7 Thermal Properties of Materials

7.1 The Atoms Matter

Recall that planets are degenerate; the electrons are in their ground state. But the classical ions, atoms and molecules are free to jiggle and will do so. This affects the internal energy and entropy and thus the free energy of the system in a significant way. It also modestly affects the equation of state (P as a function of density), e.g. at around 10%*.

*In giant planets, the ratio of thermal pressure to zero temperature pressure at the same density varies from infinity in the atmosphere to ~unity at tens of kilobars, to tens of percent at hundreds of kilobars, to less than 10% very deep down. But of course most of the mass is very deep down so it is still true in an average sense that the thermal pressure is only a small correction.

7.2 What would we like to Know?

In planetary modeling, there are four parameters of particular interest:

(viii) \( (\partial P/\partial T)_V \)

This tells us how much thermal pressure there is (i.e. by how much does the pressure increase with temperature).

(ix) \( \alpha \equiv (1/V)(\partial V/\partial T)_p \)

This is the coefficient of thermal expansion. It is essential for figuring out the properties of convection, thermal stresses in a solid body, etc.

(x) \( \gamma \equiv (\partial/\partial p/\partial/\partial n)_s \)

This is the Gruneisen parameter. It is dimensionless and it tells you how temperature varies along an isentrope (reversible adiabat). This is essential for determining the thermal state and deciding whether convection occurs. (Note: there are other mathematically equivalent definitions of gamma; derivable from the Maxwell relationships; see below. But beware! Gamma is also used to represent non-thermodynamic properties; e.g., how a given mode frequency in a lattice varies with density. This is sometimes OK and sometimes not OK as a guide to the thermodynamically defined gamma, which is the one of most interest to us.

(xi) \( C_V \) or \( C_P \)

These are the specific heats at constant volume or constant pressure, essential for the thermal budget of a planet. (In the formulas below, C has units of energy per unit mass, e.g., erg/g). Note that these parameters are not independent! The famous Maxwell relationships (which arise from fundamental calculus applied to the continuous thermodynamic potentials) tell us, for example, that

\[
\gamma = \alpha K_T/\rho C_v = \alpha K_s/\rho C_p
\]  

(7.1)

\[
(\partial P/\partial T)_V = \gamma p C_v
\]  

(7.2)
Also, \( C_p = C_v(1 + \alpha \gamma T) \); \( K_s = K_T(1 + \alpha \gamma T) \).

### 7.3 What determines Thermal Properties?

The motions of relevance include rotations of molecules (even in a solid), vibrations within a molecule (in a liquid or solid) and perhaps most importantly, the motions of species relative to each other.

In a solid, this gets us into the business of lattice dynamics, which is a complicated subject. But you can get the flavor of it (and a rough quantitative understanding) through the Debye model. Our goal is to construct a correction to the internal energy that arises from the lattice vibrations. (Remember, we already have a big internal energy coming from the electrons). From this thermal correction, we can derive anything else we need. We relegate most of the details to the Appendix of this chapter. Here is a summary of the essential ideas.

(i) Vibrational modes are quantized. They are called phonons. In accordance with quantum statistics, the energy of a phonon is \( \hbar \omega \) where \( \omega \) is the frequency. Since phonons are bosons, a given mode can have more than one phonon associated with it.

(ii) At long wavelengths these modes are indistinguishable from sound waves. These sound waves have the dispersion relationship \( \omega = kv \) where \( v \) is an appropriately averaged sound velocity and \( k = 2\pi/\lambda \) is the wavevector (\( \lambda \) is the wavelength). In the Debye approximation, this linear dispersion relationship is assumed to persist all the way up to the modes of highest frequency and wavevector.

