when applied to the data.

Where do these tensors come from? Consider an arbitrary infinitesimal material vector \( dX \) at \( X \) and associate with it a vector \( dx \) at \( x \).
Let $dX$ be of length $dS$ and $dx$ be of length $ds$ where

$$(dS)^2 = dX \cdot dX \quad \text{and} \quad (ds)^2 = dx \cdot dx$$

We suppose these vectors are related by

$$dx = F \cdot dX \quad \text{and} \quad dX = F^{-1} \cdot dx$$

where $F$ is the gradient tensor:

$$F_{ij} = \frac{\partial x_i}{\partial X_j}$$

$\eta$ and $\epsilon$ are defined in terms of the change in length of the vector:

$$(ds)^2 - (dS)^2 = 2dX \cdot \eta \cdot dX = 2dx \cdot \epsilon \cdot dx$$

Now

$$(ds)^2 - (dS)^2 = dx \cdot dx - dX \cdot dX$$

$$= dX \cdot F^T F \cdot dx - dX \cdot dX$$

$$= dx \cdot dx - dx \cdot F^{-1} F^{-1} \cdot dx$$

so

$$\eta = \frac{1}{2} [F^T F - I] \quad \text{and} \quad \epsilon = \frac{1}{2} [I - F^{-1} F^{-1}]$$

or in component form (summation over repeated indices implied)

$$\eta_{ij} = \frac{1}{2} \left[ \frac{\partial x_k}{\partial X_i} \frac{\partial x_k}{\partial X_j} - \delta_{ij} \right] \quad \text{and} \quad \epsilon_{ij} = \frac{1}{2} \left[ \delta_{ij} - \frac{\partial X_k}{\partial x_i} \frac{\partial X_k}{\partial x_j} \right]$$

These can be put in terms of the displacement $u$. For the Lagrangian case, we consider $u$ to be a function of $X$, i.e.

$$x_i = X_i + u_i(X_1, X_2, X_3)$$

thus

$$\frac{\partial x_1}{\partial X_1} = 1 + \frac{\partial u_1}{\partial X_1}, \quad \frac{\partial x_1}{\partial X_2} = \frac{\partial u_1}{\partial X_2}, \quad \text{etc.}$$

and substitution into the expression for $\eta_{ij}$ gives

$$\eta_{ij} = \frac{1}{2} \left[ \frac{\partial u_i}{\partial X_j} + \frac{\partial u_j}{\partial X_i} + \frac{\partial u_k}{\partial X_i} \frac{\partial u_k}{\partial X_j} \right]$$

For the Eulerian case, we take $u$ to be a function of $x$, i.e.

$$X_i = x_i - u_i(x_1, x_2, x_3)$$

and we have

$$\frac{\partial X_1}{\partial x_1} = 1 - \frac{\partial u_1}{\partial x_1}, \quad \frac{\partial X_1}{\partial x_2} = \frac{\partial u_1}{\partial x_2}, \quad \text{etc.}$$

and substitution into the expression for $\epsilon_{ij}$ gives

$$\epsilon_{ij} = \frac{1}{2} \left[ \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{\partial u_k}{\partial x_i} \frac{\partial u_k}{\partial x_j} \right]$$
For the special case of an isotropic strain, we can write

\[ \eta_{ij} = \eta \delta_{ij} \quad \text{and} \quad \epsilon_{ij} = \epsilon \delta_{ij} \]

where \( \eta \) and \( \epsilon \) are any of the diagonal elements of \( \eta_{ij} \) and \( \epsilon_{ij} \). \( \eta \) and \( \epsilon \) can be cast in terms of a volume change of the material (the general case is considered in Malvern). Under isotropic strain, we can consider deformation in one direction only. Consider the change in length of a small vector in the 1 direction. The length in the strained state is \( \delta x_1 \) and in the unstrained state is \( \delta X_1 \) and we have

\[ \left( \frac{\partial x_1}{\partial X_1} \right) = 1 + \frac{\partial u_1}{\partial X_1} \]

Note that

\[ \left( \frac{\partial x_1}{\partial X_1} \right)^2 = \left( 1 + \frac{\partial u_1}{\partial X_1} \right)^2 = 1 + 2\eta \]

For isotropic strain, the change in volume of an element is given by

\[ \frac{V}{V_0} = \left( \frac{\partial x_1}{\partial X_1} \right)^3 = (1 + 2\eta)^{3/2} \]

where \( V \) is the volume in the strained state and \( V_0 \) is the volume in the unstrained state. Thus, for isotropic strain, we have

\[ \eta = \frac{1}{2} \left[ \left( \frac{V}{V_0} \right)^{2/3} - 1 \right] \]

A similar analysis for the Eulerian case gives

\[ \left( \frac{\partial X_1}{\partial x_1} \right) = 1 - \frac{\partial u_1}{\partial x_1} \]

so that

\[ \left( \frac{\partial X_1}{\partial x_1} \right)^2 = 1 - 2\epsilon \]

and

\[ \frac{V_0}{V} = (1 - 2\epsilon)^{3/2} \quad \text{and} \quad \epsilon = \frac{1}{2} \left[ 1 - \left( \frac{V_0}{V} \right)^{2/3} \right] \]

We now consider the development of an isothermal EOS using an expansion of the Helmholtz free energy in powers of \( \epsilon \), i.e.

