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9798190929331

Author

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Publication Date

2026-09-11

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA

Los Angeles

Magnetic Field Generation in Earth and Super-Earths:
the Role of Iron

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Planetary Science

by

Francis Dragulet

2026

ABSTRACT OF THE DISSERTATION

Magnetic Field Generation in Earth and Super-Earths: the Role of Iron

by

Francis Dragulet

Doctor of Philosophy in Planetary Science

University of California, Los Angeles, 2026

Professor Lars Stixrude, Chair

Earth's magnetic field has persisted for at least 3.4 billion years, yet the present-day core dynamo - driven by latent heat and compositional buoyancy from inner-core solidification - cannot have operated for most of that time, as the inner core is likely less than 1 billion years old. An alternative mechanism is required. A leading candidate is a basal magma ocean (BMO): a layer of iron-enriched silicate liquid that may have persisted at the base of the mantle for billions of years following Earth's magma-ocean stage. Whether this silicate dynamo operated, and whether analogous mechanisms generate fields in larger rocky exoplanets, depends on material properties that are poorly constrained or inaccessible to laboratory experiment.

This dissertation examines the material properties governing magnetic field generation and BMO stability in rocky planets, from Earth to super-Earths, through first-principles calculations using density functional theory and *ab initio* molecular dynamics. The key quantities are the Fe - Mg distribution coefficient between silicate liquid and the dominant lower-mantle minerals bridgmanite and post-perovskite, which controls BMO gravitational stability; and the electrical conductivity, thermal conductivity, and Seebeck coefficient of iron-enriched silicate liquid and liquid iron, which

govern whether the BMO and metallic core can sustain self-generating magnetic fields.

We find that iron is strongly incompatible in bridgmanite and post-perovskite - the dominant lower-mantle phases in Earth and super-Earths, respectively - supporting gravitationally stable basal magma oceans in both. Conductivities of iron-enriched silicate liquid at BMO conditions exceed the threshold for dynamo action while permitting vigorous convection, establishing a silicate dynamo as a viable mechanism for Earth's early field. Transport properties of liquid iron from 2.5 GPa to over 3 TPa constrain core dynamo viability across the super-Earth mass range and yield the first calculation of the Seebeck coefficient at deep planetary conditions. These results form a unified, materials-physics framework for the magnetic histories of rocky planets.

The dissertation of Francis Dragulet is approved.

Jonathan Aurnou

Hao Cao

Abby Kavner

Lars Stixrude, Committee Chair

University of California, Los Angeles

2026

To my brother Ian, and my parents.

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ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under grant EAR-2223935, and by the Future Investigators in NASA Earth and Space Science and Technology under Grant 80NSSC24K1713.

I would like to express my profound appreciation to my advisor Lars Stixrude, whose thoughtful mentorship and generous support over the past six years have helped me grow not only as a scientist and critical thinker, but, most importantly, as a person.

I am also grateful to the members of my doctoral committee: Jon Aurnou, Abby Kavner, and Hao Cao. Their distinct perspectives broadened my understanding of planetary science and encouraged me to see my work from new angles.

To my lab mates: Leslie Insixiengmay, Travis Gilmore, David James, Bing Hong Chua, and Junjie Dong. Thank you for sharing in the challenges of this journey and for making it, along the way, both memorable and entertaining.

Finally, my deepest thanks go to my brother Ian, the most important person in my life, and to my parents, whose love and sacrifices have laid the foundation for everything good that has followed.

VITA

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B.S., Physics Georgetown University, 2020

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Selected Publications

1. **Dragulet, F.**, Stixrude, L. (2024). Partitioning of iron between (Mg,Fe)SiO₃ liquid and bridgmanite. *Geophysical Research Letters*, 51(12), e2023GL107979.
2. **Dragulet, F.**, Stixrude, L. (2025). Electrical and thermal conductivity of Earth's iron-enriched basal magma ocean. *Proceedings of the National Academy of Sciences*, 122(42), e2509771122.
3. Nakajima, M., Harter, SK., Jasko, AV., Polsin, DN., Szumila, I., Cone, KA., Lherm, V., Blackman, EG., **Dragulet, F.**, Stixrude, L., Trail, D., Huff, M., Rygg, R.J., Paz, A., Collins, G., LaPierre, A., Sprowal, Z. (2026). Electrical conductivities of (Mg,Fe)O at extreme pressures and implications for planetary magma oceans. *Nature Astronomy*, 10, 248-257.
4. **Dragulet, F.**, Stixrude, L. (2026). Conductivity and thermoelectricity of iron up to super-Earth core conditions. (Manuscript in prep).
5. **Dragulet, F.**, Stixrude, L. (2026). Partitioning of iron between (Mg,Fe)SiO₃ liquid and post-perovskite. (Manuscript in prep).

Selected Presentations

1. **Dragulet, F.**, Stixrude, L. "Thermoelectricity at Earth's core-mantle boundary." American Geophysical Union Conference, New Orleans, LA., 2025.
2. **Dragulet, F.**, Stixrude, L. "Iron Partitioning in super-Earth mantles." American Geophysical Union Conference, New Orleans, LA., 2025.

3. **Dragulet, F.**, Stixrude, L. “Conducting MgO liquid and planetary dynamos.” 24th Biennial Conference of the APS Topical Group on Compression of Condensed Matter, Washington, D.C., 2025.
4. **Dragulet, F.**, Stixrude, L. “Conductivity and Thermoelectricity of Super-Earth Magma Oceans.” American Geophysical Union Conference, Washington, D.C., 2024.
5. **Dragulet, F.**, Stixrude, L. “Electrical and Thermal Conductivity of Iron-enriched Basal Magma Oceans in Early Earth and Super-Earths.” American Geophysical Union Conference, San Francisco, CA, 2023.
6. **Dragulet, F.**, Stixrude, L. “Partitioning of iron between (Mg,Fe)SiO₃ liquid and bridgmanite.” American Geophysical Union Conference, Chicago, IL, 2022.

CHAPTER 1

Introduction

1.1 The geodynamo and its limits

Earth possesses a global magnetic field, and its presence pervades everyday life. The most familiar example is the compass, long used for navigation because it aligns with the local field direction. Humans are not alone in this - some animals are also thought to rely on the geomagnetic field for long-distance navigation [1]. Beyond navigation, the interaction of the solar wind with the field gives rise to the auroras at high latitudes, and governs Earth's response to space weather more broadly: severe geomagnetic disturbances can degrade GNSS/GPS positioning [2], disrupt aviation and satellite communications [3], and induce currents capable of collapsing power grids [4]. Most consequential and relevant to this work, however, are the planetary-scale implications for habitability. The field deflects the solar wind and shields the atmosphere from erosion by solar-particle bombardment [5, 6], and has been linked to the timing of atmospheric oxygenation [7] - together suggesting that a long-lived geomagnetic field is crucial for Earth's habitability.

At the surface, the field has a mean strength of $\sim 40 \mu\text{T}$ and a geometry dominated by an axial dipole approximately aligned with the rotation axis (Fig. 1.1). It is also long-lived. When iron-bearing minerals such as magnetite cool through their Curie temperature (the critical temperature below which permanent magnetization occurs) in the presence of a magnetic field, they acquire a thermoremanent magnetization aligned with that field. The orientation and intensity of this magnetization, preserved over geological time, can then be recovered in the laboratory and used to reconstruct the field at the time of mineral formation [8]. Such paleomagnetic records indicate that Earth's field has been present, and similar in strength to its present value, for at least the past 3.4 billion years [9, 10].

The present-day field is generated by dynamo action: the conversion of the kinetic energy of a flowing electrically conducting fluid into magnetic energy, sustained against ohmic dissipation by induction. The evolution of the magnetic field $\mathbf{B}$ in a moving conductor with velocity field $\mathbf{u}$, electrical conductivity σ , and magnetic permeability μ is governed by the magnetic induction

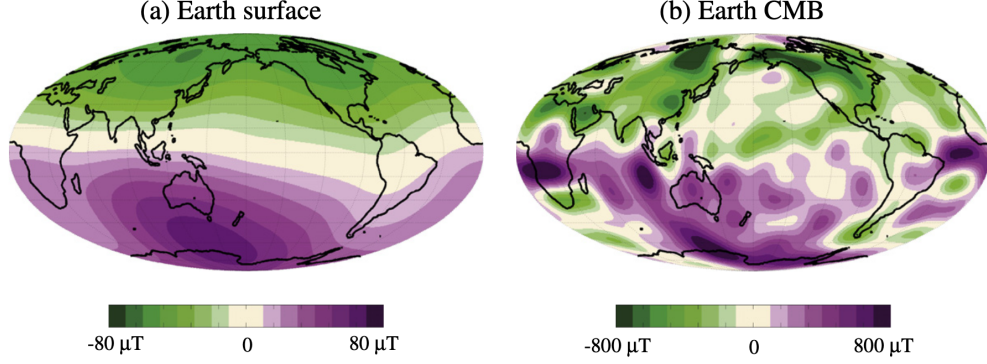


Figure 1.1: Earth’s radial magnetic field strength at the surface (left) and at the core-mantle boundary (right), from Schubert and Soderlund (2011) [11]. Color indicates whether the field is directed outwards (purple) or inwards (green).

equation,

$$\frac{\partial \mathbf{B}}{\partial t} = \nabla \times (\mathbf{u} \times \mathbf{B}) + \frac{1}{\mu\sigma} \nabla^2 \mathbf{B}, \quad (1.1)$$

in which the first term on the right represents inductive amplification of the field by the flow, and the second represents resistive diffusion. The competition between these two terms is characterized by the dimensionless magnetic Reynolds number,

$$R_m = \mu\sigma UL, \quad (1.2)$$

where U and L are characteristic velocity and length scales of the flow. When $R_m \gtrsim R_{m_c}$ — with the critical value $R_{m_c} = 10 - 100$ predicted by magnetohydrodynamic simulations [12] — induction outpaces diffusion, and a small seed field can be amplified to a self-sustaining state. Dynamo action therefore requires three ingredients: a sufficiently large layer (L) of electrically conducting fluid (σ), an energy source capable of driving flow through the fluid (U), and for sufficient rotation to organize the flow into the helical motions that sustain a large-scale field [13].