(iii) The number of degrees of freedom is \( 6N \) where \( N \) is the number of atoms. (Six comes from 3 translational and 3 vibrational; the number of 3 is of course the dimensionality of the space we live in. This is no different from an ensemble of \( N \) harmonic oscillators). Since the phase space per mode is of order \( (2\pi/L)^3 \) in a cubic box of side \( L \), and since \( N \sim (L/a)^3 \), where \( a \) is the lattice constant, it follows that the maximum wavevector in the spectrum is \( \sim \pi/a \). In the Debye model, this is called the Debye wavevector \( k_D \) and the associated frequency is the Debye frequency \( \omega_D = vk_D \). The phonon energy for this mode in temperature units is called the Debye temperature \( \theta_D = \hbar \omega_D/k_B \).

(iv) To order of magnitude, we expect \( \omega_D \sim \pi v/a \sim (3)(10^6 \text{ cm/s})/(3 \times 10^{-8} \text{ cm}) \sim 10^{14} \text{s}^{-1} \), so \( \theta_D \sim (10^{27})(10^{14})/(10^{-16}) \sim 1000 \text{K} \). The behavior of the material depends on whether the actual temperature \( T \) is above or below the Debye temperature. At \( T \ll \theta_D \), the modes are incompletely excited and the specific heat \( \propto T^3 \). At \( T \gg \theta_D \), the more common situation in planets, \( C_v \) tends towards the classical (Dulong-Petit) limit \( 3Nk_B \). (This is the number of degrees of freedom times \( k_B/2 \)). In this limit, the entropy

\[
S = 3Nk_B \ln(T/\theta_D) + \text{constant}
\]

and isentropes are lines of constant \( T/\theta_D \).
(v) From the fundamental definition of $\gamma$, it follows that

$$\gamma = \frac{d\ln\theta_D}{d\ln \rho}$$  \hspace{1cm} (7.4)

Since $\theta_D \propto \sqrt[3]{\frac{a}{v}} \propto K_{1/2} \rho^{-1/6}$, where $K$ is the bulk modulus, we obtain the approximate expression

$$\gamma = 1/2 (dK/dP) - 1/6$$  \hspace{1cm} (7.5)

This is typically about unity. (This is not a very accurate model but it provides a way of understanding how you might estimate $\gamma$).

(vi) From the above estimates of $C_v$ and $\gamma$ and our previous understanding of $K_T$ we can obtain $\alpha$, thus completing our primary goals for the Debye model.

Clearly, it is of greatest interest to decide whether $\theta_D$ is large or small compared to typical temperatures inside planets. In fact, as the table below shows, actual Debye temperatures are typically less (but not much less) than actual temperatures inside terrestrial planets. The table is taken from Anderson’s book; and the Debye temperature estimates are obtained by fitting thermodynamic properties as explained further below. Of course, there is a close relationship between the stiffness of a material (the elastic moduli) and the Debye temperature. Notice also that there is a correlation between melting temperature $T_m$ and Debye temperature. We’ll discuss this later in the chapter.

Not shown in this table are Debye temperatures for ices (which are below their melting points) and the Debye temperature for hydrogen (~1000K or less, even at 1 Megabar). The Debye model does not work very well for water ice.