\[ F(\epsilon) = a_2 \epsilon^2 + a_3 \epsilon^3 + a_4 \epsilon^4 + \cdots \]

A “third” order expansion includes terms up to \( a_3 \), a “fourth” order expansion up to \( a_4 \), and so on. The pressure-strain relationship is found by using

\[ P = -\left( \frac{\partial F}{\partial V} \right)_T = -\left( \frac{\partial \epsilon}{\partial V} \right)_T \frac{dF}{d\epsilon} \quad \text{where} \quad \left( \frac{\partial \epsilon}{\partial V} \right)_T = \frac{(1 - 2\epsilon)^{5/2}}{3V_0} \]

Successive differentiation gives

\[ K_T = -V \left( \frac{\partial P}{\partial V} \right)_T, \quad \left( \frac{\partial K_T}{\partial P} \right)_T, \quad \text{etc.} \]
as a function of $\epsilon$. Thus

$$P = -(1 - 2\epsilon)^{5/2} \left[ C_1 \epsilon + \frac{C_2}{2} \epsilon^2 + \frac{C_3}{6} \epsilon^3 + \cdots \right]$$

(52)

where $C_{n-1} = n! a_n / 3V_0$. Truncating at $C_3$ and differentiating again gives

$$K_T = (1 - 2\epsilon)^{5/2} \left[ L_1 + L_2 \epsilon + \frac{L_3}{2} \epsilon^2 \right]$$

where $C_1 = 3L_1$, $C_2 = 3L_2 + 7C_1$ and $C_3 = 3L_3 + 9C_2$. At $\epsilon = 0$ (i.e. when $P = 0$) we have $L_1 = K_0$ so $C_1 = 3K_0$. $L_2$ can be found in terms of the pressure derivative of $K_T$, i.e.

$$\left( \frac{\partial K_T}{\partial P} \right)_T = \left( \frac{\partial \epsilon}{\partial P} \right)_T \frac{dK_T}{d\epsilon} \quad \text{where} \quad \left( \frac{\partial \epsilon}{\partial P} \right)_T = -\frac{1}{3} (1 - 2\epsilon)$$

Thus

$$\left( \frac{\partial K_T}{\partial P} \right)_T = \frac{5}{3} - \frac{(1 - 2\epsilon)^{7/2}}{3K_T} [L_2 + L_3 \epsilon]$$

so $L_2 = -K_0 [3K'_T - 5]$ (where $K'_T$ is the pressure derivative of $K_T$ evaluated at $P = 0$) and $C_2 = 9K_0 [4 - K'_0]$. Repeating the procedure gives

$$\left( \frac{\partial^2 K_T}{\partial P^2} \right)_T = \frac{-1}{9K_T} (3K'_T - 5)(3K'_T - 7) + \frac{(1 - 2\epsilon)^{9/2}}{9K_T^2} L_3$$

whence $C_3 = 3K_0 [9K_0K''_0 + 9K''_0^2 - 63K_0^2 + 143]$. Equation (52) can now be fit to some $P(V)$ data along an isotherm. The fitting is non-linear since $V_0$ must also be solved for and $\epsilon$ is a function of $V_0$. Some clever ways of doing this have been devised but we won’t go into that here. The parameters that we retrieve from the fits are $V_0$, $K_0$, $K'_0$, $K''_0$, etc. It should be noted that, if we use a different definition of strain (e.g., $\eta$), the coefficients $C$ change form and the implication of fitting a truncated expansion are different. The Eulerian expansion is more efficient at fitting data largely because $K'_0 \simeq 4$ so $C_2 \simeq 0$. This should not be misinterpreted as implying that finite strain theory predicts that $K'_0 = 4$ though this would be a consequence of truncating at second order in $\epsilon$.

5. Decompressing the Earth

By converting all the isothermal derivatives to adiabatic derivatives in finite strain theory, we can fit $P(V)$ data along an adiabat (e.g. an Earth model of the lower mantle and outer core).

An application of finite strain theory to the estimation of the zero pressure properties of the different regions of the Earth can be found in Jeanloz and Knittle (Advances in Geochemistry, 1986). The procedure works reasonably well for the lower mantle and outer core but does not work well for the upper mantle or the inner core. (This probably reflects, in part, the difficulty of getting good spherically-averaged models of these regions). Using different order finite strain theories, they find:

<table>
<thead>
<tr>
<th>Property</th>
<th>Lower Mantle</th>
<th>Outer Core</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_0$</td>
<td>3.994–4.003 g/cc</td>
<td>6.66–6.73 g/cc</td>
</tr>
<tr>
<td>$K_0$</td>
<td>204.7–222.5 GPa</td>
<td>105–150 GPa</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>130–135 GPa</td>
<td>-</td>
</tr>
<tr>
<td>$K'_0$</td>
<td>3.7–4.4</td>
<td>4.2–6.4</td>
</tr>
<tr>
<td>$K_0K''_0$</td>
<td>-3 - -8</td>
<td>-4 - -20</td>
</tr>
</tbody>
</table>
Note that these zero pressure values relate to some elevated adiabatically decompressed temperature. Some corrections must therefore be made before comparing these values with low temperature laboratory data. It is interesting to note that the decompressed outer core density is less than that of liquid iron at room pressure (about 7 g/cc) though the decompressed temperature is probably very similar to the melting temperature of iron. This, of course, tells us that the outer core must have light alloying elements.