In Earth, all three ingredients are supplied by the outer core (Fig. 1.2): a layer of liquid iron alloyed with light elements that is roughly 2200 km thick today. The conductivity of liquid iron at core conditions yields R_m on the order of 10^3 for plausible core flow speeds [14], comfortably above the threshold for self-sustaining dynamo action. The energy that drives the flow, or convection, in the outer core comes from a combination of secular cooling, latent heat released as the inner core freezes, and compositional buoyancy generated when light elements are expelled from the

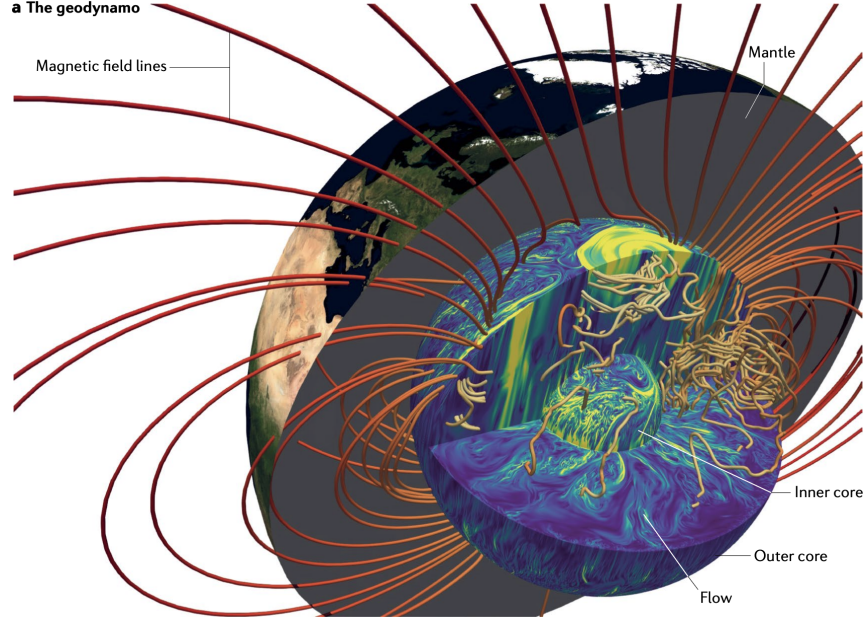


Figure 1.2: The geodynamo, from Landeau et al. (2022) [14]. Earth’s magnetic field, observed at the surface as a predominantly dipolar field with lines extending into space, is generated by convective flow of liquid iron in the outer core, with blue-to-yellow shading indicating the flow speed within the core. Other layers of the Earth’s interior (solid inner core, mantle, and crust) are also indicated.

solidifying inner core into the surrounding liquid [15]. The inner core provides two of these energy sources, and is crucial for powering the geodynamo.

However, the core-powered geodynamo as described above cannot have operated for most of Earth’s history. Geodynamo action needs convection, which requires the heat extracted through the core–mantle boundary (CMB), Q_{CMB} , to exceed the heat that can be conducted down the core adiabat,

$$Q_{\text{ad}} = 4\pi R_{\text{CMB}}^2 k \nabla T_{\text{ad}}, \quad (1.3)$$

evaluated at the CMB radius, R_{CMB} , with adiabatic temperature gradient, ∇T_{ad} . The adiabatic heat flux Q_{ad} is set by the thermal conductivity of liquid iron at core conditions, k . First-principles calculations [16, 17] predict $k \geq 100$ W/m/K, significantly larger than earlier estimates of ~ 30 W/m/K [18]. This means that Q_{ad} (around 15 TW) can exceed the heat extracted through the core–mantle boundary, with most estimates of the latter ranging from 10 to 15 TW [15, 19]. Convection in the modern core therefore depends on the compositional buoyancy supplied by inner-core solidification rather than on thermal driving alone. Thermal evolution models, however, predict a young

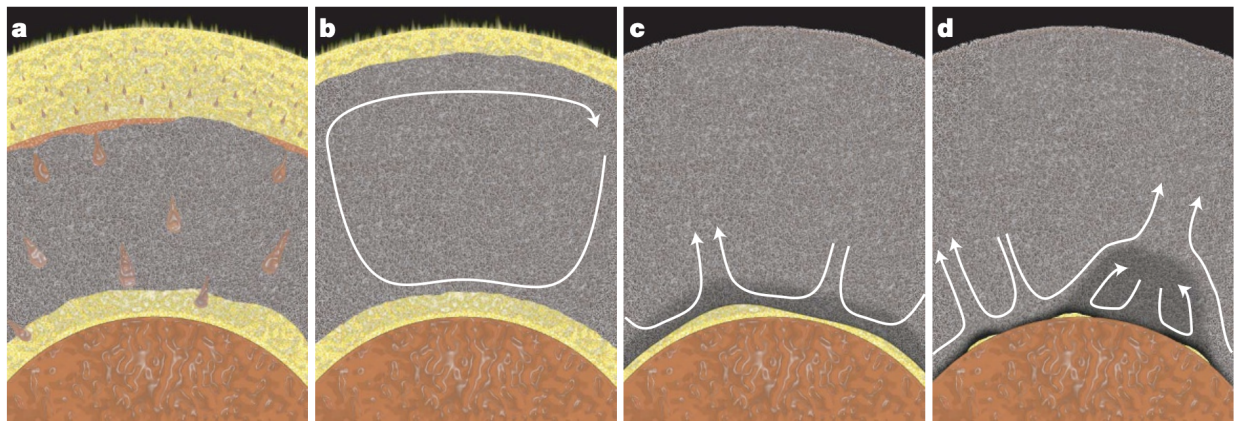


Figure 1.3: Crystallization of a molten mantle leading to a basal magma ocean, from Labrosse et al. (2007) [23]. The solid mantle is denoted by light gray, magma oceans by yellow, and iron-enriched liquid/core colored brown. Crystallization starts at mid-mantle depths, leaving a magma ocean at the surface and a basal magma ocean above the core (a). The solid layer will grow outwards b, with the surface magma ocean crystallizing well before the basal magma ocean (c), with the rate of crystallization controlled by mantle convection (white arrows). Possible entrainment of iron-enriched dense material (dark gray) at the end of crystallization (d) can explain many of the features of the present-day lower mantle.

inner core, less than 1 Gyr old [15, 20], while paleomagnetic records demonstrate that the field has existed for at least 3.4 Gyr. The magnetic field of the early Earth must therefore have been powered by a mechanism other than the one operating today.

1.2 The early Earth

To determine how the early Earth's magnetic field was powered, we must understand what the early Earth environment was like. It was extensively molten due to several large scale heat sources, including gravitational differentiation, radioactive heating, and accretionary impacts [21]. Simulations of the moon-forming impact predict that it likely melted the entire mantle, regardless of the initial configuration of the Earth-Moon system [22]. This molten mantle, or magma ocean, set the initial chemical and thermal state of the silicate mantle, and the manner in which it crystallized largely determined the deep structure that emerged from it.

The simplest, and older, picture of magma-ocean crystallization has solidification proceeding from the bottom up: as the mantle cooled, the liquidus and adiabat first intersected at the core–mantle boundary, and crystals formed there sank or remained in place while the residual liquid

retreated to the surface. This picture is consistent with the observation that, for an iso-chemical silicate system, the dominant lower-mantle mineral, MgSiO_3 bridgmanite, is denser than its coexisting liquid throughout the lower mantle [24].

An emerging view, however, has the magma ocean crystallizing from the middle outward [23, 25]. The adiabat of a deep magma ocean is steeper than its liquidus, so the two first intersect at mid-mantle depths rather than at the CMB [24]. Crystallization beginning at mid-mantle depths produces two separate magma layers: an upper layer that solidifies toward the surface, and a deeper layer trapped beneath the crystallizing mid-mantle solid, which evolves toward the base of the mantle as it cools. The latter is the basal magma ocean (BMO) [23], which being insulated from the surface by the overlying solid mantle, can persist for billions of years [26, 27]. A BMO may explain the anomalous seismic properties in the lower mantle, in large low-shear-velocity provinces (LLSVPs) and ultra-low-velocity zones (ULVZs) [28, 29], and isotopic anomalies in mantle-derived rocks [30].

