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Melting of Iron

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Summary

A theoretical melting curve for iron is determined in the pressure range of the Earth's core by a relation derived from the Ross–Lindemann melting criterium. On this basis the melting point of pure iron is estimated to be about 4800°C at the mantle–core boundary, and 6600°C at the inner core–outer core boundary with a melting point gradient of about 0·8 deg/km.

The problem treated in this paper is that of determining the melting temperature of iron, particularly under the conditions which prevail in the Earth's core.

Alder (1966), using the Lindemann law, wherein melting is assumed to occur when the root-mean-square amplitude of atomic vibrations becomes some critical fraction of the nearest-neighbour distance, has estimated the melting temperature of iron under core–mantle boundary conditions to be about 4400°C, and under inner–outer core boundary conditions to be about 7450°C.

Quite different results have been obtained more recently by Higgins & Kennedy (1971; see also, Kennedy & Higgins 1973), who assumed that the melting temperature of iron is given by a linear function of compression of the solid and extrapolated the melting curve to core conditions using the Kraut–Kennedy melting law (Kraut & Kennedy 1966). They have estimated that the temperature of iron at pressures equivalent to the inner–outer core boundary is *c.* 4250°C with a melting point gradient of approximately 500°C through the outer core.

However the hundred-fold linear extrapolation of Higgins & Kennedy (1971) for the melting curve of iron has been criticized by Verhoogen (1973) on various grounds, and by Boschi (1974) who pointed out that the Kraut–Kennedy melting law does not give the correct asymptotic behaviour. Verhoogen's (1973) views are mainly based on the significant structure calculations of the iron melting curve by Leppaluoto (1972) who has obtained figures closer to those of Alder (1966) and, namely, about 4700°C at mantle–core boundary and about 6700°C at the inner–outer core boundary. However some ambiguities inherent to the significant structure theory, when applied to melting phenomena pointed out by Tuerpe & Keeler (1967), lead to a lack of credibility on Leppaluoto's results.

Birch (1972) has discussed the validity of the procedure used by Higgins & Kennedy (1971) stressing the fact that iron exists in four crystalline forms and that present knowledge of the thermodynamic properties of the two denser phases, which are those most likely to be applicable in the core of the Earth, is extremely rudimentary.

In this paper we will use a melting equation which can be derived from the Ross-Lindemann melting criterium (Ross 1969) or, independently, from the ideal 'three-phase model' by Hiwatari & Matsuda (1972a, b) using the results of Monte Carlo calculations by Hoover *et al.* (1970). For its simplicity and elegance, we will describe in detail the Ross-Lindemann melting criterium.

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Ross has generalized the Lindemann melting law by reformulating it in terms of the statistical-mechanical partition function. In statistical mechanics, the configurational partition function Q for a system of N particles is written as:

$$Q = \frac{1}{N!}\int \dots \int \exp[- U(\vec{r}_1,\vec{r}_2, \dots \vec{r}_N)\beta]\, d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N \tag{1}$$

where $\vec{r}_1$ is the position vector of the i-th particle, U is the energy of the system, $\beta = 1/kT$, k is the Boltzmann constant and T is the temperature.

Defining a set of reduced co-ordinates, $\vec{\lambda} = \vec{r}/V^{1-3}$, where V is the volume of the entire system, we may rewrite the configurational partition function as:

$$Q = V^N Q^* \exp[- U(0)\beta]/N! \tag{2}$$

where $U(0)$ is the energy of the system with all atoms in their lattice sites and Q^* is a reduced configurational partition function given by:

$$Q^* = \int \dots \int \exp\{ - [U(\vec{\lambda}_1,\vec{\lambda}_2, \dots \vec{\lambda}_N) - U(0)]\beta\} d\vec{\lambda}_1 d\vec{\lambda}_2 \dots d\vec{\lambda}_N \tag{3}$$

with the integration performed over the reduced configuration space.

