

Theory of Melting: Thermodynamic Basis of Lindemann's Law

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Abstract

A melting equation closely resembling the differential form of Lindemann's melting law, which relates the melting point to the pressure in terms of the thermal Grüneisen parameter and incompressibility, is derived from the Clausius-Clapeyron relation with the assumption that the Mie-Grüneisen equation can be adapted directly to describe the pressure change associated with melting at constant volume. This assumption implies that melting is only a minor perturbation of the crystal structure, such that the atomic coordination is almost unaffected and that atomic bonds are merely stretched or compressed. It appears that 'normal' melting complies with this assumption reasonably closely but that departures from Lindemann's law occur when materials undergo major changes in coordination during melting. A particular merit of Lindemann's law is that it allows the extrapolation of melting points to the pressures of the Earth's deep interior. Extrapolation of data on the iron-sulphur eutectic suggests a temperature of 4160 K at the boundary of the Earth's inner (solid) and outer (liquid) cores. Adiabatic extrapolation to the core-mantle boundary gives 2940 K at the base of the mantle.

1. Introduction

The basic, thermodynamically rigorous equation for the dependence of the melting point T_M on the pressure P is the Clausius-Clapeyron relationship, the derivation of which appears in standard thermodynamic texts (e.g. Morse 1969):

$$T_M^{-1} dT_M/dP = \Delta V/L, \quad (1)$$

where ΔV and L are the volume increment and latent heat of melting (for convenience both referred to unit mass). This equation is essentially a statement that the Gibbs free energies of the solid and liquid states are equal at the melting point at any pressure. However, it contributes little to our understanding of the physics of the melting process and is not suitable for extrapolation beyond the range of laboratory data. This is because we do not have independent constraints on the pressure dependences of ΔV and L , although the assumption that the entropy of melting $\Delta S = L/T_M$ is independent of pressure for any particular solid phase appears to be a reasonably good one (Gschneider 1964; Stishov 1969). Extrapolation of melting curves of iron and its alloys and of silicates is basic to theoretical studies of the Earth's deep interior and several essentially empirical extrapolations (reviewed by Hamano 1974) have been used, but there is an urgent need for a better physical understanding of melting at high pressure.

The equation to which we now give strong support was first derived by Lindemann (1910) from the hypothesis that melting occurred when the amplitudes of thermal vibrations of atoms became large enough to cause atomic 'collisions'. This criterion

was reformulated by Gilvarry (1956) in terms of the r.m.s. amplitude of atomic vibration $\langle u^2 \rangle^{\frac{1}{2}}$ relative to the equilibrium atomic spacing r_e :

$$\langle u^2 \rangle^{\frac{1}{2}}/r_e = \delta, \quad (2)$$

δ being a constant fraction at the melting point. The Lindemann approach was inspired by the knowledge, dating from the last century, that for many materials the expansion coefficients α and melting points T_M are approximately related by

$$\alpha T_M \approx \varepsilon (\text{const.}). \quad (3)$$

For most metals $\varepsilon \approx 0.07$ if α is the volume coefficient (Gschneider 1964), which simply means that (allowing for diminution of the expansion coefficient at low temperatures) a metal melts when the density of the solid has decreased by about 6% relative to its value at absolute zero. For tetrahedrally bonded covalent materials, such as elemental silicon, which have strong intrinsic bond-angle rigidity and hence 'anomalously' low thermal Grüneisen parameters (Irvine and Stacey 1975), ε is correspondingly lower. This indicates that the amplitude of thermal vibration is not itself relevant, but that the anharmonic force law between neighbouring atoms (which relates thermal expansion to vibration amplitude) controls the melting process more directly. The relevance of the Grüneisen parameter γ is apparent in the differential form of Lindemann's melting equation, which is the useful form for our purpose:

$$T_M^{-1} dT_M/dP = 2(\gamma - \frac{1}{3})/K, \quad (4)$$

where K is the incompressibility (along the melting curve) and γ is defined by

$$\gamma = \alpha K/\rho C, \quad (5)$$

ρ being the density and C the specific heat at constant volume or constant pressure if K is the isothermal or adiabatic modulus respectively. Extensions and refinements of Lindemann's law have been reported many times (e.g. Gilvarry 1956; Ross 1969; Shapiro 1970; Boschi 1974*a*, 1974*b*) but generally without any indication of the basic reason why it happens to be so good for many materials but so poor for others.