A BMO is gravitationally stable only if the silicate liquid is denser than the coexisting crystalline assemblage at lower-mantle conditions [31, 32]. As depth increases, the density of silicate liquid approaches that of the coexisting crystals [33], and if iron, the principal heavy element in the silicate system, partitions preferentially into the liquid, the liquid density can exceed that of the solid. In this scenario, newly formed crystals are buoyant and rise away from the BMO, while iron-enriched liquid remains trapped at the base.

The gravitational stability of a basal magma ocean is therefore controlled by the degree to which iron partitions between silicate liquid and the coexisting solid. This partitioning is quantified by the Fe-Mg distribution coefficient K_D

$$K_D = \frac{X_{\text{Fe}}^{\text{sol}} / X_{\text{Mg}}^{\text{sol}}}{X_{\text{Fe}}^{\text{liq}} / X_{\text{Mg}}^{\text{liq}}}, \quad (1.4)$$

where X_i^j is the concentration of species i in phase j . While there is a consensus that iron is incompatible ($K_D < 1$) in the dominant lower-mantle phases, the value of K_D is not well constrained. This is especially the case for bridgmanite, which makes up roughly 75% of the lower mantle [34], and is likely the first phase to crystallize out of the magma ocean [35], so its buoyancy lays the foundation for the rest of the crystallization process. Experimental measurements of K_D

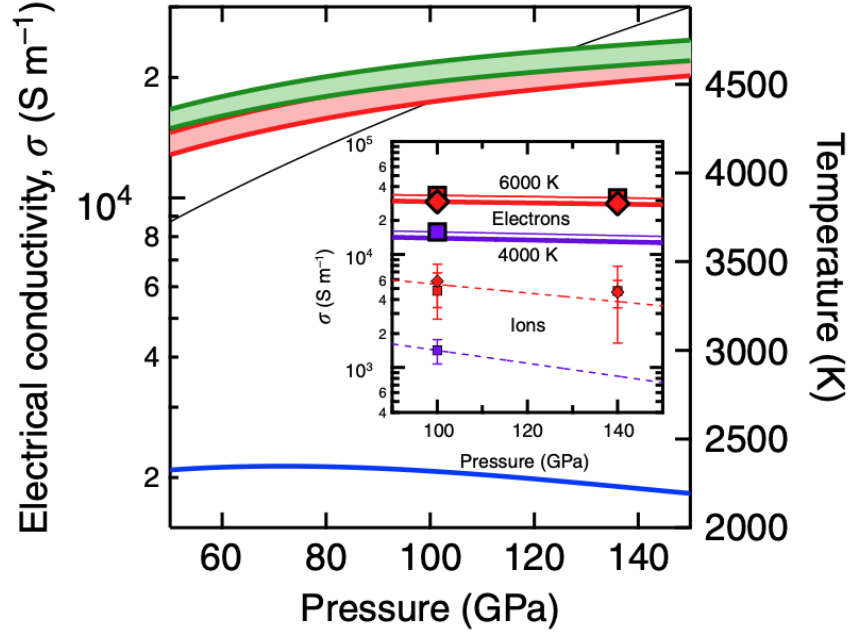


Figure 1.4: The electrical conductivity of silicate liquid at basal magma ocean pressures along the magma ocean isentrope (green), with contributions from electrons (red) and ions (blue), from Stixrude et al. (2020) [38]. The total electrical conductivity exceeds the threshold for dynamo activity ($> 10^4$ S/m) - see text.

between bridgmanite and silicate liquid range from 0.06 to 0.6 [36, 37], with values on the lower end of this range consistent with a stable basal magma ocean, and values at the upper end of this range predicting that a BMO will not exist.

Constraining K_D at lower-mantle conditions is therefore essential to determining whether a basal magma ocean existed in Earth's past. Should one have formed and persisted, it becomes a natural candidate setting for the early geomagnetic field, provided it is electrically conductive enough to host a dynamo. Whether this is the case is the question taken up next.

1.3 The silicate dynamo

Generating a magnetic field in a basal magma ocean requires the same three ingredients as generating one in the outer core: a conducting fluid, vigorous convection, and rotation. The third is supplied by the planet. The first two depend on the material properties of silicate liquid at BMO conditions, 100–140 GPa and 4000–6000 K.

The conductivity requirement is the more demanding. Silicate liquids at low pressure are elec-

trical insulators, with conductivities at upper-mantle conditions many orders of magnitude below those of metallic iron [39]. Ziegler and Stegman [40] first proposed that a BMO might nevertheless drive a dynamo, but the conductivity of silicate liquid at the lowermost mantle was at the time unknown. Stixrude et al. [38] closed this gap with first-principles molecular dynamics simulations of liquid of a bulk silicate composition at BMO conditions, finding $\sigma > 10^4$ S/m — more than two orders of magnitude larger than at ambient conditions, and large enough that the resulting magnetic Reynolds number exceeds the threshold for dynamo action (Fig. 1.4). The physical origin of this enhancement is a shift in the dominant charge carrier: at low pressure, conduction in silicate liquids is carried by mobile ions, while at extreme compression, the electronic band gap closes and conduction becomes electronic [38].

Whether a silicate dynamo could in fact have powered the early geomagnetic field, however, depends on conductivities computed for the right composition. Previous first-principles calculations of magma conductivity at high pressure have focused on simplified compositions: MgO, SiO₂, and MgSiO₃ [38, 41–43]. Bulk silicate Earth liquid, used by Stixrude et al. [38], is a more realistic representation, but it captures only the composition of the magma ocean prior to crystallization. As the BMO crystallized, iron — incompatible in bridgmanite and the other lower-mantle phases (Section 1.2) — accumulated in the residual liquid, progressively enriching it over geological time. This iron enrichment is expected to raise the electrical conductivity further, because iron is the principal carrier of conduction electrons in silicate liquid, in the same way that metallic iron carries conduction in the core. The iron enrichment might be crucial for a silicate dynamo, as the dynamo threshold for a thin BMO shell may be larger than that for the core [44]. The result is a BMO whose magnetic Reynolds number changes substantially over its lifetime, both in magnitude and in time evolution — neither of which is captured by calculations on bulk silicate Earth composition.

The same iron enrichment that raises the electrical conductivity will also raise the thermal conductivity. This matters because dynamo action requires not only a conducting fluid but also active convection (Section 1.1). If thermal conductivity rises too high, heat is transported by conduction rather than by fluid motion, and convection — and with it the dynamo — is suppressed [45]. This is the failure mode of the modern core, where the electronic thermal conductivity of liquid iron places Q_{ad} close to, or exceeding, Q_{CMB} . Whether the same limit applies to an iron-enriched BMO depends on how strongly iron raises the thermal conductivity of silicate liquid — a quantity that has

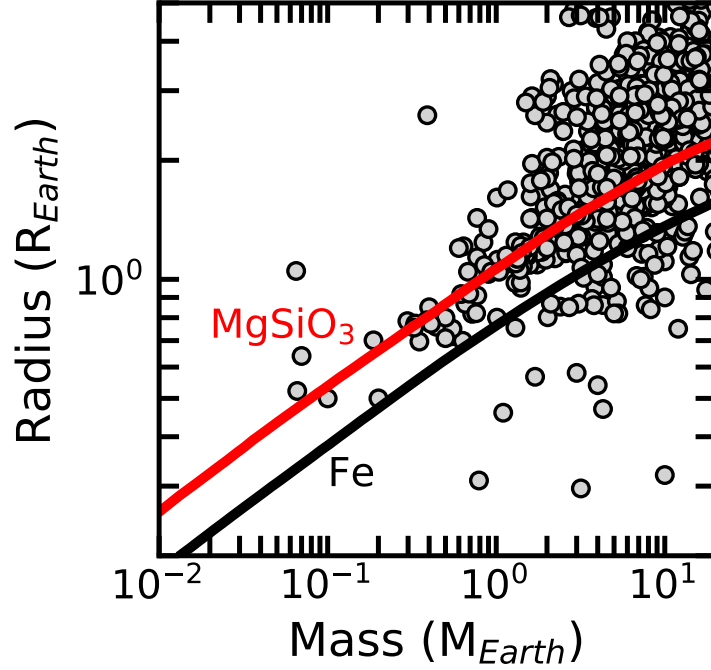


Figure 1.5: Mass–radius diagram for known small exoplanets, from the NASA exoplanet archive. Solid curves show theoretical mass–radius relations for planets of uniform composition: pure iron (black) and pure MgSiO_3 (red). Many exoplanets lie between the pure-iron and pure- MgSiO_3 bounds, consistent with rocky interiors composed of a metallic iron core and a silicate mantle, called super-Earths.

not been computed.