**Table 7.1**

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$\mu$</th>
<th>$K_T$ (GPa)</th>
<th>$\mu$</th>
<th>$\nu$</th>
<th>$\nu_m$</th>
<th>$\theta_D$ (K)</th>
<th>$T_m$ (K)</th>
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<tbody>
<tr>
<td>Iron$^1$</td>
<td>7.87</td>
<td>55.85</td>
<td>172.7</td>
<td>83.1</td>
<td>6.00</td>
<td>3.25</td>
<td>3.63</td>
<td>474</td>
</tr>
<tr>
<td>Nickel$^1$</td>
<td>8.91</td>
<td>58.69</td>
<td>185.6</td>
<td>88.2</td>
<td>5.83</td>
<td>3.15</td>
<td>3.51</td>
<td>471</td>
</tr>
<tr>
<td>Lead$^2$</td>
<td>11.34</td>
<td>207.20</td>
<td>39.9</td>
<td>9.0</td>
<td>2.14</td>
<td>0.89</td>
<td>1.00</td>
<td>96</td>
</tr>
<tr>
<td>Copper$^1$</td>
<td>8.92</td>
<td>63.55</td>
<td>144.9</td>
<td>49.4</td>
<td>4.86</td>
<td>2.35</td>
<td>2.64</td>
<td>345</td>
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<tr>
<td>Diamond$^1$</td>
<td>3.51</td>
<td>12.01</td>
<td>584.8</td>
<td>346.3</td>
<td>17.27</td>
<td>9.93</td>
<td>11.03</td>
<td>1839</td>
</tr>
<tr>
<td>Silicon$^1$</td>
<td>3.33</td>
<td>28.09</td>
<td>97.9</td>
<td>66.7</td>
<td>8.95</td>
<td>5.35</td>
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<td>129.4</td>
<td>9.68</td>
<td>6.01</td>
<td>6.63</td>
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<td>Stishovite$^2$</td>
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<td>20.03</td>
<td>277.4</td>
<td>232.2</td>
<td>11.70</td>
<td>7.36</td>
<td>8.10</td>
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<td>Corundum$^2$</td>
<td>3.99</td>
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<td>251.9</td>
<td>162.0</td>
<td>10.83</td>
<td>6.37</td>
<td>7.06</td>
<td>1030</td>
</tr>
<tr>
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<td>20.10</td>
<td>128.2</td>
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<td>8.57</td>
<td>5.00</td>
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<td>757</td>
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<td>$\beta$-phase$^3$</td>
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<td>20.10</td>
<td>174.0</td>
<td>114.0</td>
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<td>5.73</td>
<td>6.35</td>
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<td>119.0</td>
<td>9.81</td>
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<td>6.41</td>
<td>904</td>
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<td>20.16</td>
<td>176.6</td>
<td>89.6</td>
<td>9.12</td>
<td>5.02</td>
<td>5.59</td>
<td>788</td>
</tr>
<tr>
<td>Enstatite$^2$</td>
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<td>20.08</td>
<td>107.5</td>
<td>75.4</td>
<td>8.06</td>
<td>4.85</td>
<td>5.37</td>
<td>731</td>
</tr>
<tr>
<td>Ilmenite$^3$</td>
<td>3.80</td>
<td>20.08</td>
<td>212.0</td>
<td>132.0</td>
<td>10.10</td>
<td>5.89</td>
<td>6.54</td>
<td>943</td>
</tr>
<tr>
<td>Perovskite$^6$</td>
<td>4.11</td>
<td>20.08</td>
<td>264.4</td>
<td>184.2</td>
<td>10.94</td>
<td>6.69</td>
<td>7.39</td>
<td>1094</td>
</tr>
<tr>
<td>Perovskite$^6$</td>
<td>4.04</td>
<td>27.19</td>
<td>177.0</td>
<td>104.0</td>
<td>8.84</td>
<td>5.07</td>
<td>5.64</td>
<td>750</td>
</tr>
</tbody>
</table>

**Notes:** Specific mass $\rho$ in g/cm$^3$, mean atomic mass $\bar{M}$ in g/at. Melting temperature $T_m$ and Debye temperature $\theta_D$ calculated from (3.37), in Kelvin. Yolles-Resa-Hill, at room temperature and ambient pressure, bulk modulus $K_T$ and shear modulus $\mu$ in GPa.

**Sources:** $^1$Simmons and Wang (1971); $^2$Sumino and Anderson (1984); $^3$Sawamoto et al. (1984); $^4$Weidner et al. (1984); $^5$Weidner and Ito (1985); $^6$Yeganeh-Haeri, Weidner, and Ito (1988).
7.4 Liquid State Theory

Nothing as simple or successful as Debye theory exists; one cannot count up simple harmonic oscillators for obvious reasons. One can, of course, do Monte Carlo or molecular dynamics simulations. But one can define a pair distribution function $g(r)$,

![Pair Distribution Function](image)

**Figure 7.1**

which describes the probability of finding an atom at some location relative to the probability you would have if the atoms (or molecules) were distributed completely randomly in space. In other words,

$$4\pi r^2 n g(r) dr = \text{number of atoms in a shell between } r, r+dr$$  \hspace{1cm} (7.6)

given that there is an atom(or molecule) at $r=0$. Here, $n$ is the average number density.