In the following sections we derive the form of Lindemann's equation (4) from a simple adaptation of the Mie-Grüneisen equation, which has a sounder physical basis than the vibration amplitude assumption. It allows us to see the physical distinction between materials which follow the Lindemann equation and those which do not.

2. First-order Thermodynamic Approach to Melting

The definition of Grüneisen's ratio (equation 5) allows us to write a thermodynamic identity in terms of it:

$$(\partial P/\partial T)_V = \alpha K = \gamma \rho C_V, \quad (6)$$

which refers to any material in constant phase, for which γ and C_V are unambiguous quantities. The Mie-Grüneisen equation is an integrated form of the result (6), namely

$$\Delta P = \int \gamma \rho C_V dT \approx \gamma \rho (\Delta E/m), \quad (7)$$

where ΔE is the thermal energy applied to a mass m of material maintained at constant density ρ , causing an increase in pressure ΔP , and the approximate equality appeals to the assumption that, at constant volume, γ is independent of T over the range considered. This is an excellent approximation at temperatures which are not low with respect to the Debye temperature. The quantity ΔE is the normal thermal energy increment of the solid, i.e. the energy of atomic vibration, and, as the validity of the classical (Dulong–Petit) specific heat ($3R \text{ mol}^{-1}$) for normal materials at high temperatures demonstrates, ΔE is closely equipartitioned between the atomic kinetic energy and the potential energy ΔE_p associated with vibrations of atoms in their mutual force fields. Thus $\Delta E = 2\Delta E_p$ and we can rewrite equation (7) as

$$\Delta P = 2\gamma\rho(\Delta E_p/m) \quad (8)$$

Now let us consider melting as a process in which thermal energy mL (for mass m) is applied, causing atomic rearrangement such that all of the added energy appears as atomic potential energy and no temperature rise occurs. Then if we were to melt the material at constant volume we would observe an increase in pressure given by equation (8):

$$\Delta P = 2\gamma\rho L. \quad (9)$$

(Of course if the pressure is not held constant then neither is the melting point, but this is a refinement which we consider in the following section.) However, ΔP is related to the incompressibility (bulk modulus) K and to the volume increase ΔV on melting at constant pressure by

$$\Delta P = K(\Delta V/V) = K\rho\Delta V, \quad (10)$$

if ΔV refers to unit mass. Combining equations (9) and (10) and using (1), we obtain

$$T_M^{-1} dT_M/dP = \Delta V/L = 2\gamma/K. \quad (11)$$

This result closely resembles Lindemann's law (4) and demonstrates the role of γ from a thermodynamic viewpoint, with the assumption (considered in Section 4) that it is a physically meaningful parameter for material in the process of melting.

3. An Improved Thermodynamic Approach

The calculation in the previous section is made more rigorous by considering a thermodynamic cycle involving both melting (or solidification) at constant pressure and at constant volume, as illustrated in Fig. 1. Limb AB represents normal melting at pressure P , with a volume increase from V to $V+\Delta V$ and a heat input L ; limb BC represents resolidification at constant volume $V+\Delta V$, as a result of which the pressure decreases from P to $P-\Delta P$ and heat Q is released; CD is a cooling at constant pressure $P-\Delta P$ to the original solid volume V ; DA completes the cycle by heating at constant volume V . Limbs CD and DA relate the melting process to the properties of the solid phase. An alternative cycle (dashed) can be used to express melting parameters in terms of the liquid properties (and avoid possible reference to negative pressures).

With temperatures T_M on AB, $T_M - \Delta T_M$ at C and T_1 at D, the heat inputs and outputs are as shown in Fig. 1 and the net heat input balances the net mechanical work done by the material in the cycle. Thus

$$L - Q - \int_{T_1}^{T_M - \Delta T_M} C_P dT + C_V(T_M - T_1) = \Delta P \Delta V, \quad (12)$$

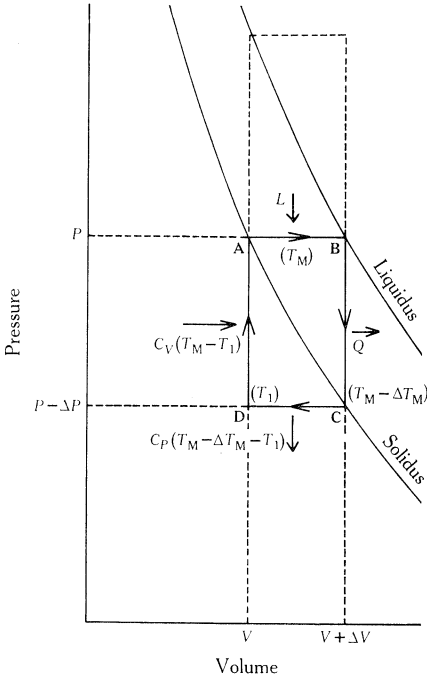


Fig. 1. Thermodynamic cycle involving melting at constant pressure and resolidification at constant volume. In detail the cycle ABCD represents:
 AB, melting at constant pressure P ;
 BC, resolidification at constant volume $V + \Delta V$;
 CD, cooling at constant pressure $P - \Delta P$;
 DA, heating at constant volume V .