Constraining the electrical and thermal conductivities of iron-enriched silicate liquid at BMO conditions is therefore essential to determining whether a basal magma ocean could have generated Earth’s early magnetic field prior to inner core nucleation.

1.4 Super-Earth interiors and their dynamos

Much of the discussion in Sections 1.1–1.3 may apply to rocky planets beyond Earth. Of particular interest are super-Earths: a population of exoplanets with masses between ~ 1 and $\sim 10 M_\oplus$ and radii between ~ 1 and $\sim 2 R_\oplus$. Thousands have been identified by transit surveys, most notably the *Kepler* mission [46]. As shown in Fig. 1.5, these super-Earths fall between mass–radius curves computed for pure iron and pure MgSiO_3 , consistent with interiors composed of an iron core overlain by a silicate mantle — the same two-layer structure as Earth [47]. These planets are therefore the natural extension of the rocky-planet population beyond the Solar System, and they

raise the immediate question of whether they, too, generate magnetic fields by the mechanisms developed in the previous three sections.

Whether super-Earths host magnetic fields, however, is currently unknown. No direct measurement of an exoplanet magnetic field has been confirmed to date, and while several detection methods are under active development, they currently favor gas giants over terrestrial planets [6]. Inferring whether a given super-Earth generates its own magnetic field therefore depends, for the foreseeable future, on theoretical assessment of whether the mechanisms developed in Sections 1.1–1.3 can operate at super-Earth interior conditions.

The interior structure of super-Earth exoplanets is also poorly constrained by mass and radius alone [47], but the thermal state of their interiors can be estimated from the energetics of accretion. The kinetic energy delivered by giant impacts, combined with the gravitational energy released during core formation and relatively short orbital radii, is sufficient to melt a super-Earth several times over, and super-Earths probably complete their accretionary phase in an entirely molten state [48]. As super-Earths cool from this initial molten state, the same competition between crystal and liquid density that controlled magma-ocean crystallization in Earth (Section 1.2) determines whether the residual liquid is concentrated at the base of the mantle, producing a long-lived basal magma ocean. The dominant lower-mantle phase in a super-Earth, however, is not bridgmanite but likely post-perovskite (ppv), the high-pressure phase of MgSiO_3 that becomes stable above ~ 120 GPa [49], and up to roughly 700 GPa [50]. Whether a basal magma ocean is gravitationally stable in a super-Earth therefore depends on the equation of state and iron partitioning (K_D) of post-perovskite at these pressures, material properties that are poorly constrained.

If a basal magma ocean does form and persist, super-Earths host two candidate sites for magnetic field generation: the metallic core, and the basal magma ocean above it. The conditions developed in Sections 1.1 and 1.3 apply directly to both. For the core, the question is whether thermal convection alone can drive a dynamo, or whether compositional buoyancy from inner-core solidification is required (as in Earth); the answer depends on the electrical and thermal conductivities of iron at pressures and temperatures well beyond those of Earth’s core. For the BMO, the question is whether the silicate-dynamo pathway, established in Section 1.3, can extend to a super-Earth lower mantle, given that BMO existence itself is contingent on the partitioning question above. Whether either operates depends on calculating the relevant material properties

using first-principles simulations across the super-Earth pressure–temperature range, which have not been systematically performed.

1.5 Thermoelectric dynamos

A third pathway for generating planetary magnetic fields, distinct from both the core and silicate dynamos that may operate in rocky planet interiors, is the thermoelectric effect. A material subject to a temperature gradient develops an electric field proportional to that gradient, characterized by the Seebeck coefficient S . At a conducting interface between two materials with different Seebeck coefficients — such as a planet’s core–mantle boundary — and in the presence of lateral temperature variations along that interface, the resulting electromotive force drives thermoelectric currents that produce a toroidal magnetic field, which can in turn be converted to a poloidal field by convective helicity in the core [51, 52]. Recent magnetohydrodynamic experiments have shown that Seebeck contrasts of order $10\ \mu\text{V/K}$ are sufficient to drive dynamically significant flows and generate induced magnetic fields, at both solid-liquid [53] and liquid-liquid [54] metal interfaces, placing the mechanism within reach of materials at planetary interior conditions.

The physical preconditions for this mechanism plausibly hold in rocky planet interiors. Lateral temperature variations of several hundred kelvin may exist at Earth’s core–mantle boundary, as inferred from seismic tomography [55], and similar or larger variations may occur in super-Earths. For the resulting thermoelectric currents to flow, however, both sides of the interface must be electrically conductive — a condition that is plausibly met in super-Earth interiors, where extreme pressures raise silicate conductivities to semi-metallic values ([43, 56]) and may permit thermoelectric circuits to close through the mantle. Despite these potential pathways to significant thermoelectric currents, this mechanism has seen little attention, in large part because the Seebeck coefficients of the relevant materials are essentially unknown. The Seebeck coefficient of liquid iron, which sets the core-side contribution to any thermoelectric circuit at the CMB, has not been measured or computed above modest pressures, and the corresponding Seebeck coefficients of the candidate mantle phases — ferropericlase, bridgmanite, post-perovskite, and iron-bearing silicate melts at lower-mantle conditions — are also unconstrained. Whether the thermoelectric mechanism contributes to the magnetic fields of Earth or super-Earths therefore depends on a set of material

properties that has not been computed.

1.6 Material properties

The questions of Sections 1.1–1.4 reduce to several material properties evaluated under conditions that are either poorly constrained or inaccessible to laboratory experiments.

For Earth, two sets of quantities are required. Whether a basal magma ocean is gravitationally stable depends on the Fe–Mg distribution coefficient K_D (Eq. 1.4) between bridgmanite and coexisting silicate liquid, together with the equations of state of both phases. Whether Earth’s BMO can host a dynamo then depends on the electrical conductivity σ_{el} and electronic thermal conductivity k_{el} of iron-enriched silicate liquid at conditions appropriate to the lowermost mantle. At these extreme conditions, the electronic contribution to charge and heat transport dominates over other contributions, and we focus on this contribution in this work.

For super-Earths, the corresponding quantities are evaluated for different phases and at substantially higher pressures. Whether a core dynamo is thermally permitted depends on σ_{el} and k_{el} of liquid iron from Earth’s core conditions out to the terapascal pressures and $\sim 10^4$ K temperatures characteristic of super-Earth core interiors. Whether a thermoelectric mechanism can contribute to the field depends, in addition, on the Seebeck coefficient S of liquid iron at these same conditions, together with the corresponding Seebeck coefficients of the overlying mantle phases. Whether a basal magma ocean is gravitationally stable depends on the same partitioning argument as for Earth, but with bridgmanite replaced by post-perovskite as the dominant lower-mantle phase, and at pressures spanning the entire super-Earth lower-mantle range.

Five material properties — K_D^{bdg} , K_D^{ppv} , σ_{el} , k_{el} , and S — evaluated across several different materials and over a pressure range spanning more than an order of magnitude, between them determine the gravitational stability of basal magma oceans, the viability of core, silicate, and thermoelectric dynamos, and the magnetic histories of rocky planets from Earth to the largest super-Earths. Besides K_D for bridgmanite, which is poorly constrained, the remaining quantities have not been systematically measured or computed across the full range of conditions required.

These quantities can, however, be computed from first principles. Density functional theory (DFT) provides a framework in which the structure and properties of a material can in principle

be determined from a remarkably minimal set of inputs: the identities of the atoms present, and the fundamental constants of physics. No empirical parameters, no fitted potentials, no laboratory calibration. The macroscopic behavior of a material — its equation of state, its phase relations, its transport coefficients — is contained in the quantum-mechanical behavior of its electrons. Solving for that behavior is computationally demanding but conceptually direct, and yields predictions at conditions that no experiment can reach.

1.7 Overview of the dissertation

The remainder of the dissertation is divided into methods and results chapters.

Chapter 2 develops density functional theory from the principles of quantum mechanics, motivating the Kohn–Sham equations and the exchange–correlation approximations used in this work. Chapter 3 develops electron transport theory from band theory through the Drude and Sommerfeld free-electron models, the Boltzmann description of the Onsager kinetic coefficients, and finally the Kubo–Greenwood expression that is the central computational tool for σ_{el} , k_{el} , and S . Chapter 4 describes the practical implementation of these theories in simulation: plane-wave basis sets, k -point sampling, projector-augmented-wave pseudopotentials, finite-temperature DFT, ab initio molecular dynamics, and thermodynamic integration.

The four results chapters apply this framework to the four material-property questions of Section 1.6.

Chapter 5 (reproduced from Dragulet & Stixrude, 2024 [57]) computes the Fe–Mg distribution coefficient between (Mg,Fe)SiO₃ liquid and bridgmanite over Earth’s lower-mantle conditions. The key result is that iron is strongly incompatible in bridgmanite at all relevant pressures, and that the resulting density crossover supports a gravitationally stable basal magma ocean in Earth’s lower mantle.

