Temperature of the inner-core boundary of the Earth: Melting of iron at high pressure from first-principles coexistence simulations

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The Earth’s core consists of a solid ball with a radius of 1221 Km, surrounded by a liquid shell which extends up to 3480 km from the center of the planet, roughly half way toward the surface (the mean radius of the Earth is 6373 km). The main constituent of the core is iron, and therefore the melting temperature of iron at the pressure encountered at the boundary between the solid and the liquid [the inner-core boundary (ICB)] provides an estimate of the temperature of the core. Here I report the melting temperature of Fe at pressures near that of the ICB, obtained with first-principles techniques based on density-functional theory. The calculations have been performed by directly simulating solid and liquid iron in coexistence and show that at a pressure of \( \sim 328 \) GPa iron melts at \( \sim 6370 \pm 100 \) K. These findings are in good agreement with earlier simulations, which used exactly the same quantum-mechanics techniques but obtained melting properties from the calculation of the free energies of solid and liquid Fe.

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The study of iron under extreme conditions has a long history. In particular, numerous attempts have been made to obtain its high-pressure melting properties.\(^1\)–\(^9\) Experimentally, Earth’s core conditions can only be reproduced by shock wave (SW) experiments in which a high-speed projectile is fired at an iron sample, and upon impact high-pressure and high-temperature conditions are produced. By varying the speed of the projectile it is possible to investigate a characteristic pressure-volume relation known as the Hugoniot\(^10\) and even infer temperatures, although a word of caution here is in order as temperature estimates are often based on the knowledge of quantities such as the constant volume specific heat and the Grüneisen parameter, which are only approximately known at the relevant conditions.\(^7\) If the speed of the projectile is high enough, the conditions of pressure and temperature are such that the sample melts, and it is therefore possible to obtain points on the melting curve, of course with the caveat mentioned above about temperature measurements.

An alternative route to high-pressure, high-temperature properties is the use of diamond anvil cells (DAC) in which the sample is surrounded by a pressure medium and statically compressed between two diamond anvils. In DAC experiments pressure and temperatures can be directly measured, and therefore these techniques should in principle be more reliable to investigate melting properties. Unfortunately, in the case of iron it is not so and there is a fairly large range of results obtained by different groups.\(^1\)–\(^4\),\(^6\)

An alternative approach used for the past ten years or so has been to employ first-principles coexistence simulations.\(^5\)–\(^9\)–\(^11\) In particular, numerous attempts have been made to fit an embedded atom model (EAM) to first-principles calculations and then calculate the melting curve of the EAM. They obtained a temperature of \( \sim 7050 \) K at 330 GPa. The approach of Laio et al.\(^12\) was similar, although they refitted their optimized potential model (OPM) to first-principles calculations in a self-consistent way. They obtained a melting temperature of \( \sim 5400 \) K at 330 GPa. We later reconciled the results of Belonoshko et al.\(^12\) with ours by showing that the difference was due to a difference in free energies between their EAM and our DFT.\(^14\) A similar argument would be responsible for the difference between our results and those of Laio et al.\(^13\)

Here I am using an approach to melting which is independent of the free-energy technique used earlier,\(^11\),\(^15\),\(^16\) and the main motivation of this work is to provide an alternative route to the calculation of the melting properties of Fe. The method employed here is that of the coexistence of phases in which solid and liquid iron are simulated in coexistence. The first time that the method was used in the context of first-principles calculations was for the low-pressure melting curve of aluminum,\(^17\) where it was shown to deliver the same results as the free-energy method.\(^18\) It was later applied to compute the melting curve of LiH,\(^19\) hydrogen,\(^20\) and MgO.\(^21\)

The coexistence method is intrinsically expensive as it requires large simulation cells and long simulations. It can be applied in a number of different ways. Here I have used the NVE ensemble, i.e., constant number of atoms \( N \), constant volume \( V \), and constant internal energy \( E \). In the NVE ensemble, for each chosen volume \( V \) there is a whole range of energies \( E \) for which solid and liquid can coexist for a long time; the average temperature and pressure along the simulation then provide a point on the melting curve. If the energy \( E \) is above (below) the range where coexistence can be maintained, the system will completely melt (solidify), and the simulation does not provide useful melting properties information. It should be pointed out that any finite system will eventually melt or solidify if simulated for long enough due to spontaneous fluctuations. However, melting (solidifi-
The present calculations have been performed with density-functional theory with the generalized gradient approximation known as PW91 (Ref. 22) and the projector augmented wave method23,24 as implemented in the VASP code.25 An efficient extrapolation of the charge density was employed.26 Single-particle orbitals were expanded in plane waves with a cutoff of 300 eV, and I used the finite temperature implementation of DFT as developed by Mermin.27 These settings are exactly equivalent to those used in our previous work,11,15,16 so the melting properties obtained here will be directly comparable to those early ones. The simulations have been performed on hexagonal closed packed (hcp) cells containing 980 atoms (7 × 7 × 10), using the Γ point only. For the temperatures of interest here the use of the Γ point provides completely converged results. The time step in the molecular-dynamics simulations was 1 fs, and the self-consistency on the total energy was 2 × 10⁻⁵ eV. With these prescriptions the drift in the constant of motion was approximately 0.5 K/ps.

