Turing Probes the Earth's Core

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We have exploited the power of the CSAR service to attack one of the great unsolved questions in the earth sciences: how hot is the Earth's core?

A report on our work just published in the journal Nature[1] was picked up by the media, and we were interviewed on Channel 4 News and the Today programme. There was even a half-page item on our work in the Daily Mirror, and on the BBC online web page[2].

The core of the Earth accounts for approximately 30% of the total mass of our planet (schematically in Figure 1.), the inner solid core is crystallizing from the liquid outer core, and the heat released flows to the surface, driving all the living geological processes of the Earth, including plate tectonics, volcanism and earthquakes.

Moreover, this heat flux is also responsible for the convective motions in the liquid core, which generate the Earth's magnetic field, shielding us from the lethal solar wind. So, a sound knowledge of the core is of fundamental importance, yet, it is one of the most difficult things to study, and its properties are poorly constrained. For example, we know that it is mainly made by iron, but it can't be pure iron, because its density is too low. So it must contain some light element, and the most likely candidates are sulphur, oxygen, carbon and silicon, but the real composition of the Earth's core remains one of the major unsolved problems. The density and the pressure are known quite accurately (within a percent), but the temperature is unknown, with estimates ranging from approx. 4000 to approx. 8000 K.
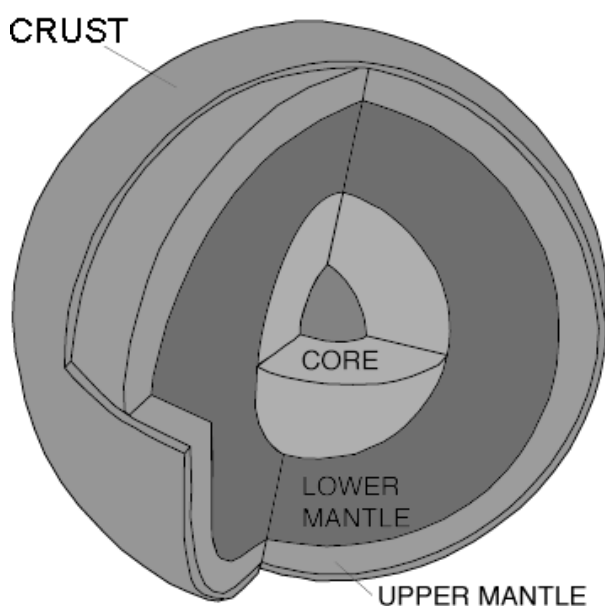

Figure 1: Schematic representation of the Earth interior

Since the main constituent of the core is iron, it is relevant to study its properties under core pressures. The pressure p at the inner-core boundary (ICB) is 330 GPa, and the melting temperature T_m of Fe is needed up to at least this value. Static compression measurements of T_m with the diamond anvil cell (DAC) have been done up to *ca*. 200 GPa, but even at lower pressures results for T_m disagree by several hundred K. Very recent DAC diffraction experiments demonstrate that in the range 60 - 80 GPa the solid phase from which Fe melts has the hexagonal close-packed (ε) structure. Shock experiments at present give the only way of going to higher pressures, but their interpretation is not simple, and there is a scatter of at least 2000 K in T_m at ICB pressures. There have also been attempts to obtain the melting curve from parameterized atomistic models for the energetics of iron, but the reliability of these models is uncertain.

Parameter-free *ab initio* techniques based on density functional theory (DFT) have recently made enormous strides[3], and for many materials, including transition metals, reliance on parameterised models is now unnecessary. With *ab initio* molecular-dynamics methods (Car-Parrinello)[4], this is true for both liquids and solids[3]. Solid iron in all its known crystal structures has been extensively studied with DFT. The accuracy of DFT depends on the approximation used for the electronic exchange-correlation energy, but with the 'generalised-gradient approximation' (GGA) the experimental properties of Fe are very accurately reproduced[5].

The calculations we present here have been done with the VASP code[6], which is extremely robust and stable for simulation of metals, we have also doubled the speed of the code for the molecular dynamics simulations using an efficient charge extrapolation[7]. Combining this with the resources of the CSAR service we have been able to do calculations of unprecedented size and length, which have been essential for the success of this work.

The strategy we follow to calculate the melting curve is very simple: we calculate the Gibbs free energy of solid and liquid iron as a function of pressure and temperature. The melting temperature T_m at any pressure is found by equalizing the free energies. In fact, we calculate the Helmholtz free energy F(V,T) as a function of volume V, and from this we obtain the pressure through the relation $p = -(\delta F/\delta V)_T$ and G through its definition $G = F + {}_pV$.