Chapter 6 (reproduced from Dragulet & Stixrude, 2025 [58]) computes the electrical and electronic thermal conductivities of iron-enriched silicate liquid at conditions appropriate to Earth’s basal magma ocean. The conductivity is sufficient to support a self-sustaining silicate dynamo, providing a viable mechanism for the early Earth’s magnetic field in the era preceding inner core nucleation.

Chapter 7 extends the transport-property calculation to pure iron across the full pressure–temperature range relevant to super-Earth cores. The electrical conductivity, electronic thermal conductivity, and Seebeck coefficient of iron are computed from 2.5 GPa to 4 TPa and from 900 K to 25,000 K. The Seebeck coefficient, in particular, has not previously been computed at deep planetary conditions; this work provides the first such calculation, benchmarked against existing low-pressure experimental measurements before extending to the super-Earth core regime. The corresponding Seebeck coefficients of mantle phases, required for a complete evaluation of the thermoelectric pathway, are left for future work. The thermal conductivities are incorporated into self-consistent interior-structure models for planets of 1–10 $M_{\oplus}$ at three core mass fractions, mapping the regimes in which thermal core dynamos are thermodynamically permitted.

Chapter 8 extends the partitioning calculation to the (Mg,Fe)SiO₃ liquid–post-perovskite system, at conditions spanning super-Earth lower mantles. Iron is found to be even more incompatible in post-perovskite than in bridgmanite, and the density crossover persists across the relevant pressure range. Basal magma oceans are therefore expected to be a generic feature of large rocky planets, and the silicate-dynamo pathway of Chapter 6 extends naturally to super-Earths.

Together, the four results chapters trace a unified materials-physics picture of magnetic field generation in rocky planets. The conventional core dynamo, the silicate dynamo of an iron-enriched basal magma ocean, and the conditions under which each operates are all governed by the same small set of first-principles material properties, computed within a common framework. Earth and super-Earths emerge not as separate problems but as different points in the same parameter space, and the magnetism of rocky planets as a property determined, in the end, by the behavior of iron at extreme conditions.

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CHAPTER 2

Background: Density Functional Theory

2.1 Introduction

The behavior of planetary interiors is governed by the properties of the materials from which they are composed. Equations of state, phase stability, elemental partitioning between coexisting phases, and the transport of heat and charge all enter directly into our understanding of how planets are structured, how they evolve, and how they generate the signals (seismic, magnetic, gravitational, etc.) by which we observe them. Constraining these material properties at the pressures and temperatures of planetary interiors is therefore central to planetary science and geophysics.

The conditions in planetary interiors are difficult to reach, or reproduce, in the laboratory. Diamond anvil cells and shock compression experiments have made remarkable progress, but each technique has its own limitations in pressure, temperature, and the range of properties that can be measured simultaneously. Many quantities of geophysical interest remain difficult or impossible to determine experimentally with confidence.

At a fundamental level, however, the material properties relevant to planetary interiors are all consequences of quantum mechanics. The compressibility of a mineral arises from how its electrons rearrange as the lattice is compressed; the partitioning of an element between two phases reflects small differences in the electronic energies of the two environments; the electrical conductivity of a metal depends on how electrons scatter and propagate through the lattice. If the equations of quantum mechanics can be solved for the electrons in a material, these properties can in principle be computed from first principles, at any conditions and compositions of interest.

The materials that make up planetary interiors are condensed matter systems - solids and liquids in which large numbers of atoms, and therefore very large numbers of electrons, interact with one another. Solving the equations of quantum mechanics exactly is not possible for any system of more than a few electrons, and condensed matter lies far beyond this limit. Practical first-principles calculations therefore rely on approximations, and the approximation framework used

throughout this work is density functional theory (DFT). The remainder of this chapter develops DFT from the principles of quantum mechanics, motivates the approximations on which it depends, and describes the practical considerations involved in applying it to condensed matter at planetary conditions.

Much of the material in this chapter is standard quantum chemistry and electronic structure theory, and the development presented here draws on these references [1–3], and material covered in graduate coursework. Specific background and methods that go beyond this are cited individually as they appear.

2.2 Wave-particle duality

Quantum mechanics began with the recognition of wave-particle duality. In classical physics, particles and waves were treated as fundamentally different: particles were localized objects with a definite position and momentum, while waves were spread out and characterized by a wavelength and frequency. By the early twentieth century, a series of experiments had shown that this distinction breaks down at small scales, and that both matter and radiation can exhibit either kind of behavior depending on the experiment performed.

The wave nature of light had been firmly established by the nineteenth century, through Young's demonstration of interference in 1801 and Maxwell's identification of light as an electromagnetic wave. The first cracks in this picture appeared in the study of blackbody radiation, where the classical electromagnetic theory predicted an unphysical divergence in emitted intensity at high frequencies, in stark disagreement with experiment. In 1900, Planck resolved this discrepancy by postulating that the oscillators responsible for emission could only exchange energy in discrete quanta of size $h\nu$, where h is Planck's constant and ν is the frequency. Einstein extended this idea in 1905 to explain the photoelectric effect, in which light incident on a metal ejects electrons whose kinetic energy depends on the frequency of the light rather than its intensity. Einstein interpreted this as evidence that light itself is composed of particle-like quanta, later called photons, each carrying energy $E = h\nu$. Light, long understood as a wave, also behaved as a particle.

In 1924, de Broglie proposed that this duality is not unique to light, and that all matter pos-

sesses a wavelength

$$\lambda = \frac{h}{p} \quad (2.1)$$

where p is the particle's momentum. For macroscopic objects λ is negligibly small and the wave-like behavior is unobservable, but for electrons it is comparable to atomic dimensions. This prediction was confirmed in 1927 by Davisson and Germer, who observed diffraction of electrons scattered from a nickel crystal. Subsequent experiments demonstrated that the diffraction pattern persists even when electrons are sent through the apparatus one at a time, indicating that each electron interferes with itself.

The wave nature of matter has profound consequences for what can be known about a particle's state. In classical mechanics, the position and momentum of a particle can in principle be specified simultaneously to arbitrary precision, and Newton's equations then determine the future evolution of the system. In quantum mechanics, this is no longer possible. Heisenberg's uncertainty principle states that the uncertainties in a particle's position and momentum along a given direction satisfy

$$\Delta x \Delta p_x \gtrsim \hbar \quad (2.2)$$

so that knowledge of one comes at the expense of knowledge of the other. The deterministic trajectories of classical mechanics must therefore be replaced by a probabilistic description, encoded in a wavefunction whose evolution is governed by the Schrödinger equation.

2.3 The Schrödinger equation

In quantum mechanics, the state of a system is described by a wavefunction Ψ , and the evolution of this wavefunction in time is governed by the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t) \quad (2.3)$$

where $\hbar = h/2\pi$ and $\hat{H}$ is the Hamiltonian operator. An operator is a rule that acts on a function to produce another function; for example, $\hat{D} = d/dt$ is the operator that returns the time derivative of whatever it acts on. The Hamiltonian has the same form as its classical counterpart, $\hat{H} = \hat{P}^2/2m + V(\hat{X})$, but with the position x and momentum p replaced by the corresponding operators

$\hat{X}$ and $\hat{P}$. The momentum operator takes the form $\hat{P} = -i\hbar d/dx$, which can be obtained by combining the de Broglie relation (Eq. 2.1) with the assumption that the wavefunction has the form of a plane wave, $\Psi(x, t) = Ae^{i(kx - \omega t)}$. For a single nonrelativistic particle moving in a three-dimensional potential, the Schrödinger equation becomes

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right] \Psi(\mathbf{r}, t) \quad (2.4)$$

Given the wavefunction at one instant in time, Eq. 2.3 determines the wavefunction at all future times. The wavefunction itself is not directly observable; instead, $|\Psi(\mathbf{r}, t)|^2 d\mathbf{r}$ gives the probability of finding the particle in a volume element $d\mathbf{r}$ around position $\mathbf{r}$ at time t . Quantum mechanics is therefore statistical in nature: even with complete knowledge of the wavefunction, only the probabilities of various measurement outcomes can be predicted.

For systems in which the potential is time-independent, the wavefunction can be separated into spatial and temporal parts, and the spatial part satisfies the time-independent Schrödinger equation,

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (2.5)$$

or, for a single nonrelativistic particle,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (2.6)$$

where E is the total energy of the system. This is an eigenvalue equation: solutions exist only for particular values of E , which correspond to the allowed energy levels of the system. Determining these energies and the associated wavefunctions is the central problem of quantum mechanics.

The time-independent Schrödinger equation can be solved exactly only for a small number of idealized systems, such as the particle in a box, the harmonic oscillator, and the hydrogen atom. For the systems of interest in this work (condensed matter consisting of many interacting nuclei and electrons), exact solutions are not possible, and a series of approximations is required. The first of these is the Born-Oppenheimer approximation.