6. EOS based on simple interatomic potentials

We include this section because it gives some insight as to why \( \frac{dK}{dP} \) is on the order of 4 (and dimensionless of course) for many materials. The assumption here is that the energy potential between atoms in a crystal depend only on interatomic spacing \( (r) \), and consist of an attractive and a repulsive part. A typical form for the Helmholtz free energy, \( F \), would be

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

where \( m \) in the attractive part would be about 2 and \( n \) in the repulsive part would be about 4. In terms of volume we have

\[
F = -aV^{-m/3} + bV^{-n/3}
\]

Differentiating with respect to volume at constant temperature gives pressure:

\[
P = -\left( \frac{\partial F}{\partial V} \right)_T = -\frac{ma}{3} V^{-(m/3+1)} + \frac{nb}{3} V^{-(n/3+1)}
\]

Similarly,

\[
K_T = -V \left( \frac{\partial P}{\partial V} \right)_T = -\frac{ma}{3} \left( \frac{m}{3} + 1 \right) V^{-(m/3+1)} + \frac{nb}{3} \left( \frac{n}{3} + 1 \right) V^{-(n/3+1)}
\]

Setting \( K_T = K_0 \) when \( P = 0 \) and \( V = V_0 \) gives

\[
a = \frac{9K_0}{m(n - m)} V_0^{(m/3+1)}
\]

\[
b = \frac{9K_0}{n(n - m)} V_0^{(n/3+1)}
\]

Hence

\[
P = \frac{3K_0}{n - m} \left[ \left( \frac{V_0}{V} \right)^{(n/3+1)} - \left( \frac{V_0}{V} \right)^{(m/3+1)} \right]
\]

\[
K = \frac{K_0}{n - m} \left[ (n + 3) \left( \frac{V_0}{V} \right)^{(n/3+1)} - (m + 3) \left( \frac{V_0}{V} \right)^{(m/3+1)} \right]
\]

Now, using the fact that \( dK/dP = dK/dV \cdot dV/dP = -dK/dV \cdot V/K \) and evaluating at zero pressure gives

\[
K'_0 = \left( \frac{dK}{dP} \right)_{P=0} = \frac{1}{3} (m + n + 6)
\]

For \( m = 2 \) and \( n = 4 \), \( K'_0 = 4 \). Any material which has attractive and repulsive components of the interatomic potential with roughly this volume dependence will have similar values of \( K'_0 \). On the other hand, materials which have strong covalent bonds or delocalized electrons (metals)) may not be well-modeled by such potentials.
The Vinet equation of state is also based upon a simple interatomic potential. Poirier shows that the effective Helmholtz potential for this EOS is given by

\[
F(a) = -F_0(1 + a)e^{-a}
\]

(53)

where \(a = (r - r_0)/l\) and \(r_0\) is the equilibrium atomic spacing when \(P = 0\) and \(l\) is some scaling length. Differentiation with respect to \(a\) gives

\[
\frac{\partial F}{\partial a} = aF_0e^{-a}
\]

Now \(V = 4/3\pi r^3\) and \(\partial a = \partial r/l\) so \(\partial V = 4\pi r^2\partial a\), thus

\[
P = -\frac{\partial F}{\partial V} = -\frac{aF_0e^{-a}}{4\pi r^2l}
\]

(54)

Differentiating again wrt \(a\) gives

\[
\frac{\partial P}{\partial a} = -\frac{F_0e^{-a}}{4\pi r^2l}[1 - a - 2\frac{al}{r}]
\]

(55)

and using the relationship between \(\partial V\) and \(\partial a\) gives

\[
K = -V\frac{\partial P}{\partial V} = \frac{F_0e^{-a}}{12\pi rl^2}[1 - a - 2\frac{al}{r}]
\]

(56)

When \(P=0, r = r_0\) and \(a = 0\) so

\[
K_0 = \frac{F_0}{12\pi r_0l^2}
\]

(57)

Next, we differentiate the equation for \(K\) wrt \(a\) and divide by the equation for \(\partial P/\partial a\) to get an expression for \(\partial K/\partial P\). Evaluating this at \(P = 0, a = 0\) gives

\[
\frac{\partial K}{\partial P}(P = 0) = K'_0 = 1 + \frac{2r_0}{3l}
\]

(58)

Note that

\[
\left(\frac{V}{V_0}\right)^{\frac{2}{3}} = \frac{r}{r_0}
\]

and using (57) and (58) allows (54) to be written as

\[
P = 3K_0\left(\frac{V}{V_0}\right)^{\frac{2}{3}}\left(1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right)exp\left[\frac{3}{2}(K'_0 - 1)\left(1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right)\right]
\]

(59)

This is the Vinet EOS with fitable parameters \(V_0, K_0,\) and \(K'_0\). This equation is quite successful but needs to be generalized to include more fitable parameters to be more generally useful.

7. Implementing the Mie-Gruneisen equation of state.

A second- or third-order Eulerian finite strain EOS is typically used to describe the "static" part of the Mie-Gruneisen equation of state which adds another 3 or 4 parameters to the 3 we already had from the thermal part (\(\gamma_0, q,\) and \(\Theta_D\)). Usually, these 6 or 7 numbers are capable of accurately explaining all the observations of compressibility, volume, thermal expansion, heat capacity, etc, for a particular mineral (see table below for an example). Note that shear properties of a mineral do not enter into the Mie-Gruneisen
description but the theory has been extended to include full elasticity by Stixrude (2005). The description of the shear modulus requires another three numbers.