The Fourier transform of $g(r)-1$ is called the structure factor and is measurable, either by X-ray diffraction or neutron scattering.

An approximate approach to the structure of liquids appeals to the detailed understanding we have of hard sphere liquids; these are liquids composed of “billiard balls”. The potential of interaction in a billiard ball fluid is:

$$\phi(r) = \infty, \quad r < \sigma$$

$$\phi(r) = 0, \quad r > \sigma$$  \hspace{1cm} (7.7)

where $\sigma$ is the collision diameter (twice the radius of each billiard ball). Of course real fluids have much more complicated potentials of interaction.

In the particular case of a hard sphere liquid, the appropriately scaled pair distribution function $g(r/\sigma)$

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**Note:** The diagram shows a graph of the pair distribution function $g(r)$ with peaks and troughs indicating the probability distribution of atoms at different distances $r$. The graph illustrates the concept of nearest neighbor distance and the transition between gas and liquid states.
7. Thermal Properties of Materials

Figure 7.2

is describable solely in terms of the packing fraction (a dimensionless number)

\[ \eta = \pi n \sigma^3 / 6 \]  

(7.8)

where \( n \) is the number density of particles. Obviously, \( \eta \) is the volume occupied by the particles (since each particle has volume \( 4\pi(\sigma/2)^3 / 3 \)) divided by the total volume. For spheres, it must thus be less than about 0.7. It is in reality less than about 0.5 in realistic liquids since higher packing causes freezing as explained below. It is not at all obvious but confirmed by experience that one can get a quite good approximation to liquid state thermodynamics by using the real potential of the liquid but giving to the atoms the spatial distribution of a hard sphere liquid. A variational principle (based on the Gibbs-Bogoliubov inequality) is employed: Minimize the free energy with respect to packing fraction. In other words:

\[
F_{\text{liquid}}(n, T; \eta) = F_{\text{hard sphere}}(n, T; \eta) + \frac{n}{2} \int g_{hs}(r; \eta) \varphi(r) d^3r
\]

From this, everything else can be determined.

7.5 The Melting Transition

This is a thermodynamic transition; equality of Gibbs energies is required. The entropy of the liquid is always larger than the solid, and the volume of the liquid is usually larger than the solid; whence these “thermodynamic” pictures of the transition:
Despite the self-evident truth that predictions of melting depend on understanding both phases, one often encounters notions about melting that are based on “instabilities” of one kind or another for just one phase. These cannot literally be true... you cannot understand melting by having merely a wonderful understanding of one phase only. But in a subtle way, there is some sense to these ideas of melting that are derived from a “one-sided” view.

### 7.5.1 Melting Viewed from the Solid Side: The Lindemann Criterion

This pre-quantum theory says that melting occurs once the lattice vibrations reach an amplitude that is some universal fraction of the lattice spacing. This universal fraction is about 0.1 (notice that it is quite small). According to the Debye model (or any simple harmonic oscillator model):

\[
M \langle u^2 \rangle \omega_D^2 \approx k_B T \quad (7.9)
\]

where \( u \) is the RMS displacement of an atom from its equilibrium position. If we say that \( u \) is some universal fraction of \( a \) at the melting temperature, and recall that \( \omega_D \) scales as \( v/a \), then it follows that:

\[
T_m \propto M v^2 \quad (7.10)
\]

You can confirm from the table above that this does rather well. It can be used to estimate the melting point at Earth’s center from seismic data, for example. From the definition of \( \gamma \), and the result that \( \theta_D \sim \rho^{1/3} \), we have

\[
T_m \propto \theta_D^2 \rho^{-2/3} \Rightarrow \frac{d \ln T_m}{d \ln \rho} = 2(\gamma - \frac{1}{3}) \quad (7.11)
\]

from which it follows that

\[
\frac{d \ln T_m}{d \ln \rho} > \frac{d \ln T_{ad}}{d \ln \rho} \iff \gamma > \frac{2}{3} \quad (7.12)
\]
This inequality is generally satisfied for Earth-forming materials, meaning that melting is most likely to occur at low pressures in an adiabatic system. The freezing of the inner core (shown below) arises because of this inequality.