The free energy of the harmonic vibrating solid is conceptually simplest, and is given (per primitive cell) by the standard high-temperature formula:

$$F = F_{\text{perf}} + N_{\mathbf{k}}^{-1} \sum_{\mathbf{k}s} \ln(\hbar\omega_{\mathbf{k}s}/k_B T)$$

where F_{perf} is the free energy of the rigid perfect lattice and w_{Ks} is the frequency of the phonon of branch *s* at wavevector **k**. The sum goes over the N_k wavevectors in the Brillouin zone of the crystal and over the branches s, the frequencies w_{Ks} were obtained by diagonalising the force-constant matrix.

To calculate the liquid free energy and the anharmonic contribution to the solid free energy, we use the technique of 'thermodynamic integration', which yields the difference $\Delta F = F - F_{ref}$ between the free energy of the *ab initio* system and that of a reference system, F_{ref}. It is a standard result that these difference is:

$$\Delta F = \int_0^1 d\lambda \, \langle U - U_{\text{ref}} \rangle_\lambda \,,$$

where the thermal average (.) is evaluated for the system governed by $U_\lambda = (1-\lambda)U_{ref} + \lambda U$ where U_{ref} and U are the internal energies of the reference system and the *ab initio* system respectively.

Even with the available CSAR power, the practical feasibility of calculating *ab initio* free energies of liquids and anharmonic solids hinges on finding a reference system for which F_{ref} is readily calculable and the difference $U - U_{ref}$ is very small.

For the liquid, the crucial discovery that makes our threshold precision achievable is that the *ab initio* energy U is extremely well reproduced by a model U_{ref} consisting of a sum of pair potentials $\phi(r)$, with $\phi(r)$ chosen to be an inverse-power repulsive potential: $\phi(r) = A/r^\alpha$. The parameters A and α are adjusted to minimise the strength of the fluctuations. We have demonstrated the excellence of this U_{ref} by doing ab initio dynamical simulations at 18 different thermodynamic states spanning the (p,T) range of interest, and we find that a single choice of A and α is almost equally good over the whole range.

Figure 2: The ab initio melting curve of iron compared with experimental results. Chain curve shows ab initio results; solid and dotted curves are interpolations of DAC measurements; points are more recent measurements, and represent a lower bound rather than the melting curve itself; open squares and open diamond with error bar are shock data.

The inverse-power model is not a good enough reference system for the anharmonic solid, but we find that an outstandingly good reference system for this case can be obtained by suitably combining the inverse-power and harmonic ab initio total energies. We stress that the choice of reference system affects only the efficiency of the calculations, and not the final results.

Figure 2 compares our *ab initio* melting curve with experimental results from both DAC and shock measurements. For pressures $p < 200$ GPa covered by DAC, our curve lies *ca.* 1000 K above the lower set of experimental data and *ca.* 500 K above the more recent values represented by two points in the figure (whose authors stress that their values are only a lower bound to T_m); our agreement with the higher values is close. In comparing with shock data, we recall the well-known difficulties of obtaining temperature in shock experiments. Our curve falls significantly below some of the T_m measurements, in which temperature was deduced by measuring optical emission, but accords quite closely with the other single point, obtained by estimating the shock temperature using thermodynamic calculation.
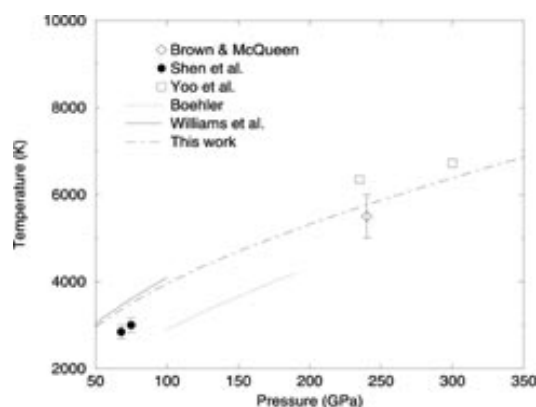
Our T_m of 6670K at the ICB pressure is close to the values inferred from some previous estimates, and gives evidence against the much higher or lower estimates sometimes proposed.

How good is our melting curve? Based on the analysis of the non cancelling errors in the Gibbs free energies for the liquid and the solid, and on the possible systematic errors due to GGA, we believe that our predictions for T_m are good to +/- 600K. This suggests that they are consistent with some of the recent DAC T_m; at high pressures, we are consistent with some of the shock T_m.

The *ab initio* techniques for calculating thermodynamic properties under extreme conditions are expected to find application to many other problems concerning the Earth's deep interior.

We conclude by remarking again that this work involved enormous computational effort, which has been possible only thanks to the CSAR service.

References

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