For a particular \( V \) and \( T \), we can now calculate all the properties of a mineral component of the mantle. We would first calculate \( \epsilon \) in the finite strain theory

\[
\epsilon = \frac{1}{2} \left[ 1 - \left( \frac{V_0}{V} \right)^{2/3} \right]
\]

and then evaluate equation (52) to get the pressure (at 300K):

\[
P(300) = -\left(1 - 2\epsilon\right)^{5/2} \left[ 3K_0\epsilon + \frac{C_2}{2} \epsilon^2 \right]
\]

where \( C_2 = 9K_0[4 - K'_0] \) and we have assumed \( C_3 = 0 \). We can also use the EOS to compute \( K_T \) at 300K:

\[
K_T(300) = (1 - 2\epsilon)^{5/2} \left[ K_0 + L_2\epsilon + \frac{L_3}{2} \epsilon^2 \right]
\]

where \( L_2 = -K_0(3K'_0 - 5) \) and \( L_3 = -3C_2 \).

We now want to correct the pressure for the thermal pressure between \( T \) and 300K (with volume fixed) which we do using equation (27):

\[
P(V,T) = P(V,300) + \frac{\gamma(E(T) - E(300))}{V}
\]

Since \( \gamma \) is a function only of volume, we can calculate \( \gamma \) using

\[
\gamma = \gamma_0 \left( \frac{V}{V_0} \right)^q
\]

We now compute the energy difference using the Debye form for \( E \) given in equation (17)

\[
E = \frac{9}{8} Nk\theta_D + \frac{9NkT}{x_D^3} \int_0^{x_D} \frac{x^3}{e^{x} - 1} \, dx
\]

where \( \theta_D \) is the Debye temperature of the material and \( x_D = \theta_D/T \). Note that the Debye temperature is proportional to the Debye frequency which is a function of the volume of the material. Thus, we have to first correct the Debye temperature to volume \( V \). Remember that Gruneisen’s ratio is related to the logarithmic
dependence of the mode frequencies (equation 24) and that we have assumed that all mode frequencies (including the Debye frequency) have the same volume dependence, thus

$$\gamma = \left( \frac{\partial \ln \theta_D}{\partial \ln V} \right)_T$$

(66)

If we use the expression for $\gamma$ above, we can integrate to get an expression for $\theta_D$:

$$\theta_D = \theta_{D0} \exp \left( \frac{\gamma_0 - \gamma}{q} \right)$$

(67)

where $\theta_{D0}$ is the value of the Debye temperature when $V = V_0$. After computing the energy, we can compute $C_v$ using equation (19):

$$C_v = 3Nk \left[ \frac{3}{x_D} \int_0^{x_D} \frac{x^4e^x}{(e^x - 1)^2} dx \right]$$

(68)

Now we want to correct the bulk modulus for the difference in temperature between $T$ and 300K (at constant volume). We can compute the thermal part of the bulk modulus by differentiating the thermal pressure wrt volume at constant temperature, i.e.,

$$K_{th} = -V \left( \frac{\partial P_{th}}{\partial V} \right)_T$$

$$P_{th} = \frac{\gamma E}{V}$$

(69)

so

$$K_{th} = -E \left( \frac{\partial \gamma}{\partial V} \right)_T - \gamma \left( \frac{\partial E}{\partial V} \right)_T + \frac{\gamma E}{V}$$

(70)

and using the definition of $q$, we have

$$K_{th} = \frac{\gamma E}{V} (1 - q) - \gamma \left( \frac{\partial E}{\partial V} \right)_T$$

(71)

Now

$$\left( \frac{\partial E}{\partial V} \right)_T = \frac{T \gamma^2 C_v}{V} - \gamma \left( \frac{\partial E}{\partial V} \right)_T$$

(72)

So we get:

$$K_{th} = \frac{\gamma E}{V} (1 + \gamma - q) - \frac{T \gamma^2 C_v}{V}$$

(73)

and the bulk modulus is just

$$K_T = K_T(300) + \frac{\gamma}{V} (1 + \gamma - q) [E(T) - E(300)] - \frac{\gamma^2}{V} [TC_v - 300C_{v0}]$$

(74)

We can now compute $\alpha$ from

$$\alpha = \frac{\gamma C_v}{K_T V}$$

(75)

and then

$$K_S = K_T(1 + \alpha T \gamma) \quad \text{and} \quad C_p = C_v(1 + \alpha T \gamma)$$

(76)

So finally we can compute the bulk sound speed for comparison with seismological models. You should consult Stixrude for the calculation of the shear modulus.
8. Other treatments of Gruneisen’s ratio

Up till now, we have considered the case where the volume dependence of $\gamma$ is given by

$$\left( \frac{\partial \ln \gamma}{\partial \ln V} \right)_{T} = q$$  \hspace{1cm} (77)

where $q$ is taken to be a constant so $\gamma$ is given by equation 64. From equation 44, we find that $q$ is given in terms of thermodynamic quantities as

$$q = 1 + \delta T - \left( \frac{\partial K_{T}}{\partial P} \right)_{T} + \left( \frac{K_{T}}{C_{v}} \frac{\partial C_{v}}{\partial P} \right)_{T}$$  \hspace{1cm} (78)

where the last term is small. Evaluating $q$ for a variety of materials shows that it is typically between 1 and 3, however, it is not usually independent of volume. This can be a limitation when you are fitting an equation of state to data over a wide pressure range (e.g., including shock wave data at very high pressures).