Ross (1969) has reformulated the Lindemann principle by stating that for a given substance, at all points along its melting curve, the solid always occupies the same fraction of configurational phase space. In other words, in configuration space we would always see the same scaled picture at all points along the melting curve. In statistical mechanical language it is required that Q^* be a constant at all melting temperatures T_m and all volumes V_m along the melting curve, and this is formally written as:

$$Q^*(T_m, V_m) = \text{constant}. \tag{4}$$

The solid is represented by means of the single-particle cell model, in which the volume V is divided up into a lattice of N cells with one particle in each cell. In this approximation the configurational partition function, now denoted as $Q^{(1)}$, may be written (Hill 1960) as:

$$Q^{(1)} = v_f{}^N .\ \exp[- NE(0)/2\beta] \tag{5}$$

where v_f is the one-particle free volume given by:

$$v_f = \int_v \exp\{ - [E(\vec{r}) - E(0)]\beta\} d\vec{r} \tag{6}$$

where the integral is over v, the volume of the cell. $E(r)$ is the potential field in which the particle moves, and $E(0)$ is the potential at the centre of the cell. Defining a set of reduced co-ordinates $\vec{\lambda} = \vec{r}/v^{1/3}$, enables us to express v_f as:

$$\left.\begin{aligned} v_f &= v v_f{}^* \\ v_f{}^* &= \int_0^1 \exp\{ - [E(\vec{\lambda}) - E(0)]\beta\} d\vec{\lambda} \\ Q^{(1)} &= v^N v_f{}^{*N} \exp[- NE(0)/2\beta]. \end{aligned}\right\} \tag{7}$$

Here v_f is the volume of configuration space that a single particle moving in its cell will occupy. Then $v_f{}^*$ is the dimensionless reduced volume occupied by a single particle and is the cell-analogue of the function Q^*. Consequently, in terms of the cell model, Ross melting principle is postulated as:

$$v_f{}^*(T_m, v_m) = \text{constant}. \tag{8}$$

Consider now the case in which the atoms of the solid interact by pairwise additive repulsive forces of the inverse power form:

$$\Phi(r) = \epsilon(r^*/r)^n. \tag{9}$$

The Z nearest neighbours surrounding an atom in its cage are considered to be smeared over that shell, then the potential in which the atom in the cell moves is given by (Hill 1960; Barker 1963)

$$E(\lambda) - E(0) = Z\epsilon(v^*/v)^{n/3} l(\lambda^2) \tag{10}$$

where r^*, ϵ, and n are constants, and $v^* = r^{*3}/d$; d depends on the crystal structure $l(\lambda^2)$ is a polinomial expansion in λ^2 and can be written in closed form.

In the limit of harmonic approximation, it can be shown that:

$$E(\lambda) - E(0) = Z\epsilon(v^*/v)^{n/3} a_n \lambda^2 \tag{11}$$

where a_n is a constant depending on the crystal srtucture and the number of neighbouring shells included

To satisfy the melting condition of equation (8), it is necessary that:

$$(Z\epsilon/kT_{\mathrm{m}})(v^*/v_{\mathrm{m}})^{n/3} a_n = \text{constant.} \tag{12}$$

Let us write:

$$v_{\mathrm{m}} = v_0 - \Delta v$$

substituting in equation (12), we get:

$$\frac{Z\epsilon}{kT_{\mathrm{m}}} \left[\frac{v^*}{v_0(1 - \Delta v/v_{\mathrm{n}})}\right]^{n/3} a_{\mathrm{n}} = \text{constant.} \tag{13}$$

We may evaluate the constaut at $\Delta v = 0$ for which $T_{\mathrm{m}} = T_0$ and $v_{\mathrm{m}} = v_0$, where T_0 and v_0 refer to some point of the melting curve. We obtain:

$$T_{\mathrm{m}}/T_0 = (v_0/v_{\mathrm{m}})^{-n/3} = (1 - \Delta v/v_0)^{-n/3} \tag{14}$$

which is the equation which we will use to determine the melting curve of iron.

