Ab initio calculations on iron and iron alloys at Earth’s core conditions

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Can mineral physics match seismology?

Is there an inner core composition that has the same elastic properties \((V_P, V_S)\) as the observation?
Talk Outline

• Why is the core interesting?

• What are ab initio calculations?
  o Simulating pressure
  o Simulating temperature

• What composition matches seismology?
  o Pure iron phases
  o Effect of light elements
  o Effect of nickel
The Earth’s Core

Seismology tells us the core is close to pure Fe
• The Earth’s core is mainly Fe with Ni and light elements

• The outer core is liquid and runny, ~10% less dense than Fe with T~4000-6000K

• The inner core is solid, 3-4% less dense than Fe

• IC is crystallising from the OC.

• Light alloying elements may be things like Si, S, O, C, H....
The outer core: the geodynamo


Glatzmaier and Roberts 1995
The outer core: stratification?

Buffett, EPSL, 2010

Ozawa et al., Science, 2011

Huang et al. rule out O altogether (Nature yesterday!)
Hemispherical solidification/melting of inner core?

Alboussière et al, Nature 2010

Monnereau et al., Science 2010

Gubbins et al, Nature 2011
The Inner Core

- Layering with OIC and IIC
- Significant anisotropy
- Hemispherical variations in anisotropy for OIC
- Melting of inner core
- IIC distinct: either different phase or different crystalline alignment
- Preferred orientation of crystals over time leading to texture?

Sun & Song 2008
Finding out about the core: Computational Mineral Physics

- Seismology is the direct observation
- Gives elastic properties and their variations as a function of depth including lateral variations
- Calculate these properties on iron and iron alloys
- Match the seismology
What does CMP involve?

• Atomistic scale modelling of bonding in minerals and fluids

• The bonding is described by *quantum mechanics*; calculate how energy varies with structure.

• Solve Schrodinger’s equation, but problem with more than one electron
Ab initio techniques (or tricks)

- VASP code using DFT with PAW and GGA
  This is the trick that gets us past one electron

- Numerically solving Schrodinger’s equation
- No parameterisation
- Can predict:
  - $V(P)$, $K$, EoS
  - $\omega_i$
  - $C_{ij}$, $V_P$, $V_S$
  - Free energies
  - Defects and diffusion
  - Viscosities and melting....
Potential energy as a function of atomic separation, $r$; the equilibrium bond length, $r_0$, corresponds to an energy minimum.
Simulation of pressure

- Choose V
- Vary atom positions and cell dimensions to produce minimum energy
- No residual forces on the atoms (dE/dx = 0)
- Calculate energy
- Change V and repeat
- Fit to an Equation of State
Equation of state for iron

Simulation of Temperature

- Computationally more difficult than modelling P
- Two approaches:
  - Lattice Dynamics
  - Molecular Dynamics
- Very, very cpu expensive
Simulation of Temperature:

Lattice Dynamics
Any complex motion, such as the trace at the top, can be decomposed into a set of simple sine waves, each with a frequency, $\omega_i$, and wavelength, $\lambda$. 
Thermodynamic Properties

\[ S, C, E, c_{ij}, \text{ etc.} = f(\omega_i) \]

\[ K, G, V_p, V_s = f(c_{ij}) \]

Free energy: \[ F = k_B T \sum_i \frac{h \omega_i}{2k_B T} + \ln \left( 1 - e^{\frac{h \omega_i}{k_B T}} \right) \]
Simulation of Temperature:

Molecular Dynamics
Ab initio molecular dynamics simulations of iron showing the time evolution of the temperature of the system calculated from the particle velocities. A similar trace is seen for many time-evolving properties (stress, energy…).
What’s the problem?

• What causes observed inner core complexity?
• Need to know what the core is made of
• Composition determined by stable phase(s) of Fe-X alloys
• First need to know stable phase of pure iron at core P&T
• Can we match $V_P$ and $V_S$?
• Need to know effect of light elements
• Need to know the effect of nickel
What is the stable phase of iron?

Phase diagram of pure iron

Solid lines from DAC experiments; symbols from shock experiments; broken lines from first-principles calculations.