A natural extension would be to write

$$q = q_{0} \left( \frac{V}{V_{0}} \right)^{q'}$$  \hspace{1cm} (79)

where $q_{0}$ and $q'$ are new constants. Integrating equation 77 above now gives

$$\gamma = \gamma_{0} \exp \left( \frac{q - q_{0}}{q'} \right)$$  \hspace{1cm} (80)

but the calculation for the volume dependence of the Debye temperature is more complicated. For reference, the exact solution is

$$\theta_{D} = \theta_{D0} \exp \left[ c_{1}(E_{i}(q/q') - E_{i}(q_{0}/q')) \right]$$  \hspace{1cm} (81)

where $c_{1} = -\gamma_{0}/q' \exp (-q_{0}/q')$ and $E_{i}$ is the exponential integral. When $q'$ is small, $q$ doesn’t change very much and we can approximate it by its volume average $\bar{q} = (qV - q_{0}V_{0})/((q' + 1)(V - V_{0}))$. Combine equation 66 and 77 to give

$$\left( \frac{\partial \ln \theta_{D}}{\partial \gamma} \right)_{T} = -\frac{1}{q} \approx -\frac{1}{\bar{q}}$$  \hspace{1cm} (82)

This is trivial to integrate giving

$$\theta_{D} = \theta_{D0} \exp \left( \frac{\gamma_{0} - \gamma}{\bar{q}} \right)$$

This approximation is good for most situations except, perhaps, when $q'$ is very big. When $q'$ is greater than about 5, an even better approximation to equation 81 is given by

$$\theta_{D} = \theta_{D0} \left( \frac{q}{q_{0}} \right)^{c_{1}} \left( \frac{\gamma}{\gamma_{0}} \right)^{c_{2}}$$

where $c_{2} = c_{1}[1 + (q + q_{0})/(4q')]$

Yet another description of the volume dependence of $\gamma$ also comes from a desire to model the high compressions found in shock-wave experiments by including the possibility of a finite $\gamma$ at infinite compressions. This value of $\gamma$ is called $\gamma_{\infty}$ and the resulting form for $\gamma(V)$ is

$$\gamma = \gamma_{\infty} + (\gamma_{0} - \gamma_{\infty}) \left( \frac{V}{V_{0}} \right)^{\beta}$$  \hspace{1cm} (83)

Using equation (77) gives
\[ q = \beta \left( \frac{V}{V_0} \right)^\beta \frac{\gamma_0 - \gamma_\infty}{\gamma} = \beta \frac{\gamma - \gamma_\infty}{\gamma} \]  
\text{and using equation (81) gives}

\[ \theta_D = \theta_{D0} \left( \frac{V}{V_0} \right)^{-\gamma_\infty} \exp \left[ \frac{\gamma_0 - \gamma}{\beta} \right] \]  

Note that if \( \gamma_\infty = 0 \) then 84 gives \( \beta = q \) and 83 reduces to 64 and 85 reduces to 67.

A completely different approach is taken by Stixrude who suggests that the squared mode frequencies can be expanded in a finite strain expansion:

\[ \omega^2 = \omega_0^2 \left[ 1 + a_1 f + \frac{1}{2} a_2 f^2 + \ldots \right] \]  
where \( f = -\epsilon \) and we have taken \( \omega \) to be some average of all the mode frequencies. Since

\[ \gamma = -\left( \frac{\partial \ln \omega}{\partial \ln V} \right)_T \]

we find that differentiation of equation 86 (truncating at \( a_2 \)) leads to

\[ \gamma = \frac{1 + 2f \omega_0^2}{6 \omega_0^2} [a_1 + a_2 f] \]  

with \( a_1 = 6\gamma_0 \) and \( a_2 = 36\gamma_0^2 - 18\gamma_0 q_0 - 12\gamma_0 \) Stixrude argues that this gives a better fit to the observed volume dependence of \( \gamma \) than the power laws discussed above. Since the Debye temperature is proportional to the Debye frequency and we assume that all mode frequencies have the same volume dependence, we simply have

\[ \theta_D = \theta_{D0} \left[ 1 + a_1 f + \frac{1}{2} a_2 f^2 \right]^{\frac{1}{2}} \]  

The finite strain approach can also be used to get an expression for \( q(f) \). This expression predicts a value for \( q' \) in terms of \( \gamma_0 \) and \( q_0 \):

\[ q' = 2\gamma_0 - \frac{c(c - 2)}{9q_0} \]

where \( c = a_2/a_1 = 6\gamma_0 - 3q_0 - 2 \). Typical values of \( \gamma_0 \) and \( q_0 \) lead to a value of \( q' \) of about 3 so \( q \) is quite a strong function of volume in the Stixrude approach. If this value is used in equation 79 then the two approaches give very similar results for both \( \gamma \) and \( \theta_D \) to compressions of 30\% \( (f \approx 0.1) \). If \( q' \) has been given independently then it is possible to add another term in equation 86 \( (a_3 f^3/6) \) and we find that

\[ \theta_D = \theta_{D0} \left[ 1 + a_1 f + \frac{1}{2} a_2 f^2 + \frac{1}{6} a_3 f^3 \right]^{\frac{1}{2}} \]

where \( a_3/a_1 = 9q_0(q_0 - 2\gamma_0) + c(c - 2) \).