2.4 Born-Oppenheimer approximation

The systems of interest in this work consist of many interacting nuclei and electrons. Treating the nuclei and electrons as point particles, and neglecting relativistic and spin-orbit effects, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{\nabla_{\alpha}^2}{m_{\alpha}} - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{r_{\alpha\beta}} - \sum_{\alpha, i} \frac{Z_{\alpha} e^2}{r_{i\alpha}} + \sum_{i \neq j} \frac{e^2}{r_{ij}} \quad (2.7)$$

where α and β index the nuclei and i and j index the electrons. The first two terms are the kinetic energies of the nuclei and electrons, and the remaining three are the Coulomb interactions between pairs of nuclei, between nuclei and electrons, and between pairs of electrons.

This Hamiltonian can be simplified by exploiting the large mass difference between nuclei and electrons. Even the lightest nucleus, the proton, is roughly two thousand times heavier than the electron, and so the electrons respond to changes in the nuclear positions on timescales much shorter than those on which the nuclei themselves move. To a good approximation, the electrons can therefore be treated as adjusting instantaneously to any nuclear configuration, while the nuclei see only the time-averaged electronic distribution. This is the Born-Oppenheimer approximation, and it allows the full problem to be separated into an electronic problem at fixed nuclear positions and a nuclear problem on the resulting potential energy surface.

In the electronic problem, the nuclei are held fixed, so the nuclear kinetic energy does not appear, and the nuclear-nuclear Coulomb repulsion is a constant for a given nuclear configuration that can be added to the total energy at the end. What remains is the time-independent Schrödinger equation for the many-electron wavefunction,

$$\left[-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i, \alpha} \frac{Z_{\alpha} e^2}{r_{i\alpha}} + \sum_{i \neq j} \frac{e^2}{r_{ij}} \right] \Psi = E \Psi \quad (2.8)$$

solved at a given configuration of nuclei.

Eq. 2.8 is the foundation of the quantum-mechanical theory of electronic structure, but it is far too complex to solve directly for any system of practical interest. The difficulty lies in the dimensionality of the many-electron wavefunction, which depends on the coordinates of all N electrons

and therefore lives in a space of $3N$ dimensions. Suppose, for instance, that representing the wavefunction along a single spatial dimension required only three values on a coarse grid; the full wavefunction would then require 3^{3N} values to specify. For the body-centered cubic unit cell of iron, which contains two iron atoms and a total of 52 electrons, this is $3^{156} \sim 10^{74}$ values. Even on the fastest current supercomputers, which perform on the order of 10^{18} operations per second, evaluating this many quantities would take roughly 10^{56} seconds — many orders of magnitude longer than the age of the universe, $\sim 10^{17}$ seconds.

Storage poses a similar problem. The number of bits required to record an approximate wavefunction is $B = q^{3N}$, where q is the number of bits used per coordinate. Even with the optimistic choice $q = 3$, a system of only $N = 100$ electrons would require $B \sim 10^{150}$ bits, vastly exceeding the number of atoms in the observable universe! The many-electron Schrödinger equation cannot, then, be solved directly.

2.5 The variational principle

The many-electron Schrödinger equation cannot be solved exactly, but a powerful tool for approximating its ground-state solution is provided by the variational principle. The principle states that for any normalized trial wavefunction ψ , the expectation value of the Hamiltonian

$$E[\psi] = \int \psi^* \hat{H} \psi d\tau \quad (2.9)$$

is an upper bound on the true ground-state energy E_0

$$E[\psi] \geq E_0 \quad (2.10)$$

with equality if and only if ψ is the true ground-state wavefunction. The quantity $E[\psi]$ is a *functional* of ψ : it takes a function as input and returns a number.

The variational principle turns the search for the ground-state energy into a minimization problem. If the trial wavefunction is allowed to depend on a set of parameters, the parameters can be varied to minimize $E[\psi]$, with the minimum providing the best approximation to E_0 achievable within the chosen functional form. The accuracy of the result therefore depends on how flexibly the

trial wavefunction can represent the true ground state. This idea underlies most of the approximations developed in the remainder of this chapter: the Hartree and Hartree-Fock methods restrict the trial wavefunction to particular forms and minimize the energy with respect to single-electron orbitals, while density functional theory recasts the minimization in terms of the electron density rather than the wavefunction itself.

2.6 The Hartree approximation

The simplest way to make the many-electron Schrödinger equation tractable is to assume that each electron moves independently in an average potential generated by the others. In the Hartree approximation, this is implemented by writing the many-electron wavefunction as a product of single-electron wavefunctions,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \cdots \psi_N(\mathbf{r}_N) \quad (2.11)$$

Each electron is described by its own one-particle wavefunction, and correlations between the motions of different electrons are neglected.

Applying the variational principle to this trial wavefunction, the expectation value of the many-electron Hamiltonian (Eq. 2.8) is minimized with respect to the single-electron wavefunctions, subject to the constraint that they remain orthonormal. The result is a set of coupled single-particle equations, the Hartree equations,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \sum_{\alpha} \frac{Z_{\alpha} e^2}{|\mathbf{r} - \mathbf{R}_{\alpha}|} + e^2 \sum_{j \neq i} \int \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2.12)$$

where $\mathbf{R}_{\alpha}$ are the positions of the nuclei and ϵ_i is the single-particle energy of orbital ψ_i . The first term is the kinetic energy, and the second is the Coulomb attraction between the electron and the nuclei. The third term, the Hartree potential V_H , describes the electrostatic interaction of the electron with the mean charge density of all other electrons. Recognizing that the total electron density is $n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$, the Hartree equation can be written compactly as

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2.13)$$

The Hartree equations are nonlinear, because the potential acting on each electron depends on the densities of all the others, and they must be solved self-consistently. One starts with a guess for the orbitals ψ_i , computes the resulting density $n(\mathbf{r})$ and Hartree potential V_H , solves the Hartree equations to obtain a new set of orbitals, and iterates until the input and output orbitals agree to within a chosen tolerance. This self-consistent field procedure is common to nearly all of the methods developed in the rest of this chapter, including Hartree-Fock and Kohn-Sham DFT.

Despite reducing the many-electron problem to a tractable set of single-particle equations, the Hartree approximation has serious shortcomings. It treats each electron as moving in a smooth average density rather than responding to the instantaneous positions of the other electrons, so the correlated motion that arises from Coulomb repulsion is entirely absent. More fundamentally, the product wavefunction in Eq. 2.11 fails to respect the antisymmetry required of fermionic wavefunctions, and so the consequences of the Pauli exclusion principle, including the exchange interaction, are missing. Both of these omissions must be addressed before the theory can describe real electronic systems.

2.7 Pauli exclusion and Slater determinants

The failure of the Hartree approximation to capture the antisymmetric character of the many-electron wavefunction must now be addressed. Electrons are fermions, particles characterized by half-integer spin and obeying Fermi-Dirac statistics, and their wavefunctions are subject to two related constraints. The first is the Pauli exclusion principle, which states that no two electrons can occupy the same single-particle quantum state. The second, from which the Pauli principle follows, is that the many-electron wavefunction must be antisymmetric under the exchange of any two electrons.

The antisymmetry requirement can be motivated by considering a system of two indistinguishable electrons described by a wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$. Because the electrons are indistinguishable, the probability density must be unchanged when their labels are exchanged,

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2 \quad (2.14)$$

which permits the wavefunction itself to be either symmetric ($\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1)$) or antisymmet-

ric ($\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$) under the exchange. Particles whose wavefunctions are symmetric are bosons; those whose wavefunctions are antisymmetric are fermions, and electrons fall into the latter category. The antisymmetric two-electron wavefunction constructed from single-particle orbitals ϕ_1 and ϕ_2 is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)] \quad (2.15)$$

which can be written compactly as the determinant

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) \end{vmatrix} \quad (2.16)$$

Exchanging the two electrons corresponds to swapping the rows of the determinant, which changes its sign, automatically enforcing antisymmetry. If $\phi_1 = \phi_2$, the determinant vanishes, recovering the Pauli exclusion principle.

This construction generalizes naturally to N electrons. The Slater determinant

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix} \quad (2.17)$$

is antisymmetric under the exchange of any two electrons and vanishes whenever two orbitals are identical. The factor $1/\sqrt{N!}$ ensures normalization. Replacing the Hartree product (Eq. 2.11) with the Slater determinant of Eq. 2.17 as the trial wavefunction in the variational principle leads to Hartree-Fock theory.

2.8 Hartree-Fock theory

Hartree-Fock theory extends the Hartree approximation by replacing the product wavefunction (Eq. 2.11) with the antisymmetric Slater determinant (Eq. 2.17) as the trial wavefunction in the variational principle. Minimizing the expectation value of the many-electron Hamiltonian with re-

spect to the single-particle orbitals, subject to orthonormality, leads to the Hartree-Fock equations,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r}) \right] \psi_i(\mathbf{r}) - \sum_j \delta_{s_i s_j} e^2 \int \frac{\psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \psi_j(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2.18)$$

where the Hartree potential $V_H(\mathbf{r}) = e^2 \sum_j \int |\psi_j(\mathbf{r}')|^2 / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}'$ now includes the contribution from $j = i$ as well. Compared to the Hartree equations, two changes have appeared. First, the Hartree potential includes a spurious self-interaction, in which an electron interacts with its own charge density. Second, a new term has emerged: the exchange term, which contains the Kronecker delta $\delta_{s_i s_j}$ enforcing that the contribution is non-zero only when the orbitals ψ_i and ψ_j have the same spin. The $j = i$ contribution to the exchange term exactly cancels the self-interaction in V_H , leaving an equation that is free of self-interaction and that introduces a genuine new piece of physics through the $j \neq i$ exchange contributions.