which gives the heat required to melt the material at constant volume $V + \Delta V$, namely

$$Q = L + C_V \Delta T_M - \int_{T_1}^{T_M - \Delta T_M} (C_P - C_V) dT - \Delta P \Delta V, \quad (13)$$

where C_V is treated as a constant but C_P is a function of P and T such that

$$C_P - C_V = C_V \gamma \alpha T \ll C_V, \quad (14)$$

α being the volume expansion coefficient. In terms of the Mie-Grüneisen equation (7) and its modification (8), Q is related to the pressure increment on melting at volume $V + \Delta V$. We note that Q includes a contribution $C_V \Delta T_M$ associated with the temperature change ΔT_M and that the balance $(Q - C_V \Delta T_M)$ is the atomic potential energy of the melting process at constant volume, so that

$$\Delta P = \frac{2\gamma'(Q - C_V \Delta T_M)}{V + \Delta V} + \frac{\gamma' C_V \Delta T_M}{V + \Delta V} = \frac{\gamma'}{V + \Delta V} (2Q - C_V \Delta T_M), \quad (15)$$

where γ' is the Grüneisen ratio appropriate to describe the melting process.

From limb DA of the cycle in Fig. 1 we also have

$$\Delta P = (\gamma/V)C_V(T_M - T_1) \quad (16)$$

and from limb CD

$$\Delta V = V\bar{\alpha}(T_M - T_1 - \Delta T_M) = (\bar{\gamma}C_V/K_1)(T_M - T_1 - \Delta T_M), \quad (17)$$

where $\bar{\alpha}$ and $\bar{\gamma}$ indicate mean values over the range CD and K_1 is the incompressibility of the solid phase at pressure $P - \Delta P$, which is related to the value K at pressure P by the Murnaghan (1951) relationship

$$K_1 = K - K' \Delta P, \quad (18)$$

K' being the pressure derivative of K . We are entitled to assume equation (18) over a limit pressure range ΔP .

Noting that the integral in equation (13) represents a small correction term since $C_P - C_V$ is small, we can solve it by using average values of α and γ as in equation (17):

$$\begin{aligned} \int_{T_1}^{T_M - \Delta T_M} (C_P - C_V) dT &= C_V \bar{\gamma} \bar{\alpha} \int_{T_1}^{T_M - \Delta T_M} T dT \\ &= \frac{1}{2} C_V \bar{\gamma} \bar{\alpha} (T_M - \Delta T_M - T_1) \times (T_M - \Delta T_M + T_1) \\ &= \frac{1}{2} C_V \bar{\gamma} (\Delta V/V) (T_M - \Delta T_M + T_1), \end{aligned} \quad (19)$$

the final simplification being a substitution for $\bar{\alpha}$ from equation (17).

Equations (16) and (17) allow us to write $T_M - T_1$ and ΔT_M in terms of ΔV and ΔP as

$$T_M - T_1 = \frac{V \Delta P}{\gamma C_V}, \quad \Delta T_M = \frac{V \Delta P}{\gamma C_V} - \frac{K_1 \Delta V}{\bar{\gamma} C_V}, \quad (20)$$

which are used to eliminate $T_M - T_1$ and ΔT_M from equations (13) and (15). Substituting also for the integral in equation (13) by (19), from equations (15) and (13) respectively we then obtain two expressions for Q :

$$Q = \frac{1}{2} V \Delta P \left(\frac{1}{\gamma} + \frac{1}{\gamma'} \right) + \frac{\Delta V \Delta P}{2\gamma'} - \frac{K_1 \Delta V}{2\bar{\gamma}}, \quad (21)$$

$$Q = L - \bar{\gamma} C_V T_M \frac{\Delta V}{V} + \left(\frac{\bar{\gamma}}{\gamma} - 1 \right) \Delta V \Delta P + \frac{V \Delta P}{\gamma} - \frac{K_1 \Delta V}{\bar{\gamma}} - \frac{K_1 (\Delta V)^2}{2V}. \quad (22)$$