9. Properties of composites

Before we can compare the calculations of the predicted seismic properties of mantle mineral assemblages with those of the Earth, we must be able to compute the elastic properties of composites of different minerals. Consider a volume \( V \) with elastic modulus tensor \( C_{ijkl} \):

\[ T_{ij} = C_{ijkl} \varepsilon_{kl} \]

and define the mean stress and strain as:
\[< T_{ij} > = \frac{1}{V} \int_V T_{ij} \, dV\]
\[< \epsilon_{ij} > = \frac{1}{V} \int_V \epsilon_{ij} \, dV\]

It is easy to show these averages do not depend on constitutive relation. Now define:

\[< T_{ij} > = C_{ijkl}^* < \epsilon_{kl} >\]

where \(C^*\) is the effective modulus tensor of the composite. We usually try to bound this tensor – we do this by introducing the compliance tensor:

\[\epsilon_{ij} = S_{ijkl} T_{kl}\]
\[< \epsilon_{ij} > = S_{ijkl}^* < T_{kl} >\]

Consider a composite of two isotropic phases and write

\[< \epsilon > = V_1 < \epsilon^1 > + V_2 < \epsilon^2 >\]
\[< T > = V_1 < T^1 > + V_2 < T^2 >\]

where

\[< \epsilon^k_{ij} > = \frac{1}{V_k} \int_{V_k} \epsilon^k_{ij} \, dV\]

\((V_k\) is the volume fraction of the \(k\)’th phase). We can now write

\[< \epsilon > = V_1 S_1 < T^1 > + V_2 S_2 < T^2 >\]
\[< T > = V_1 C_1 < \epsilon^1 > + V_2 C_2 < \epsilon^2 >\]

The average strain in each phase depends upon the average strain so we write:

\[< \epsilon^1 > = A_1 < \epsilon > \quad \text{and} \quad < \epsilon^2 > = A_2 < \epsilon >\]

where the \(A\)’s are some tensors. Note that we also have

\[V_1 A_1 + V_2 A_2 = I\]

Similarly, we can write

\[< T^1 > = B_1 < T > \quad \text{and} \quad < T^2 > = B_2 < T >\]

\[V_1 B_1 + V_2 B_2 = I\]

Finally, we have

\[< \epsilon > = (V_1 S_1 B_1 + V_2 S_2 B_2) < T >\]
\[< T > = (V_1 C_1 A_1 + V_2 C_2 A_2) < \epsilon >\]

so
Different effective moduli can now be determined by making different assumptions about the stress and strain in the composite. If we make the extreme assumption that strain is uniform in the composite ($A_1 = A_2 = I$), so

\[ C^* = \sum V_i C_i \]

This is called the Voigt average. If we make the extreme assumption that stress is uniform, ($B_1 = B_2 = I$)

\[ S^* = \sum V_i S_i \]

This is called the Reuss average. As we are dealing with an isotropic composite, we can write for the effective bulk modulus (or rigidity):

\[ K^*_V = \sum V_i K_i \quad \text{and} \quad K^*_R = (\sum V_i/K_i)^{-1} \]

The assumption of uniform strain gives an overestimate of the effective moduli and the assumption of uniform stress gives an overestimate of the compliance so

\[ K^*_R \leq K^* \leq K^*_V \]

This result was proved by Hill – the VRH average is just the mean of the Voigt and Reuss estimates. It is the VRH average that is typically used in the computation of the elastic properties of composites for comparison with seismologically determined properties. Other, tighter, bounds can be derived (see Watt et al, 1976 Rev Geophys, v14, 541 for a review). To get a feel for why the Reuss and Voigt averages bound the moduli, consider the following situation. Consider a composite of two materials where the volume fractions are exactly 0.5 and let the modulus of material 1 be slightly stiffer than the modulus of material 2:

\[ V_1 = V_2 = \frac{1}{2} \quad \text{and} \quad C_1 = C_2 + \delta \quad \text{and} \quad A_1 + A_2 = 2I \]

Thus the Voigt average is given by

\[ \frac{1}{2} C_1 + \frac{1}{2} C_2 = C_2 + \frac{1}{2} \delta \]

The true average is given by

\[ C^* = V_1 C_1 A_1 + V_2 C_2 A_2 = \frac{1}{2} C_2(A_1 + A_2) + A_1 \frac{1}{2} \delta = C_2 + A_1 \frac{1}{2} \delta \]

Now $A_1$ measures the amount of average strain in phase 1:

\[ < \epsilon_1 > = A_1 < \epsilon > \]

but phase 1 is slightly stiffer than phase 2 so we expect the strain to be smaller there so

\[ |A_1| < I \]

i.e. it will deform less. This means that $C^*$ is less than the Voigt average as advertised. A similar argument can be made for the compliances.