Equation (14) can be derived in an independent way in the framework of the 'ideal three-phase model' proposed by Hiwatari & Matsuda (1972a, b), using the results of Monte Carlo calculations of Hoover *et al.* (1970; see also, Hansen 1970; Hoover & Ross 1970; Ree 1971). The Hiwatari–Matsuda model is characterized by the pair potential:

$$\Phi(r) = A/r^n - \alpha B^3 \exp(-Br)$$

where $n(>3)$, $A(>0)$, and $\alpha(>0)$ are the constant parameters specifying the substance in the scheme of the model. The positive constant B is a quantity to be made to tend to zero after having taken the thermodynamic limit. This model has considerable merit because of its simple scaling properties (Matsuda 1969).

A series expansion of equation (14) leads to the following relationship:

$$T_{\mathrm{m}} = T_0 \left\{ 1 + \frac{n}{3}\frac{\Delta v}{v_0} + \frac{n}{6}\left(\frac{n}{3} + 1\right)\left(\frac{\Delta v}{v_0}\right)^2 + \dots \right\} \tag{15}$$

which is similar to the one proposed by Kraut & Kennedy (1966):

$$T_{\mathrm{m}} = T_0(1 + C\Delta v/v_0).$$

An inspection of the ratio of the quadratic to the linear term in equation (15) reveals that for any reasonable value of n the quadratic term becomes 10 per cent of the linear at $\Delta v/v_0$ of about 0·05. Therefore for transition metals such as iron in which core-core interaction are important, equation (15), with higher order terms neglected, appears to be a much more adequate description of melting phenomena than the Kraut–Kennedy relationship. However Kraut & Kennedy (1966) claim that alkali metals obey their linear expression up to compressions of 0·4, wherein quadratic and higher terms, if present, should have begun to manifest themselves. Nevertheless it is well known that at normal densities there is no appreciable core-core interaction in the alkali metals (Royce 1967). Consequently equation (15), which is derived from a potential that is appropriate to a system in which strong core–core repulsions dominate, should not be applicable to the alkali metals. Ross (1969) has also derived a melting law using potential that is more appropriate to such systems.

To obtain the melting curve of iron we use for n the value 8·4, obtained by Hiwatari & Matsuda (1972) studying the isothermal compression in the solid phase.

En passant, we may observe that if we accept the following relation:

$$\frac{2}{3} - 2\gamma = \frac{d \log T_m}{d \log v_m} \tag{16}$$

where γ is Grüneisen's parameter, we obtain $\gamma = 1{\cdot}6$, since in our case $d \log T/d \log v_m$ is $-n/3$. Equation (16) has been obtained by Knopoff & Shapiro (1969) in their study of the various methods of computing Grüneisen's parameter taking also into account the effects of melting and fluidity.

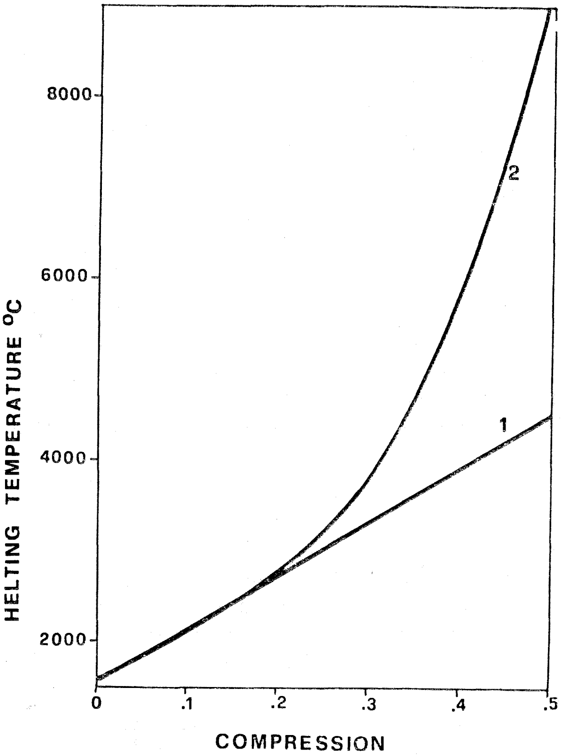

FIG. 1. Melting temperature of iron versus $\Delta v/v_0$. Curve 1: Higgins–Kennedy (1971) of the Kraut–Kennedy melting law. Curve 2: present work.