**Figure 7.4**

Pressure release melting of silicates (the dominant form of volcanism in terrestrial planets) also arises because the melting curve is usually steeper in the adiabat. In all real cases, however, this is at best an *approximate argument* since we are dealing with multicomponent systems and the argument strictly only applies to univariant systems. Moreover, melting curves can sometimes be anomalously flat (e.g. Earth’s transition zone).
In molecular and metallic hydrogen, $\gamma$ is less than $2/3$, but it is irrelevant because the actual temperature is well above freezing (as we shall see).

### 7.5.2 Melting Viewed from the Liquid Side: The Hard Sphere Criterion

It is found from numerical simulations that a liquid will freeze when its hard sphere packing fraction (determined variationally as described above) is about 0.45. (An actual hard sphere liquid freezes at 0.49 packing fraction.) This is also consistent with Lindemann in the following sense: If the packing fraction is fixed at melting and the entropy difference is fixed at melting then you can write

$$S(\text{liquid}) = S(\text{Debye}) + \text{const}$$

$$\Rightarrow \ln(T^{3/2}/\rho) = 3\ln(T/\theta_D) + \text{const}$$

$$\Rightarrow T \propto \theta_D^2/\rho^{2/3} \propto K/\rho \sim v^2 \ [v=\text{sound speed}] \quad (7.13)$$

This is the same result for the melting curve gradient as that given above based on the solid state considerations.

### 7.6 Appendix: Lattice Dynamics and the Debye Model

Lattice vibrations are normal modes of the crystal. Consider a simple solid (a single atom on each lattice site). In the continuum limit (ordinary sound waves, seismology, ordinary sound waves, seismology, ordinary...
acoustics) we can set up waves whose wavelength is long compared to the distance between atoms. These waves exist because of the elastic restoring forces arising from the forces between atoms. If we think of a wave whose amplitude is of the form \( \exp[i(k \cdot r - \omega t)] \), then the relationship between the wavevector (magnitude \( k = 2\pi/\lambda \) where \( \lambda \) is the wavelength) and frequency (\( \omega = 2\pi/P \) where \( P \) is the wave period) is of course

\[
\omega = kv
\]

where \( v \) is the wave velocity. The relationship between \( \omega \) and \( k \) is called the dispersion relationship (although in this particular case, it is linear, meaning there is no dispersion at long wavelengths.) But in reality, there are three polarizations (two transverse, one longitudinal) and the relationship depends on the direction of the wavevector relative to the crystallographic axes. Even cubic crystals are acoustically anisotropic. But most importantly, the continuum limit must breakdown when \( k \) approaches \( 2\pi/\lambda \), where \( \lambda \) is the lattice spacing. In fact, the waves are dispersive when this limit is approached (i.e., the relationship between \( \omega \) and \( k \) is not linear).

These waves are quantized. Here, the word quantum is used in its original sense to mean discreteness (countable modes) and not to mean the particular use of quantum in the context of Schroedinger’s equation. The waves also satisfy Bose-Einstein statistics, the same statistics satisfied by photons, but different from electrons, because the “particles” are indistinguishable but more than one can occupy a given energy level. The quanta are called phonons.

Let’s look at this quantization. Imagine, for simplicity, a string of atoms spaced a distance \( a \) apart, and of total length \( L \).

![Figure 7.6](image)

As in the electron case, it is convenient to impose periodic boundary conditions on the system for any normal mode, which means that \( \exp[ikL] = 1 \). So it follows that

\[
k = 2\pi/L, \, 4\pi/L, \, 6\pi/L, \, 8\pi/L \ldots
\]

But the displacements can only be evaluated at atomic positions. Consider the wavevector \( k^* = 2\pi/a + k \). If we only evaluate \( \exp[ikx] \) at \( x = 0, a, 2a, 3a, \ldots, L \) then \( k^* \) will yield the same set of displacements as wavevector \( k \). So there is a maximum acceptable wavevector \( 2\pi/a \) and the number of acceptable wavevectors is \( L/a \), which is equal to the number of atoms.