Now equations (21) and (22) may be equated to obtain the following expression for $L/\Delta V$ which is needed in the Clausius–Clapeyron equation (1),

$$\frac{L}{\Delta V} = \frac{K_1}{2\bar{\gamma}} + \frac{1}{2} K_1 \left(\frac{\Delta V}{V} \right) + \frac{1}{2} V \left(\frac{1}{\gamma'} - \frac{1}{\gamma} \right) \frac{\Delta P}{\Delta V} + \Delta P \left(1 - \frac{\bar{\gamma}}{\gamma} + \frac{1}{2\gamma'} \right) + \frac{\bar{\gamma} C_V T_M}{V}. \quad (23)$$

This is an equation with the form (11), plus a series of correction terms which depend on the volume dependence of γ and on γ' , the effective melting Grüneisen ratio.

The largest correction term is the last one. The pressure increment ΔP is related to ΔV by the incompressibility along the melting curve, K_M , which differs from K only by a small factor, similar to but slightly larger than the factor distinguishing adiabatic and isothermal moduli:

$$\Delta P = - \int_V^{V+\Delta V} (K_M/V) dV, \quad (24)$$

where

$$K_M = K_T \left(1 - \alpha K_T \frac{dT_M}{dP} \right)^{-1} \approx K_T \left(1 - 2(\gamma - \frac{1}{3}) \alpha T_M \right)^{-1}, \quad (25)$$

K_T being the isothermal modulus, which is assumed to be pressure-dependent as in equation (18).

We now have all of the equations necessary for a numerical integration of the melting point curve as a function of pressure for a material for which we have a knowledge of γ and the solid density-pressure equation of state. In materials whose atomic forces are approximately central, the equation of state also gives the value of γ at any density by the Vashchenko-Zubarev relationship (Irvine and Stacey 1975). However, some of the correction terms in equation (23) are clearly smaller than the uncertainties in the equation of state for any material, and it is more instructive to make approximations which introduce only small percentage errors by neglecting terms of second order in small quantities. First we neglect the second term in the denominator of equation (25) and then we can relate ΔP and ΔV via the integrated form of Murnaghan's equation (18):

$$\Delta P = \frac{K}{K'} \left\{ 1 - \left(1 + \frac{\Delta V}{V} \right)^{-K'} \right\} = K \left\{ \frac{\Delta V}{V} - \frac{1}{2}(K' + 1) \left(\frac{\Delta V}{V} \right)^2 + \dots \right\}, \quad (26)$$

and, since ΔP itself only enters as a correction term, we can simply put

$$\Delta P \approx K \Delta V / V. \quad (27)$$

Now we may consider alternative extreme assumptions about the behaviour of γ , bracketing the properties of real materials. First we suppose γ to be independent of V and that $\gamma' = \gamma$. Then equation (23) reduces to

$$\frac{L}{\Delta V} = \frac{K}{2\gamma} \left(1 + \frac{(\gamma+1)\Delta V}{V} \right) + \frac{\gamma C_V T_M}{V}. \quad (28)$$

In connection with the Earth's core we are especially interested in values for iron. At atmospheric pressure these give $(\gamma+1)\Delta V/V = 0.1$ while at core pressures, by our estimate, the corresponding value is 0.06. We therefore introduce an error of less than 10% by ignoring this term. To put equation (28) into a form more directly comparable with the Lindemann law (4) we then substitute for γ in the second term of equation (28) by the (5), so that

$$T_M^{-1} \frac{dT_M}{dP} = \frac{\Delta V}{L} = \frac{2\gamma}{K(1+2\gamma\alpha T_M)} \approx \frac{2(\gamma-2\gamma^2\alpha T_M)}{K}. \quad (29)$$

The term $2\gamma^2\alpha T_M$ has a very limited range for 'normal' metals and may be regarded

as a constant for the purpose of an approximate melting law; for iron at atmospheric pressure, $2\gamma^2\alpha T_M = 0.4$. Allowing also for the 10% correction for the $\Delta V/V$ term in equation (28) we obtain

$$T_M^{-1} dT_M/dP = 2(\gamma - 0.23)/K. \quad (30)$$

Substitution of numerical values at core pressures gives the same result exactly. Clearly these equations are very close indeed to the differential form of the Lindemann relationship (4).