10. Static high pressure experimental techniques

One of the most popular instruments used to explore the $P$ and $T$ conditions of the mantle is the diamond anvil cell (DAC). The DAC is capable of attaining pressures up to 5Mbars and diamond is transparent to
a broad range of electromagnetic radiation so the sample can be directly observed through the anvils. A typical experimental arrangement is shown in the figure below, where a sample is placed between the flat faces of two opposed diamond anvils. Pressure is generated by pushing the anvils together, with the force multiplied by a nutcracker like device. It is critical that the faces (culets) of the anvils be kept in close alignment (a tenth of a micron is typical). If misalignment occurs, non-uniform stresses are induced in the sample making pressure determination very difficult (apart from the fact that the diamonds will probably crack). The gasket (usually a metal foil with a hole in it for the sample) provides support at the ends of the culets and helps to minimize pressure gradients. The sample will usually be about ten microns thick at high pressures and has a diameter of about 100 microns. The sample is suspended in a pressure medium along with ruby grains (or some other material with a known equation of state) which are used to calibrate the pressure. Ideally the pressure medium would be a fluid so that the pressure would be hydrostatic in the sample. No fluid is known above about 14GPa so “soft” solids are used – the noble gases (e.g. argon) are particularly useful in this respect and special equipment has been devised for loading the DAC with gas pressure media (which of course turn to solids at high pressure).

At room temperature, laser light is used to excite a fluorescence line in ruby which shifts into the deep red part of the visible spectrum with increasing pressure. The pressure shift has been calibrated to well over 100GPa using shock-wave data. The laser light can be focused on an area a few microns in dimension so point-wise pressure measurements can be made across the sample. Crystal structure and lattice parameters can be determined using X-ray diffraction through the diamond anvils. These days, these measurements are almost always made at synchrotron facilities which provide brilliant X-ray sources so that diffraction patterns can be established very quickly (sometimes in real time). High temperatures are achieved by external heating or laser heating. External heating is limited to temperatures of about 1200° K since higher temperatures cause softening of the DAC superstructure and misalignment of the diamonds. External heating allows steady temperatures to be attained. Laser heating (using near infrared gives radiation absorbed by the minerals, but not most diamonds) is capable of achieving very high temperatures (6000° K) but the narrowness of the beam means that heating is highly non-uniform leading to large thermal stresses. A large variety of physical properties can be measured in the DAC: in addition to the usual $P(V)$ studies, elastic moduli can be measured using Brillouin scattering and gigaHz interferometry; viscosity and electrical conductivity measurements are also being made.
Many problems still exist with DAC technology. One problem is the accurate measurement of pressure at elevated temperature. The ruby fluorescence cannot be used at temperatures above about 700K because of line broadening. This means that chemically inert materials with known equations of state must be used – gold, platinum, and MgO are favorites, though it is only recently that attempts have been made to get consistent pressure scales with these materials. Thus it is common for the results of compression of a material from older experiments to be inconsistent because of the use of different pressure calibrants. Another issue is the presence of deviatoric stresses in the DAC which can often mean that one is effectively measuring the strength of a material rather than the true $P(V)$ relationship. Thus, early DAC EOS measurements prior to about 1995 which didn’t strive for hydrostatic conditions are often treated with suspicion.

Finally, it should be noted that conventional high pressure equipment (eg. multi-anvil designs) have also been undergoing development and are capable of reproducing conditions in the Earth at the top of the lower mantle. Multi-anvil devices are often called "large-volume" presses though we are usually talking about samples with dimensions of a millimeter or so – this is sufficiently large that conventional acoustic methods of determining elastic moduli can be used (though we are still talking about kHz to MHz frequencies which are very different from seismic frequencies). Pressure is often measured simply by calibrating the force used to compress the multi-anvil cell. Temperature is often measured using thermocouples though you will find that most papers have a disclaimer that the pressure effect on the temperature measured by the thermocouple has not been calibrated – clearly more work on $P$ and $T$ calibration needs to be done.

Shock waves provide another means of achieving high pressure and establishing equations of state – we shall look at these later.

11. Composition and temperature in the lower mantle

The lower mantle between pressures of 30GPa and 120Gpa is believed to be relatively homogeneous and of fairly simple mineralogy. Above this pressure, upper mantle minerals are still transforming to their high pressure counterparts, and, at higher pressures, new phase transformations are now thought to be possible.

Therefore, between 30GPa and 120Gpa, we think we can use 1D seismic models of the Earth in concert with equilibrium thermodynamics to determine the bulk composition of the mantle (later in the class, we shall discuss other types of transitions such as spin transitions which may violate these conditions).

Below about 800km depth, we believe that only 3 mineral species may be abundant: magnesiowustite (or ferropericlase) $(Mg, Fe)O$; magnesium-iron silicate perovskite $(Mg, Fe)SiO_3$; and smaller amounts of calcium silicate perovskite $CaSiO_3$. Aluminum is probably accommodated in the magnesium-iron silicate perovskite but its effect on seismic velocities is currently controversial (and possibly negligible). This means that a small number of parameters can be used to describe the composition of the lower mantle:

- $X_{Pv}$ – the mole fraction of magnesium-iron silicate perovskite
- $X_{Ca}$ – the mole fraction of calcium silicate perovskite
- $X_{Mw}$ – the mole fraction of magnesiowustite. This doesn’t have to be specified since $X_{Mw} = 1.0 - X_{Pv} - X_{Ca}$
- $X_{Fe}$ – the fraction of Mg/Fe sites occupied by Fe: $Fe/(Mg+Fe)$ which, from geochemical constraints, is close to 0.1.
- $K_D$ – the partition coefficient which describes the partitioning of iron between magnesiowustite and magnesium-iron silicate perovskite. This is defined as

$$K_D = \frac{X_{Fe}^{Pv} / X_{Pv}}{X_{Fe}^{Mw} / X_{Mw}}$$

The value of this parameter is not very certain. Some experiments indicate that most of the iron goes into magnesiowustite with $K_D \approx 0.25$ but other experiments, in the presence of aluminum, indicate that iron goes equally into both phases implying $K_D \approx 1$. Equilibrium thermodynamics indicates a $K_D$ of about 0.8 (Mattern et al, 2005). Fortunately, this parameter does not seem to have much effect on the properties of the resulting phase assemblage though you are encouraged to play with it.

The final parameter we need to specify to calculate the seismological properties of a particular mineral assemblage is the temperature. In the code you are given, we assume that the temperature profile is adiabatic.
and this is specified by the temperature at the 660km discontinuity (thought to be about 1900K though, in certain circumstances, could be larger). The code extrapolates this through the lower mantle using the thermal properties of magnesium-iron silicate perovskite which is the dominant mineral in the lower mantle. The resulting temperature profile is rather insensitive to the thermal properties assumed (except for the boundary condition on temperature at the 660).

Thus, the following five numbers specify a mantle composition and temperature:

\[ X_{Fe}, K_D, X_{Pv}, X_{Ca}, T_{660} \]

You can find typical values in the Mattern et al paper. For example, for a pyrolite composition, \( X_{Pv} \approx 0.62, X_{Ca} \approx 0.05, X_{Fe} \approx 0.10 \). \( K_D \) is probably between 0.25 and 1. For a composition closer to a chondritic meteorite, \( X_{Pv} \) is larger, on the order of 0.75, at the expense of \( X_{Mw} \).

Program eos_{mu2} allows you to experiment with these numbers to see what composition/temperature combinations can fit the lower mantle of PREM. We use the density, bulk sound speed, and the shear velocity to do this comparison. We use the Mie-Gruneisen equation of state to specify the properties of each candidate mineral: \( MgO, FeO, MgSiO_3, FeSiO_3, CaSiO_3 \). The properties of each mineral at a particular, P,T state are computed then averaged according to their molar fractions and iron partitioning to get the final properties of the assemblage. These are then compared with PREM at a discrete number of pressures and a couple of measures of misfit for each parameter are returned: \( \chi^2/N \) and the maximum deviation in terms of standard deviations. (Given our discussion of resolving power of 1D models, we take the uncertainty in density to be 0.5% and the uncertainty in seismic velocities to be 0.1%). The mineralogical data on shear velocity is sparse and so comparisons with \( V_s \) are less reliable than comparisons with density and \( V_c \) – however, it turns out that \( V_c \) is critical for eliminating some compositions.

You are asked to do a homework problem

12. Note on Handling iron partitioning

When running the M-G code we describe the system by mole fractions \( (X_{pv}, X_{ca}, X_{mw} \) though we specify only the first two since

\[ X_{mw} = 1 - X_{pv} - X_{ca} \]

We also specify the total iron number of the whole assemblage, \( X_{fe} \) and \( X_{mg} = 1 - X_{fe} \). Thus

\[ \left( \frac{X_{fe}}{X_{mg}} \right)_{total} = \frac{X_{fe}}{1 - X_{fe}} \]

The way iron is partitioned between perovskite and magnesiowustite is specified by the "partition coefficient", \( K_D \) where

\[ \left( \frac{X_{fe}}{X_{mg}} \right)_{pv} = K_D \left( \frac{X_{fe}}{X_{mg}} \right)_{mw} \]

Since no iron goes into the calcium silicate perovskite, the total mole fraction we are interested in is just \( X_{pv} + X_{mw} \) so

\[ (X_{pv} + X_{mw}) \left( \frac{X_{fe}}{X_{mg}} \right)_{total} = X_{pv} \left( \frac{X_{fe}}{X_{mg}} \right)_{pv} + X_{mw} \left( \frac{X_{fe}}{X_{mg}} \right)_{mw} \]

Thus

\[ (X_{pv} + X_{mw}) \frac{X_{fe}}{1 - X_{fe}} = (X_{pv}K_D + X_{mw}) \left( \frac{X_{fe}}{X_{mg}} \right)_{mw} \]

so
\[
\left( \frac{X_{fe}}{X_{mg}} \right)_{mw} = \frac{(X_{pv} + X_{mw})X_{fe}}{X_{pv}K_d + X_{mw}}
\]

and

\[
\left( \frac{X_{fe}}{X_{mg}} \right)_{pv} = K_d \frac{(X_{pv} + X_{mw})X_{fe}}{X_{pv}K_d + X_{mw}}
\]

and

\[
(X_{fe})_{mw} = \frac{\left( \frac{X_{fe}}{X_{mg}} \right)_{mw}}{1 + \left( \frac{X_{fe}}{X_{mg}} \right)_{mw}} \quad \text{and} \quad (X_{fe})_{pv} = \frac{\left( \frac{X_{fe}}{X_{mg}} \right)_{pv}}{1 + \left( \frac{X_{fe}}{X_{mg}} \right)_{pv}}
\]