This is trivially generalizable to three dimensions. For a cube of sides \( L \), (and a simple cubic lattice of lattice spacing \( a \)) the acceptable wavevectors are
\[ k = (2\pi \ell/L, 2\pi m/L, 2\pi n/L) \quad ; \quad \ell, m, n = 1, 2, 3, \ldots, L/a \] (7.15)

So the number of acceptable wavevectors exactly equals the number of atoms (in this simple case).

### 7.6.1 The Debye Model

This model replaces the above general case with an exactly dispersionless law \( \omega = kv \), and imposes a spherically symmetric limiting wavevector, called the Debye wavevector \( k_D \).

![Debye Model Diagram](image)

**Figure 7.7**

Since the volume per allowable wavevector (in \( k \) space) is \((2\pi/L)^3\), it follows that

\[
N = \frac{4}{3} \pi k_D^3 \left( \frac{2\pi}{L} \right)^3
\] (7.16)

(where \( N \) is the number of atoms in the cube) or equivalently, \( k_D^3 = 6\pi^2 n \), where \( n \) is the atomic number density. Obviously, \( k_D \sim 1/a \).

This leads to a cutoff frequency \( \omega_D = k_D v \) where \( v \) is a mean sound-speed; and thus to a highest energy phonon, with energy \( h\omega_D \). If we set this to \( k_B \theta_D \), we get what is called the Debye temperature. It is the characteristic scale of the energy of the lattice excitations.

The Internal (Vibrational) Energy of a Debye Crystal is given by

\[
E = \int_0^{\omega_D} \langle n(\omega,T) \rangle h\omega g(\omega) d\omega
\] (7.17)
where \( \langle n(\omega, T) \rangle = \frac{1}{\exp(\hbar \omega / kT) - 1} \), the Bose-einstein occupanct factor, and \( g(\omega) \) is the density of states (number of modes per unit frequency interval). From this, one can calculate everything else. (You can find details in Poirier’s book).

Here’s how to think about it: The internal energy of an ensemble of \( N \) oscillators (atoms on lattice sites) can be written as

\[
E = (\text{# polarizations}).(\text{#phonons per mode}).(\text{phonon energy}).(\text{fraction of modes excited})
\] (7.18)

The number of polarizations is three. The number of phonons per mode is given by the Bose-Einstein occupancy factor \( \exp(\hbar \omega / kT) - 1 \) and is thus roughly \( kT/\hbar \omega \) for \( kT > \hbar \omega \) and small otherwise. The phonon energy is \( \hbar \omega \). The fraction of modes excited is the volume of the sphere in \( k \)-space for which \( \hbar \omega < kT \), and thus must be \( (T/\theta_D)^3 \) for \( T < \theta_D \) and 1 for \( T \geq \theta_D \). So the internal energy associated with these oscillations (remember this is only part of the internal energy) is

\[
E = 3NkT.f(\theta_D/T)
\] (7.19)

where \( f(x) \rightarrow 1 \) for \( x \) small, and \( f(x) \sim x^3 \) for \( x \) large. To be precise,

\[
f(x) = \frac{3}{x^3} \int_0^x \frac{y^3 dy}{(e^y - 1)} \] (7.20)

This function is not expressible in terms of elementary functions but it is easily evaluated and tabulated. So as expected, \( E \propto T \) at high \( T \) and \( E \propto T^4 \) at low \( T \). (The latter is just like a photon gas, with the distinction that there is no maximum photon energy.) The Debye temperature \( \theta_D \) is derived from \( k_B \theta_D = \hbar \omega_{\text{max}} \), where (from the dispersion relationship) \( \omega_{\text{max}} = k_{\text{max}}v \) with \( k_{\text{max}} \), the maximum wavevector being of order \( 2\pi/a \). But \( a \) is \( \sim \) cube root of the volume per atom, so that \( k_{\text{max}} \sim (\rho/M)^{1/3} \) where \( M \) is the ion mass and \( \rho \) is the mass density. So

\[
\theta_D \propto v(\rho/M)^{1/3}
\] (7.21)

where \( v \) is the mean sound speed.