Fig. 1 shows the plot of our melting temperatures of iron versus the compression v/v_0, compared with those of Higgins & Kennedy (1971). Fig. 2 shows the plot of the melting curve of iron versus pressure, where use has been made of the pressure–density plot for iron derived by Higgins & Kennedy (1971) from shock-wave data (Van Thiel 1966). At a pressure of 1·4 Mbar (core–mantle boundary) the melting temperature of pure iron is about 4800°C, and at a pressure of 3·2 Mbar (inner–outer core boundary) the melting temperature is about 6600°C.

An interpretation which has found favour for many reasons is that the inner core is the solid phase corresponding to the liquid outer core (Birch 1940, 1952; Bullen 1946, 1949, 1950; Ramsey 1950). Recent analyses of the periods of free oscillations (Pekeris, Alterman & Jarosh 1962; Alsop 1963; Derr 1969; Jordan & Franklin 1971; Dziewonski & Gilbert 1971, 1972; Dziewonski 1971; Julian, Davies & Sheppard 1972) appear to support this idea. Thus it is generally postulated that the temperature at the boundary, at the depth of 5120 km, lies on the melting curve of core material. Though argument continues concerning the amount and the nature of alloying elements, there remains little ground for doubting that both inner and outer core consists mainly of iron. However, it is generally believed that iron is too dense to meet the requirement of the outer core (Birch 1952, 1964; MacDonald & Knopoff 1958; Knopoff & MacDonald 1960; McQueen, Fritz & Marsh 1964; Boschi & Caputo 1969, 1970, 1972) and of possible alloying elements, silicon and sulphur have been proposed as suitably abundant and likely to enter a phase composed mainly of iron. Birch (1972) has discussed the influence of this alloying element on the melting point of iron and has concluded that to estimate the temperatures in the real core, the melting temperature of iron at the inner–outer core boundary must be lowered by no more than 1000°C.

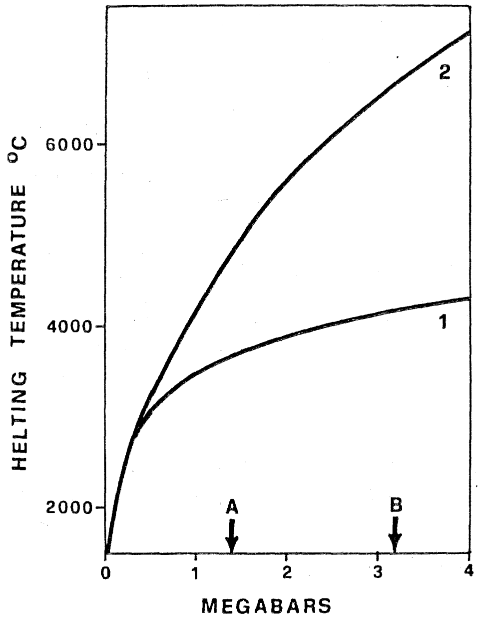

FIG. 2. Melting temperature of iron versus pressure. Curve 1: Higgins–Kennedy (1971) Curve 2: present work. A and B correspond to the pressures of mantle-core boundary and inner–outer core boundary respectively.

However, here, we have to mention that recently Cook (1972) has estimated the values of the bulk-modulus and the density for the inner core as a consequence of the observation of Bolt & Qamar (1970) and of the determination of the velocity of shear waves, concluding that there may be some indication that the material of the inner core differs in composition from that of the core.

Concluding, in Table 1 we compare some of the existing estimates of the melting temperature of iron at the mantle–core boundary conditions.

Table 1

Method	Iron melting temperature at 1·4 Mbar (°C)	Reference
Simon equation with different values of the empirical parameters	3120	Simon (1953)
	2950	
	2810	
	3320	Bullard (1954)
	2950	
	4610	
	3920	Gilvarry (1956)
	3360	
	2340	Strong (1959)
	4750	Birch (1963)
Lindemann equation with semi-empirical considerations	4000	Valle (1955)
	4250	Zharkov (1959)
	4400	Alder (1966)
Kraut–Kennedy equation	3750	Higgins & Kennedy (1971)
Significant structure theory	4700	Leppaluoto (1972)
Ross–Lindemann criterium	4800	Present work

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