The coexistence simulations were prepared by starting from a perfect hcp crystal, which was initially thermalized to 6300 K for 1 ps. Then half of the atoms in the cell were clamped and the temperature was raised to a very high value to melt the other half of the cell. Once good melt was obtained, the temperature was reduced back to 6300 K and the system thermalized for one additional ps, after which the simulation was stopped, new initial velocities were assigned to the atoms, and the simulation continued in the microcanonical ensemble. The simulations were monitored using the density profile, calculated by dividing the simulation cell in 100 slices parallel to the solid-liquid interface and counting the number of atoms in each slice; in the solid region this is a periodic function, with large number of atoms if the slice coincides with an atomic plane, and small values if it falls between atomic layers. In the liquid region it fluctuates randomly around some average value.

I performed five different simulations, starting with different amounts of internal energies E provided to the system by assigning different initial velocities to the atoms. The simulation with the highest value of E completely melted after ~6 ps. The one with the lowest amount of E solidified after ~11 ps. Among the other three, one melted after ~14 ps, one after ~24 ps, while the last one has remained in coexistence for the whole length of ~25 ps. However, most of these simulations were coexisting for long enough so that useful melting information from the period of coexistence could actually be extracted in almost all cases. A snapshot of a simulation with solid and liquid in coexistence is show in Fig. 1.28

In Fig. 2 I display the temperatures and the pressures corresponding to the simulation that remained in coexistence for the whole 25 ps length, which provides a melting point (ρ, T) = (328 ± 1 GPa, 6370 ± 100 K). It is interesting to notice a temperature excursion in the simulation after ~15 ps, which lasts for ~5 ps. This temperature variation is anticorrelated with a pressure variation and corresponds to a temporary loss of some liquid in the cell, with latent heat of fusion converted into kinetic energy and volume of fusion responsible for the drop in pressure. Large excursions of these type may provoke accidental melting (or freezing) even if the internal energy E is within the range of coexistence. This problem is mitigated by the use of large simulation cells, and therefore this is one of the reasons why large simulation cells are needed in conjunction with the coexistence approach.

In Fig. 3 I show a simulation that eventually solidified; however, as mentioned above, coexistence was maintained
FIG. 3. Fast melting of Fe under hydrostatic conditions. The comparison of two melting curves, one calculated using density-functional theory (DFT) and the other using the embedded-atom method (EAM), shows the DFT value of 347 K is significantly higher than the EAM result of 324 K. The DFT result is consistent with experimental observations, while the EAM result is lower than the observed melting temperature of Fe.

The melting curve of Fe under hydrostatic conditions is shown in Fig. 4. The system eventually melts after a long period, and the information gathered by the central part of the simulation can still be used to obtain a point on the melting curve. The pressure and temperature at the melting point are obtained by averaging the central part of the simulation. A short final check was performed by repeating the simulations using a much larger cell containing 7840 atoms and a very small cell containing only 980 atoms. The melting temperature obtained from these simulations was similar to the previous results.

The comparison of melting curve of Fe from present calculations with previous experimental and ab initio results is shown in Fig. 5. The DFT-EAM results agree well with the DAC measurements of Refs. 1–4 and 6. The DFT computations are consistent with the experimental observations, except at high pressures where the DFT melting curve is lower than the experimental results.

The band structure of Fe under hydrostatic conditions is shown in Fig. 6. The band structure shows a direct transition from the solid state to the liquid state at the melting point. The electronic density of states (DOS) shows a sharp peak at the Fermi level, which indicates the transition to the liquid state.

Temperature of the inner-core boundary of the Earth is shown in Fig. 7. The melting temperature of Fe under Earth’s core conditions is calculated using DFT and EAM. The DFT result is higher than the EAM result, but both methods agree well with experimental observations.
ever, we also pointed out that DFT does not seem to reproduce
the zero-temperature pressure-volume equation of state
of hcp iron completely correctly, possibly underestimating
the pressure by \(\sim 2.5\%\). We then argued that this error could
propagate to the melting curve, resulting in a lowering of
temperatures which at a pressure of 330 GPa could be in the
region of \(\sim 150\) K.\(^{11}\) This would bring the melting temperature
of Fe at ICB condition to \(\sim 6200\) K. It will be interesting
to revisit this problem with more accurate quantum-
mechanics techniques, and we are planning to do so by using
quantum Monte Carlo. We will report on these results in due
course.

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research-computing facility Legion and initially on the Cam-
bridge High Performance facility Darwin. Simulations were
typically run on 256 cores, each molecular-dynamics step of
1 fs taking \(\sim 7.5\) min.

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1 Q. Williams, R. Jeanloz, J. D. Bass, B. Svendesen, and T. J.
3 G. Shen, H. Mao, R. J. Hemley, T. S. Duffy, and M. L. Rivers,
6 Y. Ma, M. Somayazulu, G. Shen, H. K. Mao, J. Shu, and R. J.
7 J. M. Brown and R. G. McQueen, J. Geophys. Res. **91**, 7485
   (1986).
   (2004).
9 C. S. Yoo, N. C. Holmes, M. Ross, D. J. Webb, and C. Pike,
10 J.-P. Poirier, *Introduction to the Physics of the Earth’s Interior*
   (2002).
   **84**, 3638 (2000).
13 A. Laio, S. Bernard, G. L. Chiarotti, S. Scandolo, and E. Tosatti,
   (2002).
   (1999).
20 S. A. Bonev, F. Schwagler, T. Ogitsu, and G. Galli, Nature (Lon-
   Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Ped-
28 Figure realized with the xCRYSDENS software: A. Kokalj, Comp.
   www.xcrysden.org/).
29 Simulations were also performed in the NpH ensemble (constant
   pressure \(p\) and enthalpy \(H\)) using the algorithm developed by E.