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On the Melting Curve at High Pressures

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Summary

The asymptotic behaviour of the melting curves for substances with close-packed structures is analysed by means of Monte Carlo calculations on model systems of hard spheres. The Kraut–Kennedy melting law does not show the correct asymptotic behaviour. On this basis some recent results on the physics of the Earth's core are rejected.

Higgins & Kennedy (1971) have estimated that the melting temperature of iron at pressures equivalent to the inner core–outer core boundary is circa 4500 °K with a melting point gradient of approximately 500° through the outer core. Their estimate is based on a hundred-fold linear extrapolation of the 30 kbar experimental results of Sterret, Klement & Kennedy (1965), by assuming that the melting point is a linear function of the volume of the solid (Kraut & Kennedy 1966).

Birch (1972) has discussed the validity of such a procedure, 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. Birch (1972) concludes that the melting temperatures of the γ-phase may be some 700° above those estimated by Higgins & Kennedy (1971); the melting temperatures of the ε-phase may still be higher.

Verhoogen (1973) has suggested that the Higgins–Kennedy estimate is grossly wrong on several grounds but mainly basing his views on significant structure calculations by Leppaluoto (1973). The significant structure theory is based on the idea that molecules of liquids are more or less free to move about in a structure which is basically solid-like. This view is then translated into mathematical language, that is a partition function, from which all of the thermo-dynamic properties of the liquid are calculated (for a recent review in this subject see John & Eyring 1971). However the significant structure theory of liquids has been used by Tuerpe & Keeler (1967) to predict melting curves at high pressures obtaining anomalous results, which indicate that, although successful in predicting some thermal properties of liquids at moderate temperatures and pressures, the theory may not be suitable to describe the phenomenon of melting, as Kennedy & Higgins have pointed out.

Jacobs (1971, 1973) has re-estimated the adiabatic gradient in the core, assuming that there is a linear relationship between the reciprocal of the thermal expansion coefficient and pressure in analogy with Bullen's compressibility-pressure hypothesis, finding that in the core the adiabatic temperature gradient is less than the melting point gradient of Higgins & Kennedy. Jacobs (1973) concludes that actual temperatures in the core are probably very close to those of the melting temperature.

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In consequence it appears worthy of interest to speculate on the general asymptotic behaviour of the melting curve, which could constitute a necessary condition for the validity of every melting law at high pressures. At the present stage of our knowledge of the physics of phase-transitions, that is all what we may do. To this end we will use some results obtained by Monte Carlo calculations on model systems of hand spheres. In this context, the term Monte Carlo refers to a probablistic method of sampling configurations specified in various ensembles. Using configurations specified in this manner, estimates can be made for most equilibrium averages of interest in statistical mechanics and thermodynamics.

The chief advantage of this approach lies in the fact that we can control the shape of the intermolecular potential energy to be used and the independent external variables with the desired accuracy. A complete review of this subject has been given by Ree (1971).

It is reasonable to assume that at high densities a system of solid spheres can exist in two different states, namely, the crystal-like state (the spheres' centres are statistically located at the nodes of a periodic spatial lattice) and the non-ordered liquid-like state (the statistical spatial correlation of the sphere exists only over a distance of the order of several sphere diameters).

Computer studies cannot provide the locations of the melting and freezing densities since they do not give any information on the entropy constant which would allow the solid state entropy to be evaluated from the same reference state used for the entropy of the fluid branch. If an ideal gas state is chosen as the reference state, entropies of the fluid can be measured from a low density state. This is achieved by integrating on the fluid branch the relationship

$$\beta P = \rho^2 \partial A/\partial \rho$$

where $\beta = (kT)^{-1}$, T is the temperature, P is the pressure, ρ is the number of particles in the unit volume, A is the free energy and k is the Boltzmann constant. We get

$$A = A_{\text{ideal}} + \int_0^\rho \{[(\beta P/\rho) - 1]/\rho\} d\rho$$

where A_{ideal} is the free energy for the ideal gas at g. However a similar approach cannot be used in the case of the solid branch because this branch terminates at a dense state. Hoover & Ree (1967; see also Ree 1971) have overcome this difficulty by using the single-occupancy system, i.e. a similar system with a constraint in the volume, in which a particle can move around. This constraint assigns each particle to its own Wigner–Seitz cell within which the centre of the particle is confined. For the single-occupancy system at high densities, a particle with a repulsive core would predominantly collide with neighbouring particles, and only very rarely it would collide with the wall of its own cell. Since the particle cannot feel the pressure of the wall, thermodynamic properties at high densities could be satisfactorily approximated by those without the wall constraint. This fact plus the fact that the artificial wall forces the single-occupancy system to remain in a solid phase at all densities offers a practical way to extend the real isotherm to lower fluid densities by using the isotherm of the artificial solid. The free energy has an expression similar to that of the fluid branch, i.e.

$$A^* = A_{\text{ideal}} + \int_0^\rho \{[(\beta P^*/\rho) - 1]/\rho\} d\rho$$

where the asterisk means single-occupancy thermodynamic quantities. In this way a reversible path which links the solid and the fluid branches is achieved. The melting pressure and the co-existence densities of solid and fluid are then determined by a systematic use of a Maxwell double-tangent construction drawn using A and A^*. By the method here outlined Hoover & Ree (1967) conclude that hard spheres systems melt at $(0{\cdot}736 \pm 0{\cdot}003)\,\rho_0$ and freeze at $(0{\cdot}667 \pm 0{\cdot}003)\,\rho_0$ and the pressure of the co-existence region is $(8{\cdot}27 \pm 0{\cdot}13)\,\rho_0 k\, T_m$, where ρ_0 is the density of the system in the state of closest packing, and T_m is the melting temperature.