The specific heat at constant volume is given by

\[
C_v = \left( \frac{\partial E}{\partial T} \right)_V = 3Nk[f(y) - yf'(y)]_{y = \theta_D/T}
\] (7.22)

which has the limit \( 3Nk \) at high temperature (equivalently \( 3R \) per mole of atoms). This is known as the Dulong-Petit limit; it associates \( 3kT \) of energy with each atom: half is kinetic energy and half is potential energy.... i.e. equivalent to a set of independent harmonic oscillators.
Figure 7.8

At low temperatures, it is obvious that the specific heat is cubic in temperature. Note that it depends only on the ratio of actual to Debye temperature.

The entropy $S$ is given by:

$$S = \int_0^T \frac{C_v}{T} \, dT$$

(7.23)

and thus depends only on the ratio of actual to Debye temperature. At high $T$,

$$S_{\text{Debye}} = \text{constant} + 3Nk\ell_n(T/\theta_D)$$

(7.24)

Most importantly, the dependence of $S$ only on the ratio of actual to Debye temperature means that isentropes (reversible adiabats) are defined by lines of constant $T/\theta_D$. From the definition of the Gruneisen gamma, we thus have:

$$\gamma = \frac{d \ln T}{d \ln \rho} = \frac{d \ln \theta_D}{d \ln \rho}$$

(7.25)

from which one can derive an estimate for gamma from knowing the seismic (i.e. sound speed) of materials in a planet, using seismology. Remember that this is only an approximation! From the above scaling law for Debye temperature, and remembering that sound speed scales as $(K/\rho)^{1/2}$, one finds one simple approximation for gamma in the form

$$\gamma = \frac{d \ln \rho^{1/3}(K/\rho)^{1/2}}{d \ln \rho} = -\frac{1}{6} + \frac{1}{2} \frac{dK}{dP}$$

(7.26)

because $d\ln K/d\ln \rho = dK/dP$. Typically, as discussed previously, $dK/dP$ is around 4 in many materials, whence gamma is somewhat smaller than 2. It turns out (in more precise models) that gamma decreases with pressure. This model is only approximately correct for solids and even then is sometimes inaccurate.
Recall that $F = E - TS$. From the relationship $S = \left(\frac{\partial F}{\partial T}\right)_V$, we get that

$$E = \frac{\partial(F/T)}{\partial(1/T)} \Rightarrow F = -3NkT \int_{\theta_D}^{\infty} f(u\theta_D) du / u$$

(7.27)

from which we get the thermal pressure:

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

(7.28)

where the $E$ used is of course coming from the Debye model. This is called the Mie-Gruneisen equation of state. Remember (as always) that to get total pressure you must add the (dominant) term which comes from the electrons. Last but not least, the coefficient of thermal expansion is best obtained from the Maxwell relations (a thermodynamic identity):

$$\alpha K_T = \gamma pC_V$$

(7.29)

where, of course, $K_T$ does not come (primarily) from the Debye model but is dominated by the electron gas. The RHS (and therefore also the LHS) of this equation varies only slowly with pressure. It can easily be confirmed that alpha is very small and that it becomes even smaller at high pressure because $K$ increases substantially with $P$ (look at any seismic model for Earth).

So this completes what we wanted to get out of the Debye model.

**Ch. 7 Problems**

7.1) Ice III is soft (lower elastic moduli and therefore lower Debye temperature than Ice I). However, it is more dense than Ice I. Explain why the Ice I-Ice III transition is endothermic, i.e., has negative $dT/dP$. (The ice phase diagram in the text in Chapter 6 is not sufficiently well drawn that you can see the negative slope in that diagram.) This turns out to have important consequences for the thermal history of large icy satellites. It has a similar effect to the 660km discontinuity in earth’s mantle.