What is the stable phase of iron?

**Free energy from molecular dynamics**

- $\rho = 13,155 \text{ kgm}^{-3}, T = 5500 \text{ K}$
- $F_{\text{hcp}}(\text{eV})$ $F_{\text{bcc}}(\text{eV})$ $F_{\text{fcc}}(\text{eV})$
  - $-10.668$ $-10.633$ $-10.654$

\[ \Delta F_{\text{bcc-hcp}} = 35 \text{ meV} \]
\[ \Delta F_{\text{fcc-hcp}} = 14 \text{ meV} \]

So for an inner core of pure Fe, stable phase is hcp now confirmed experimentally by Tateno et al. (2010)

**BUT** there are light elements to consider

Vočadlo et al. 2003, 200
Can we match $V_P$ and $V_S$? Both $f(C_{ij})$

Seismic velocities of pure iron from elastic constants

- Only $C_{11}$, $C_{12}$ and $C_{44}$
- Deformation matrix:
  $$
  \begin{pmatrix}
  1 + \delta & \delta / 2 & 0 \\
  \delta / 2 & 1 & 0 \\
  0 & 0 & 1
  \end{pmatrix}
  $$

- For hcp need two strain matrices in order to get $C_{11}$, $C_{12}$ $C_{13}$, $C_{33}$ and $C_{44}$

All done at core P&T
Can we match $V_P$ and $V_S$?

Must remember to match “real” data.
Can we match $V_P$ and $V_S$?

Not yet......

- AIMD elasticity calculations show high $V_S$ for all phases (Vočadlo 2007, Vočadlo et al., 2008)

<table>
<thead>
<tr>
<th></th>
<th>$\rho$ (kgm$^{-3}$)</th>
<th>$T$ (K)</th>
<th>$V_P$ (kms$^{-1}$)</th>
<th>$V_S$ (kms$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hcp-Fe</td>
<td>13155</td>
<td>5500</td>
<td>11.14</td>
<td>4.01</td>
</tr>
<tr>
<td>bcc-Fe</td>
<td>13155</td>
<td>5500</td>
<td>11.29</td>
<td>4.11</td>
</tr>
<tr>
<td>fcc-Fe</td>
<td>13155</td>
<td>5500</td>
<td>11.64</td>
<td>4.64</td>
</tr>
</tbody>
</table>

- Incompatible with seismology: $V_S$ (PREM) = 3.5-3.67 kms$^{-1}$
- Calculated $V_S >$ seismology by 10-30 %
- Needs a lot of melt in the IC to account for difference in $V_S$: 
  \[
  \%: >8_{bcc} >12_{hcp} >25_{fcc}
  \]
  (% melt estimate from Hashin–Shtrikman bound for effective $\mu$ of 2-phase media)
What about light elements?

The effect of light elements

- Cold calculations predict transition to the CsCl-FeSi at ~13 GPa (Vočadlo et al. 1999)
- CsCl-FeX iso-structural with bcc
  - CsCl-FeSi (Dobson et al., 2002)
  - CsCl-FeS (Sata et al., 2008)
  - CsCl-FeO (Ozawa et al., 2011)
- At zero K, 330 GPa, few atm. % Si, S, O, C stabilises bcc-Fe (Côté et al. 2008)
Problem is even worse.....

<table>
<thead>
<tr>
<th>Material</th>
<th>ρ (kgm⁻³)</th>
<th>T (K)</th>
<th>V_p (kms⁻¹)</th>
<th>V_s (kms⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hcp-Fe</td>
<td>13155</td>
<td>5500</td>
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<td>13155</td>
<td>5500</td>
<td>11.64</td>
<td>4.64</td>
</tr>
<tr>
<td>cubic-FeSi</td>
<td>10212</td>
<td>5500</td>
<td>13.53</td>
<td>6.26</td>
</tr>
<tr>
<td>cubic-FeS</td>
<td>10353</td>
<td>5500</td>
<td>12.02</td>
<td>4.43</td>
</tr>
<tr>
<td>fcc-Fe₃S</td>
<td>13155</td>
<td>5500</td>
<td>11.97</td>
<td>4.55</td>
</tr>
</tbody>
</table>

- Incompatible with seismology: V_s (PREM) = 3.5-3.67 kms⁻¹
- Calculated V_s > seismology by 10-50+ %
- Needs a lot of melt in the IC to account for difference in V_s:
  \[ %: >8_{bcc} >12_{hcp} >25_{fcc} \]
Possible explanations include

- partial melt
- anelasticity
- lateral density inhomogenities
- aggregates and defects in iron
- composition effects
What about nickel?