The exchange term is non-local: the operator acting on ψ_i at position $\mathbf{r}$ depends on the values of ψ_i at all other positions $\mathbf{r}'$. Physically, exchange reflects the consequence of antisymmetry on electron-electron interactions: two electrons of the same spin cannot occupy the same point in space, and so each electron is surrounded by a region of reduced same-spin density, often referred to as the exchange hole. The presence of this hole lowers the Coulomb repulsion energy relative to a system of independent electrons, and capturing it correctly is essential to any quantitative description of electronic structure.

Like the Hartree equations, the Hartree-Fock equations are nonlinear and must be solved self-consistently. Hartree-Fock treats exchange exactly within the single-determinant ansatz, which is a substantial improvement over the Hartree approximation. However, by restricting the wavefunction to a single Slater determinant, it neglects *correlation*: the additional reduction in energy that arises when electrons of opposite spin avoid one another due to their mutual Coulomb repulsion. In condensed matter systems, correlation contributes meaningfully to the total energy and to most properties of physical interest, and any quantitative theory must account for it. Density functional theory provides a route to including both exchange and correlation while retaining the computational efficiency of a single-particle framework.

2.9 Thomas-Fermi theory

Hartree and Hartree-Fock theory work directly with the many-electron wavefunction, and even after the simplifications of the previous sections, this remains a complex object: a function of $3N$ spatial coordinates plus spin. Thomas-Fermi theory, developed independently by Thomas and Fermi shortly after the formulation of quantum mechanics, takes a different approach. Rather than seeking the wavefunction at all, it expresses the total energy as a functional of the electron density $n(\mathbf{r})$ alone, a function of just three spatial coordinates. While Thomas-Fermi theory is not accurate enough to be used in practice, the conceptual move from wavefunction to density is the same one that underlies modern density functional theory, and it is for this reason that Thomas-Fermi theory is included here.

The central approximation in Thomas-Fermi theory is to treat the electrons locally as a uniform non-interacting Fermi gas, in which the kinetic energy density depends only on the local value of $n(\mathbf{r})$. In a uniform Fermi gas at zero temperature, the electrons fill momentum states up to the Fermi momentum p_F , and the density is related to p_F by

$$n(\mathbf{r}) = \frac{8\pi}{3h^3} p_F^3(\mathbf{r}) \quad (2.19)$$

The kinetic energy per unit volume is obtained by integrating $p^2/2m_e$ over the occupied momentum states,

$$t(\mathbf{r}) = \frac{3h^2}{40m_e} \left(\frac{3}{\pi}\right)^{2/3} [n(\mathbf{r})]^{5/3} = C_k [n(\mathbf{r})]^{5/3}, \quad (2.20)$$

where $C_k = (3h^2/40m_e)(3/\pi)^{2/3}$. The total kinetic energy is then $T[n] = C_k \int [n(\mathbf{r})]^{5/3} d\mathbf{r}$, an explicit functional of the density.

The electron-nucleus and electron-electron Coulomb interactions are treated classically, as functionals of the density:

$$E^{TF}[n] = C_k \int [n(\mathbf{r})]^{5/3} d\mathbf{r} + \int n(\mathbf{r}) V_N(\mathbf{r}) d\mathbf{r} + \frac{1}{2} e^2 \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.21)$$

where $V_N(\mathbf{r}) = -\sum_{\alpha} Z_{\alpha} e^2 / |\mathbf{r} - \mathbf{R}_{\alpha}|$ is the electrostatic potential of the nuclei. The ground-state density is then obtained by minimizing this functional with respect to $n(\mathbf{r})$, subject to the constraint

that the density integrates to the total number of electrons.

Despite its conceptual appeal, Thomas-Fermi theory performs poorly in practice. The local kinetic energy approximation misses the shell structure of atoms, fails to describe chemical bonding, and is the dominant source of error in the predicted total energies. The Hartree-like Coulomb term contains a spurious self-interaction, and exchange and correlation are absent entirely. These shortcomings make Thomas-Fermi theory unsuitable for quantitative work. Its enduring contribution is conceptual: it demonstrates that the total energy can, in principle, be written as a functional of the density alone, and so reduces the basic variable of the problem from a $3N$ -dimensional wavefunction to a three-dimensional density. The challenge is to construct an energy functional that does this reliably, and the Hohenberg-Kohn theorems show that such a functional exists.

2.10 Hohenberg-Kohn theorems

Thomas-Fermi theory established that the total energy can, at least in some approximate form, be written as a functional of the electron density. The Hohenberg-Kohn theorems make this idea rigorous, providing the formal foundation for density functional theory.

The first theorem states that for a system of interacting electrons in an external potential $V_{\text{ext}}(\mathbf{r})$, the ground-state density $n_0(\mathbf{r})$ uniquely determines $V_{\text{ext}}(\mathbf{r})$, up to an irrelevant additive constant. The proof, due to Hohenberg and Kohn, proceeds by contradiction: assuming that two different external potentials produced the same ground-state density leads to an inconsistent pair of variational inequalities, so the assumption must be false. Because the external potential determines the Hamiltonian, and the Hamiltonian determines the wavefunction and all of its observable properties, the ground-state density therefore determines every property of the system. In particular, the total energy is a functional of the density, which can be written as

$$E[n] = \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r}) d\mathbf{r} + F[n] \quad (2.22)$$

where $F[n]$ contains the kinetic energy of the electrons and their mutual Coulomb interaction. The functional $F[n]$ is *universal*: it depends only on the density and is the same for every electronic system, regardless of the external potential. The system-specific information enters Eq. 2.22 only through the first term.

The second theorem states that for any trial density $n(\mathbf{r})$ satisfying $n(\mathbf{r}) \geq 0$ and $\int n(\mathbf{r}) d\mathbf{r} = N$, the energy functional satisfies

$$E[n] \geq E_0 \quad (2.23)$$

with equality if and only if $n(\mathbf{r})$ is the true ground-state density $n_0(\mathbf{r})$. This is the density-based counterpart of the variational principle for wavefunctions: the search for the ground-state energy is reduced to a minimization over densities, with the basic variable now a function of three spatial coordinates rather than $3N$.

The Hohenberg-Kohn theorems establish that an exact energy functional of the density exists, and that minimizing it yields the true ground-state energy and density. They do not, however, specify the form of the universal functional $F[n]$. The Thomas-Fermi expression for the kinetic energy is one approximation to the kinetic part of $F[n]$, but it is not accurate enough for quantitative work, and an analogously simple expression for the electron-electron part is not available. Direct minimization of the energy functional in the form of Eq. 2.22 is therefore not a practical strategy. The Kohn-Sham approach, developed in the following section, provides a way to bypass this difficulty by reformulating the problem in terms of an auxiliary system of non-interacting electrons.

2.11 Kohn-Sham equations

The Hohenberg-Kohn theorems guarantee that an exact density functional exists, but they say nothing about its form. The most damaging unknown is the kinetic energy: the Thomas-Fermi local approximation is not accurate enough for quantitative work, and no simple closed-form expression for the true interacting kinetic energy as a functional of the density is known. Kohn and Sham proposed a clever way around this difficulty. Rather than approximate the interacting kinetic energy directly, they introduced an auxiliary system of *non-interacting* electrons constructed to have the same ground-state density as the real, interacting system. The kinetic energy of this auxiliary system, which can be computed exactly from its single-particle orbitals, is taken as the principal contribution to the kinetic energy, and the difference between it and the true kinetic energy is absorbed into a separate term to be approximated.

In this framework, the total energy functional is written as

$$E[n] = T_s[n] + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} + E_H[n] + E_{XC}[n] \quad (2.24)$$

Here $T_s[n]$ is the kinetic energy of the auxiliary non-interacting system,

$$T_s[n] = \sum_{i=1}^N \int \psi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \psi_i(\mathbf{r}) d\mathbf{r} \quad (2.25)$$

expressed in terms of single-particle orbitals ψ_i whose density is constrained to equal that of the true system. The second and third terms are familiar: the external potential energy due to the nuclei and the classical Hartree energy of the electron density,

$$E_H[n] = \frac{1}{2} e^2 \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.26)$$

The final term, the exchange-correlation functional $E_{XC}[n]$, is defined as everything missing from the other three: the difference between the true interacting kinetic energy and $T_s[n]$, plus the difference between the true electron-electron interaction energy and $E_H[n]$. By construction, Eq. 2.24 is formally exact; the only approximation in the Kohn-Sham scheme enters through the choice of approximate form for $E_{XC}[n]$.