*Solution:* Since the entropy per particle $S = 3k_B\ln(T/\theta_D) + \text{constant}$, lower Debye temperature means higher entropy. By the Clausius–Clapeyron equation, $dT/dP$ will be negative if the higher entropy phase has lower specific volume. This is indeed the case for ice III.

7.2) Estimate the coefficient of thermal expansion $\alpha$ for dense, liquid metallic hydrogen (i.e., density $\rho$ well in excess of 1g/cm$^3$) from Maxwell’s relationships using the following approximations: $C_V = 2k_B/\text{proton}$, $P = 10^{5.53}$ Mbar (the Fermi gas limit), and $\gamma = 1/2(dK/dP)-1/6$ where $K = \rho dP/d\rho$. Your answer should be in the form of the function $\alpha(\rho)$. What must $T(\rho)$ be in order that $\alpha T = 0.1$? Does $\alpha T$ change along an isentrope as $\rho$ changes? What must $T(\rho)$ be in order that the thermal pressure is 0.1 of the electron (Fermi) pressure? These results are most relevant for planets several times more massive than Jupiter up to brown dwarfs.
7.3) Why must the Gruneisen parameter $\gamma$ and the coefficient of thermal expansion $\alpha$ have the same sign? *Hint:* Think about the signs of bulk modulus and specific heat, based on the fundamental principles of thermodynamics and stability.

(Commentary: In case you’re wondering, both $\alpha$ and $\gamma$ are negative in liquid water between 0 and 4 degrees Celsius, so this is not an abstract question. A negative $\alpha$ can be profoundly important because it shuts off thermal convection in planets. It affects the ability of Europa’s ocean to convect. Negative $\alpha$ and $\gamma$ have also been suggested for the deep interior of Jupiter where molecular hydrogen dissociates and metallizes.)

*Solution:* Thermodynamic stability demands that both the bulk modulus and the specific heat are positive. If the bulk modulus were negative then infinitesimal disturbances would exponentiate (i.e., the frequency of sound waves would be imaginary). If the specific heat (as conventionally defined) were negative then you could violate the second law of thermodynamics. From Maxwell’s relationships, $\gamma = \alpha K_T / \rho C_v = \alpha K_s / \rho C_P$ so $\gamma$ and $\alpha$ must therefore have the same sign since everything else is positive.

7.4) (a) By how much has Earth’s core cooled since the onset of formation of the inner core? (b) Assuming that the Earth cools at constant rate (i.e., $dT/dt =$ constant where $T$ is temperature at some fixed pressure in the core), show that $R_{ic} \propto t^{1/2}$ where $R_{ic}$ is the radius of the inner core, and $t$ is the time elapsed since inner core nucleation.

Proceed as follows: The inner core has a current radius of 1220 km. Assume the outer core is always adiabatic. Assume that the solid inner core-liquid outer core boundary is a simple freezing transition (ignore compositional effects). Assume Lindemann’s law and assume $\gamma = 4/3$. The bulk modulus is 14 Megabars = $1.4 \times 10^{12}$ Pa. The actual $T$ is around 5000K and the amount of cooling is small compared to this. The pressure difference between Earth center and inner core surface can be well approximated by hydrostatic equilibrium at constant density using a mean density of $13 \text{ g/cm}^3 = 13000 \text{ kg/m}^3$. (This formula will be accurate for evaluating pressure difference; you can’t calculate actual pressures inside Earth with this formula except extremely crudely. But you don’t need to know actual pressures. Ignore the consequences of the density change due to freezing). The amount by which the Earth’s core has cooled can therefore be adequately approximated by the temperature decrease at the fixed pressure corresponding to the current pressure at the inner core surface.

*Commentary:* If you know $dT/dt$ then this question can be extended to ask: How much time has elapsed since the inner core nucleated? The “real” answer to this question is hotly debated and depends on what you believe about earth cooling. A common estimate is $dT/dt \sim 100 \text{K to 200/Ga}$ deep in the core. This will be discussed later in the text.