Alternatively, let us suppose that γ is proportional to volume but that γ' has the value of γ at volume $V + \Delta V$, so that

$$\bar{\gamma} = \gamma(1 + \frac{1}{2}\Delta V/V) \quad \text{and} \quad \gamma' = \gamma(1 + \Delta V/V).$$

Then to first order in $\Delta V/V$ equation (23) becomes

$$\frac{L}{\Delta V} = \frac{K}{2\gamma} \left(1 - \frac{\Delta V(K' - \frac{1}{2} - \gamma)}{V} \right) + \frac{\gamma C_V T_M}{V} \left(1 + \frac{\Delta V}{2V} \right). \quad (31)$$

This does not differ significantly from the $\gamma = \text{const.}$ result (28). Thus we have a thermodynamic justification for the Lindemann-based melting law, subject to the validity of the assumption implicit in equations (8), (9) or (15).

4. Discussion of Assumptions, Difficulties and Exceptions

Section 3 is an elaboration of Section 2 which avoids certain simplifying approximations and so gives a more rigorous justification of Lindemann's law, but does not add anything to the physical understanding of melting. The essential novelty in the present approach is conveyed in Section 2 in the steps between equations (7) and (9). Equation (7) is a standard relationship which falls short of a thermodynamic identity only to the extent that γ may not be perfectly independent of temperature at constant volume, as both theory and observation agree that it is at temperatures which are not low with respect to the Debye temperature. The representation of $(\partial P/\partial T)_V$ in terms of γ emphasizes the fact that normal thermal expansion is an anharmonic effect, resulting from asymmetry of the potential wells in which solid atoms are held. Since it is easier to pull neighbouring atoms apart than to push them together, thermal vibration causes an average increase in atomic spacing at constant pressure, or an increase in pressure on heating at constant volume. At any instant some atoms are closer than their equilibrium spacing and others further apart, but at constant pressure the forces are balanced and γ (or α) expresses the net dilation resulting from the balance of forces between compressed and extended bonds.

If melting may be regarded as a process in which atomic rearrangement causes some bonds to be extended and others compressed, but neither breaking of bonds nor formation of new ones, then precisely the same asymmetry operates as in normal thermal expansion; the volume and energy changes result from a balance between compressed and extended bonds and γ relates the pressure and thermal energy increments, as in heating at constant phase. In this circumstance equation (9) is justified. Thus the validity of Lindemann's law is restricted to those materials that undergo no dramatic changes in coordination on melting. Obvious exceptions include water and bismuth, which have negative volume changes on melting and

negative dT_M/dP , but clearly have more dramatic structural rearrangements, including coordination changes, which therefore invalidate the assumption made here.

We may also anticipate difficulty with materials, such as both elemental silicon and silica, in which intrinsic rigidity of bond angles restricts thermal vibrations, giving anomalously low γ (Irvine and Stacey 1975), and also low Poisson's ratio. The development of a physically sound melting law for such materials may be possible in terms of the dislocation theory of melting. If so, it may then be related to a generalization of the Vashchenko-Zubarev (1963) relationship, giving Grüneisen's ratio in terms of elastic constants for materials which cannot be described by a central atomic force law.

'Anomalous' melting curves, that is, those which do not follow a steady trend of increasing T_M with compression, were explained by Stishov (1969) in terms of phase changes in the liquid and solid states. In particular, maxima in T_M versus P curves occur when the liquid phase undergoes transformation to a denser atomic arrangement at a lower pressure than the solid phase. When the pressure is high enough to ensure that both phases are approximately close-packed, melting must become 'normal', by which we mean that it obeys equation (4). Thus we believe that exceptions to Lindemann's law become progressively fewer with increasing pressure and that it may be applied reliably to simple materials (such as iron) in the Earth's deep interior.

5. Application to Earth's Core

The conventional assumption that both the inner (solid) and outer (fluid) regions of the Earth's core are composed largely of iron, and may plausibly have identical composition, has led numerous authors to identify the temperature at the boundary as the melting point of iron or of an iron alloy at the appropriate pressure (3.2 Mbar , i.e. $3.2 \times 10^{11} \text{ Pa}$). If a reliable extrapolation of melting point can be made, this 'fixed' point provides the best calibration available for the temperature profile of the whole of the Earth's interior. In this connection the melting law advocated by Kennedy and co-workers (Kraut and Kennedy 1966; Higgins and Kennedy 1971) has stirred a vigorous debate about melting laws (Ross and Alder 1966; Gilvarry 1966; McLachlan and Ehlers 1971; Leppaluoto 1972; Boschi 1974*a*, 1974*b*; Hamano 1974). In principle the Lindemann relationship (4) can accommodate any pressure dependence of T_M if suitable variations of γ and K are permitted, but a particular feature of the Kennedy approach which aroused so much interest was the assertion that the melting point gradient in the core was less steep than the adiabatic gradient (the 'core paradox' of Higgins and Kennedy 1971; see also Kennedy and Higgins 1973). Since we have the thermodynamic identity