But.... Ni works the opposite way to light elements

DAC experiments of Huang et al. (1988); qualitatively in agreement with calculations of Vočadlo et al., 2006
What about nickel?

LHDAC at ~300 GPa and ~2000 K


- Triple point is “possibly” located at ~10-20 wt% Ni
- Crystallising phase depends on % Ni present
- Could have early crystallising of fcc phase, then hcp on cooling (3rd figure)
- Could explain layering in inner core
- However, we calculate ~40% Ni required before fcc transition
What about nickel?

**Ab initio** $V_p$, $V_s$ on hcp-Fe-Ni

NB These are cold calculations done at 360 GPa…
hot calculations in progress!
Summary: a very simple explanation

- Observed $V_S$ are at least 10% lower than those of Fe and Fe-light element alloys at core conditions.

- Do not need assorted complicated explanations.

- Ni has an unexpectedly large effect on the velocities, particularly $V_S$, of the hexagonal close-packed (hcp) phase.

- Depending on the concentration of Ni in the core, our results show that the observed velocities in the Earth’s inner core are consistent with an Fe-Ni alloy in the hcp structure, with a low concentration of light-element.
Birch (1952): High Pressure Language

High pressure form:  

ordinary meaning: 

pure iron  

uncertain mixture of 

certain mixture of all the elements
Core solutions? Or more problems….

- Seismology giving much more detailed (interesting) structure of the core
- Inner core phase *if it was pure iron* would be hcp
- The presence of light elements and nickel changes everything
- But the free energy difference is always very very small
- Likely to be an “uncertain mixture of all the elements”

- The high $V_S$ for all phases is incompatible with seismology
- Needs a lot of melt in the inner core (%: >8$_{bcc}$ >12$_{hcp}$ >25$_{fcc}$)
- Anisotropy can be accounted for by fcc and hcp, not bcc!
What about light elements?

- Cold calculations predict transition to the CsCl-FeSi at ~13 GPa (Vočadlo et al. 1999)
- CsCl-FeX iso-structural with bcc
- CsCl-FeSi (Dobson et al., 2002)
- CsCl-FeS Sata et al., 2008
- At zero K, 330 GPa, few atm. % Si, S, O, C stabilises bcc-Fe (Côté et al. 2008)
What about light elements?

Free energy from lattice dynamics

\[
F = k_B T \sum_i \frac{\hbar \omega_i}{2k_B T} + \ln \left( 1 - e^{-\frac{\hbar \omega_i}{k_B T}} \right)
\]

\[
G = F + PV
\]

- \( \omega_i \) from phonon calculations
- Calculations zero \( K; T \) added at this stage
The Core: the only way out is in…….

**Phonon spectra of iron**

- Phonon dispersion as \( f(P) \)
- \( \text{bcc} \) becomes unstable at core \( P \)
- \( \text{hcp} \) and \( \text{fcc} \) vibrationally stable
- \( \text{hcp} \) more stable than \( \text{fcc} \)
- Cannot compare \( F_{\text{bcc}} \) with \( F_{\text{hcp}} \) or \( F_{\text{fcc}} \)
Phonon dispersion for \( bcc-Fe \) with \( Si \)

\( P = 330 \text{ GPa} \)

- Pure \( Fe \)
- 6.7 wt.\% \( Si \)
- 10.4 wt.\% \( Si \)

Silicon stabilises the \( bcc-Fe \) phase at high pressure
The Core: the only way out is in…….