Let us now confine our attention to substances with close packed structures.

It is well established that the melting point of a substance with close-packed structure rises as the pressure increases. In other words

$$dT_m/dP_m > 0$$

where P_m is the melting pressure. It is well established also that

$$d^2T_m/dP_m{}^2 < 0,$$

in other words, the slope of the melting decreases as the pressure increases. This leads to a more rapid decrease in the volume jump ΔV during the melting than the corresponding entropy jump ΔS. It can be stated that $\Delta V/V_s$, where V_s is specific volume for the solid at melting, decreases very rapidly at low pressures. This has been experimentally shown for some metals by Urlin (1965). The fact is also substantiated by some observations made by Bridgman (1931) who established that the compressibility of liquids under low pressures greatly exceeds the compressibility of the corresponding solids, but, already at moderately high pressures, it becomes very near to the compressibility of solids. Urlin's experimental data show also that the rate of variation in $\Delta V/V_s$ diminishes greatly as pressure increases and it can be assumed that this ratio tends to a non-vanishing constant. Corresponding conclusions apply to the entropy discontinuity at melting, which rapidly reaches a nearly constant value as the pressure is increased.

Thus the available experimental data lead to the conclusion that

$$\left.\begin{aligned} \lim_{P\to\infty} (\Delta V/V_s) &= \text{const} \\ \lim_{P\to\infty} \Delta S &= \text{const} \end{aligned}\right\}.$$

For the melting of model systems of hard sphere particles, we have the following relations

$$\left.\begin{aligned} \Delta V/V_s &= \text{const} \\ \Delta S &= \text{const} \end{aligned}\right\}. \qquad (1)$$

Thus it is reasonable to suppose that close packed systems can be represented by hard sphere models at sufficiently high pressures.

As already mentioned the equation of the melting curve for a system of hard spheres is (Hoover & Ree 1967)

$$P_m V_0 = 8{\cdot}27\, NkT_m, \qquad (2)$$

where V_0 is the volume of the model system in the state of closest packing and N is the number of particles.

Assuming an identical melting behaviour in both model and real systems, we can re-write equation (2) for the real system in the following manner

$$P_m V_0^R = \text{const} \times kT_m \tag{3}$$

where V_0^R is the volume of the real system in its closest packing. V_0^R is temperature dependent and can be derived from the energy conservation principle:

$$\phi(r_0^R) = \tfrac{1}{2}kT \tag{4}$$

where $\phi(r)$ is the interaction potential. If we consider power-law repulsion only, as is reasonable for very high pressures, $\phi(r)$ can be written as

$$\phi(r) \sim r^{-n}$$

and we get

$$V_0^R \sim T_m^{-3/n}. \tag{5}$$

Then from the relations (3) and (5), it follows that

$$P_m \text{ is proportional to } T_m^{1+3/n}, \tag{6}$$

or

$$\frac{d\ln P_m}{d\ln T_m} = 1 + \frac{3}{n},$$

which gives the asymptotic expression for the melting curve.

The Kraut–Kennedy relation (Kraut & Kennedy 1966) relates the melting temperature linearly to the compression

$$T_m = T_m^0\left(1 + \frac{m\Delta V}{V^0}\right) \tag{7}$$

where T_m^0 and V^0 are the melting temperature and the volume at room conditions and m is a constant characteristic of the considered substance. Equation (3) implies that the volume at a given temperature is proportional to V_0^R. We may therefore replace V in the Kraut–Kennedy relation by a constant times V_0^R and so obtain a linear dependence of V_0^R on T_m, which is clearly in contradiction with our relation (5).

Incidentally we may observe that the asymptotic behaviour of the melting curve here discussed, is formally consistent with the Simon empirical equation

$$(P/P_*) = (T/T_t)^c - 1$$

where T_t is the temperature of the triple point, P_* and c are empirical parameters. The experimental values of c generally lie between 1·2 and 1·5 for pressures up to 10^3 atm, but this pressure is not high enough for quantitative comparisons.

Concluding we can state that the Kraut–Kennedy equation does not behave in the asymptotic manner to be expected from hard sphere models and the geophysical results based on it about the core (Higgins & Kennedy 1971) must be open to question.

Birch's (1972) assumption that the melting curves of each phase of iron are straight lines in the temperature–volume plane following the Kraut–Kennedy relation also cannot give the correct asymptotic behaviour.

The values of the resistivity of liquid iron at high pressures calculated by Evans & Jain (1972) in the basis of Higgins–Kennedy melting curve should be revised.

Higgins & Kennedy (1971) have also pointed out that the temperature gradient is much less than the adiabatic gradient in the outer core which would then be thermally stably stratified, thereby inhibiting radial convection which is necessary to drive the geomagnetic dynamo. Various ways have been developed to circumvent this difficulty. Bullard & Gubbins (1971) have pointed out that a stable fluid can have internal wave motions and their calculations indicate that a body of fluid could act as dynamo, even when its motion is purely oscillatory. Busse (1972), Malkus (1972) and Elsasser (1972) have all independently proposed that the liquid in the outer core can have a temperature distribution along a melting point curve, but they propose that the liquid is a slurry made up of extremely fine iron particles suspended in an iron-rich liquid. They show that such a liquid, given the proper distribution of solid particles, can behave as an adiabatic fluid. At the light of present knowledge all these suggestions, although ingenious, appear no more than speculations.

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