$$T^{-1}(\partial T/\partial P)_S = \gamma/K_S, \quad (32)$$

K_S being the adiabatic bulk modulus, in terms of Lindemann's law the Higgins-Kennedy paradox means simply that $\gamma < \frac{2}{3}$, compared with the value for laboratory iron of $\gamma = 1.6$. Such a strong decrease in γ with pressure is completely inconsistent with the Vashchenko-Zubarev (1963) formulation for γ , which we strongly support (Irvine and Stacey 1975), so that we agree with those authors who have rejected the core paradox.

The main problem in estimating core temperatures is now in guessing the composition. Certainly the core is less dense than pure iron and a substantial admixture of lighter components is required to explain it (see e.g. Stacey 1977). The favoured

alternative is a eutectic of iron and sulphur, for which relevant data are given by Usselman (1975), who found that at pressures up to about 55 kbar the eutectic temperature is almost constant at about 1265 K, as the eutectic composition tends toward Fe_2S , but that at this point there is a clear break. Above 55 kbar the eutectic composition remains virtually constant and the temperature follows a Lindemann relationship. We therefore estimate the melting point T_M of core material at megabar pressures P by extrapolating from Usselman's 55 kbar (P_1) datum (T_{M_1}) by Lindemann's equation:

$$\ln(T_M/T_{M_1}) = \int_{P_1}^P \frac{2(\gamma - \frac{1}{3})}{K} dP. \quad (33)$$

We do not have a continuous profile for γ over the relevant pressure range, but the variation is small; $\gamma = 1.6$ at laboratory pressures and the average over the core range is $\gamma \approx 1.4$ (Irvine and Stacey 1975), so that as a sufficient approximation for the present purpose we can put $\gamma = 1.5 = \text{const.}$, that is, $2(\gamma - \frac{1}{3}) = 2.33$, in equation (33) and then make use of the fact that

$$\int_{P_1}^P K^{-1} dP = \ln(\rho/\rho_1).$$

Thus

$$T_M/T_{M_1} = (\rho/\rho_1)^{2.33},$$

from which we obtain at 3.29 Mbar (the pressure at the boundary of the solid inner core) a value for T_M of 4160 K, to which an uncertainty of several hundred degrees must be understood. This is an improvement upon the estimate given by Stacey (1977). Assuming an adiabatic regime throughout the outer core, by integrating equation (32) over the outer core we obtain the temperature at the core-mantle boundary ($P = 1.35$ Mbar) as $T = 2940$ K.

6. Conclusions

Lindemann's melting law, equation (4), has a sound theoretical basis in thermodynamics with the proviso that it is not appropriate for any material which undergoes a major change in coordination on melting. At laboratory pressures it is most satisfactory for close-packed materials in which the volume change on melting is small, indicating a good approximation to close packing in the liquid state as well as in the solid. We expect all materials to adopt close-packed structures at pressures exceeding about 0.25 Mbar, so that for extrapolation to the pressures of the Earth's deep interior (up to 3.6 Mbar) Lindemann's law is particularly appropriate.

Extrapolation of melting temperatures to pressures at which there are first-order changes in density relies upon knowledge of the volume dependence of Grüneisen's ratio γ , which is quite variable in different types of material (Irvine and Stacey 1975) and is even quite different for different metals, e.g. sodium and iron. However, the Vashchenko-Zubarev (1963) formulation for γ allows us to estimate its value for any material for which the pressure-dependence of elasticity is known. This is so for the deep interior of the Earth.

Extrapolation of the iron-sulphur eutectic data of Usselman (1975) gives a melting point of 4160 K at the boundary of the Earth's solid inner core and, by

adiabatic extrapolation upward, a temperature of 2940 K at the core–mantle boundary. Within the limitation of the assumption that the inner core boundary marks the solid–liquid equilibrium of iron–sulphur eutectic, these temperatures provide fixed points on the Earth's temperature profile which appear to be valid to within a few hundred degrees.

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