Effect of light elements

$\Delta H_{(\text{bcc-hcp})}$ (meV)

atm. % concentration of ...

- Oxygen
- Silicon
- Sulphur
- Carbon

NB Zero K

Côté et al. (2008)
Stability of Fe with 10.4 wt.% Si at 330 GPa
Dihedral angle and planetary segregation

High T, 4 GPa

Fe-S in Fe

Fe-O in Fe

Low $\gamma$ (~27°) results in segregation

High $\gamma$ (138°) results in isolation

Immiscible system = high $\gamma$; low $\gamma$ = miscible system

What happens at planetary core P? What about Si, C....??

Implications for crystallisation dynamics of terrestrial cores (Fe-Si-O alloys)
But.... Ni works the other way....

DAC experiments of Huang et al. (1988); qualitatively in agreement with calculations of Vočadlo et al., 2006
What about nickel? Phonon dispersion for \textit{bcc-Fe} with Ni
\textit{P} = 330 GPa

6.25 atm. %  
9.375 atm. %
Phonon dispersion for \textit{hcp- and fcc-Fe} with Ni
\( P = 330 \text{ GPa}, \) \(12.5\text{ atm} \% \text{ Ni}\)

\[ \Delta G \sim 20-30 \text{ meV at } 5500 \text{ K} \]

These are not big numbers!
Stable phase of Fe in the IC according to UCL:

- It’s hcp.... (1999)
- No, it’s bcc... (2003)
- Oh, ok, it’s hcp..... (2008)
- No it’s fcc...... (2009)
- It’s an uncertain mixture of all the elements.... (2011)
Is it because of anelasticity.....

The reduction in $V_S$ due to shear wave attenuation is given by:

$$V(\omega, T) = V_0(T) \left(1 - \frac{1}{2} \cot \left( \frac{\pi \alpha}{2} \right) Q^{-1}(\omega, T) \right)$$

For the inner core:

- Quality factor, $Q = 100$ \textit{(Resovskiy et al., 2005)}
- freq dep of Q, $\alpha = 0.2-0.4$ \textit{(Jackson et al., 2000)}

This results in a decrease in the shear velocity of only 0.5-1.5%, nowhere near the >8% difference between the seismological observations and the calculated materials properties.
Single crystal S-wave velocities in fcc-Fe as a function of propagation direction:

a) $V_{S1}$
b) $V_{S2}$
c) $dV_S$

- Anisotropy strikingly large....
- Much larger than bcc- and hcp-Fe
• Single crystal P-wave velocities for fcc-Fe, fcc-Fe$_3$S and c) fcc-Fe$_3$Ni projected onto a sphere at inner core conditions with the colourscale denoting the P-wave velocity. (Unicef Careware, Mainprice, 1990).

• P-wave anisotropy 10-15%

• But not achievable along mutually perpendicular directions
Phonon dispersion for *bcc-Fe* with C

P = 330 GPa

- Unstable at low concentrations; stable with 4.73 wt. % C
- hcp unstable at this concentration, so cannot compare F
Phonon dispersion for \textit{bcc-Fe} with S or O

\( P = 330 \text{ GPa} \)

Unstable at all tested concentrations

\(<18.75 \text{ atm. } \% \equiv 11.7 \text{ wt}\% \text{ S, 6.2 wt}\% \text{ O})
The Core: the only way out is in......
Stability of Fe at 330 GPa and 5500 K

Gibbs free energy vs. Si concentration at 330 GPa and 5500 K
Can we match seismic anisotropy?

Tkalčić H. (2010)  
Sun & Song 2008
Single crystal P-wave velocities for:
   a) fcc-Fe
   b) bcc-Fe
   c) hcp-Fe

Max anisotropy 13.5%, 3.3% and 11.47%
But not mutually perpendicular directions

For fcc-Fe:
   ~1% <110>, ~3% <111> and 6% <100>
   Significant to full alignment required
   For <111>, increase anisotropy by layering

For bcc-Fe:
   the maximum anisotropy <2%
   so anisotropy could not be alignment alone

For hcp-Fe:
   ~3% with c-axis in equatorial plane
   need full alignment.