The orbitals ψ_i are determined by applying the variational principle to Eq. 2.24. To see how this leads to a tractable single-particle equation, it is useful to first consider the simpler case of the Hartree approximation, in which E_{XC} is set to zero. Minimizing the resulting energy with respect to the orbitals, subject to orthonormality, yields the Hartree-like equations

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2.27)$$

Reintroducing the exchange-correlation contribution adds a corresponding term to the effective potential. Defining

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})} \quad (2.28)$$

as the functional derivative of E_{XC} with respect to the density, the Kohn-Sham equations take the

form

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \sum_{\alpha} \frac{Z_{\alpha} e^2}{|\mathbf{r} - \mathbf{R}_{\alpha}|} + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \quad (2.29)$$

These are the central equations of practical density functional theory.

The Kohn-Sham equations have the form of a single-particle Schrödinger equation, with all of the many-body effects folded into the effective potential through V_{XC} . They are nonlinear — the effective potential depends on the density, which in turn depends on the orbitals — and must be solved self-consistently. The procedure is the same as for the Hartree and Hartree-Fock equations: starting from a guess for the density, one constructs the effective potential, solves the Kohn-Sham equations to obtain a new set of orbitals, recomputes the density, and iterates until self-consistency is reached.

The density is constructed from the Kohn-Sham orbitals as

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 \quad (2.30)$$

where f_i is the occupation of orbital i . At zero temperature, the lowest N orbitals are fully occupied and the rest empty. At finite electronic temperature, which is non-negligible at the conditions of planetary interiors relevant to this work, the occupations follow the Fermi-Dirac distribution,

$$f_i = \frac{1}{\exp[(\epsilon_i - \mu)/k_B T] + 1} \quad (2.31)$$

where μ is the chemical potential, fixed by the condition $\sum_i f_i = N$

A subtlety worth noting is that the Kohn-Sham orbitals ψ_i and eigenvalues ϵ_i are mathematical constructs of the auxiliary non-interacting system. They are chosen so that the resulting density matches that of the true interacting system, but they are not in general the wavefunctions or energies of physical electrons. Despite this, they are routinely interpreted as approximations to single-particle states and are widely used in practice to compute band structures, densities of states, and other electronic properties.

If the exact form of $E_{XC}[n]$ were known, the Kohn-Sham equations would yield the exact ground-state energy and density of the interacting system. In practice, $E_{XC}[n]$ must be approximated, and the accuracy of any DFT calculation depends on the quality of this approximation. The

remainder of this chapter is concerned with the structure of the exchange-correlation functional and with the specific approximations relevant to this work.

2.12 Exchange and correlation

The Kohn-Sham scheme reduces the many-electron problem to a set of single-particle equations, with all of the genuinely many-body physics absorbed into the exchange-correlation functional $E_{XC}[n]$. Although E_{XC} is typically a small fraction of the total energy of a solid, it is responsible for nearly all of the energy differences that determine chemical and physical behavior — bond formation, structural stability, magnetic ordering, and the cohesion of condensed phases. Approximating E_{XC} accurately is therefore the central practical challenge of density functional theory.

The two physical effects encoded in E_{XC} can be understood by considering how electrons in a real system avoid one another. The first effect, exchange, arises from the antisymmetry of the many-electron wavefunction: two electrons of the same spin cannot occupy the same point in space, and so each electron is surrounded by a region of reduced same-spin density. This is the exchange hole introduced in the discussion of Hartree-Fock theory, and it lowers the energy by reducing the Coulomb repulsion that would be present if the electrons were independent. Exchange is a purely quantum-mechanical consequence of the Pauli principle and acts only between electrons of the same spin.

The second effect, correlation, arises from the Coulomb repulsion between electrons themselves. Even if antisymmetry were not enforced, electrons would still avoid one another because of their mutual electrostatic repulsion, and this avoidance further lowers the energy. Correlation acts between electrons of both same and opposite spin, and is missing from Hartree-Fock theory, which restricts the wavefunction to a single Slater determinant in which the only avoidance comes from antisymmetry.

In the Kohn-Sham formulation, $E_{XC}[n]$ contains both effects, together with a small kinetic-energy correction: the difference between the true interacting kinetic energy and that of the auxiliary non-interacting system. The exact form of $E_{XC}[n]$ is unknown and is unlikely ever to be derived in closed form for general inhomogeneous systems, and the practical accuracy of any DFT calculation is determined by the quality of the approximation used. The remainder of this chapter

describes the hierarchy of approximations relevant to this work, beginning with the simplest — the local density approximation — and building up to the generalized gradient approximation and the specific functional, PBEsol, used throughout our work.

2.13 Local density approximation

The simplest approximation to the exchange-correlation functional is the local density approximation (LDA), introduced by Kohn and Sham in their original 1965 paper [4]. LDA is constructed by exploiting one special case in which E_{XC} can be computed essentially exactly: the uniform electron gas.

The uniform electron gas is a system of interacting electrons of constant density n moving in a uniform compensating positive background. Despite its idealized character, it is one of the very few interacting many-electron systems for which the exchange-correlation energy per electron, $\epsilon_{xc}^{\text{unif}}(n)$, is known to high accuracy. The exchange contribution can be evaluated analytically in closed form,

$$\epsilon_x^{\text{unif}}(n) = -\frac{3}{4\pi}(3\pi^2n)^{1/3} \quad (2.32)$$

while the correlation contribution $\epsilon_c^{\text{unif}}(n)$ has been computed to high precision by quantum Monte Carlo simulations and is available in convenient parametrized forms [5].

In LDA, the exchange-correlation energy of an inhomogeneous system is approximated by treating each volume element as if it were locally a uniform electron gas of the same density,

$$E_{XC}^{\text{LDA}}[n] = \int n(\mathbf{r}) \epsilon_{xc}^{\text{unif}}(n(\mathbf{r})) d\mathbf{r} \quad (2.33)$$

By construction, LDA is exact when the density is genuinely uniform, and it is expected to be accurate when the density varies slowly on the scale of the local Fermi wavelength. Many real systems do not strictly satisfy this condition — atomic and molecular densities vary rapidly near nuclei, and surfaces and interfaces have abrupt density changes — yet LDA performs remarkably well across a wide range of solids, often much better than its underlying assumption would suggest.

LDA’s quantitative performance is mixed. The magnitude of the exchange-correlation energy is systematically underestimated, with the result that binding energies of solids and molecules are

typically overestimated by 10–20% and bond lengths and lattice constants are typically 1–2% too short. Despite these errors, LDA captures the qualitative trends across a wide range of systems and remains a useful baseline. It is also the conceptual foundation on which the more sophisticated functionals discussed below are built: most modern exchange-correlation approximations reduce to LDA in the limit of a uniform density, and the effort to understand why LDA performs better than its derivation suggests has been an important driver in the development of higher-level functionals.

2.14 Spin polarization and LSDA

The treatment of LDA above implicitly assumes that the spin-up and spin-down electron densities are equal at every point. This is appropriate for non-magnetic, closed-shell systems, but it fails for any system in which the two spin channels are not equivalent — magnetic materials, atoms or molecules with unpaired electrons, and systems in which an applied magnetic field breaks the spin symmetry.

Spin is an intrinsic quantum-mechanical property of the electron, with no classical analog. Each electron carries a spin angular momentum of magnitude $\hbar/2$, and along any chosen quantization axis the spin component takes one of two values, conventionally labeled "up" ($\uparrow$) and "down" ($\downarrow$). Because the Pauli exclusion principle forbids two electrons from occupying the same single-particle state, each spatial orbital can accommodate at most one electron of each spin, and the total number of electrons in a system divides into a spin-up population and a spin-down population. The corresponding spin densities $n_{\uparrow}(\mathbf{r})$ and $n_{\downarrow}(\mathbf{r})$ sum to the total electron density, $n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$, and their difference $n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})$ is the spin polarization.

When the two spin populations differ, the exchange-correlation energy depends on each separately rather than on their sum alone, because exchange acts only between electrons of the same spin (Section 2.12) and the same-spin and opposite-spin correlation contributions differ in magnitude. The local spin density approximation (LSDA) generalizes LDA accordingly,

$$E_{XC}^{\text{LSDA}}[n_{\uparrow}, n_{\downarrow}] = \int n(\mathbf{r}) \epsilon_{xc}^{\text{unif}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) d\mathbf{r} \quad (2.34)$$

where $\epsilon_{xc}^{\text{unif}}(n_{\uparrow}, n_{\downarrow})$ is the exchange-correlation energy per electron of a uniform electron gas with the specified spin densities. LSDA reduces to LDA in the unpolarized limit $n_{\uparrow} = n_{\downarrow} = n/2$. In the

Kohn-Sham equations, allowing for spin polarization means solving two coupled sets of equations, one for each spin channel, with the corresponding effective potential $V_{\text{eff}}^{\sigma}(\mathbf{r})$ depending on both spin densities through $V_{XC}^{\sigma}(\mathbf{r}) = \delta E_{XC} / \delta n_{\sigma}(\mathbf{r})$.

Spin polarization is relevant to much of the work presented in this dissertation because iron, the central element in nearly all of the systems studied, is magnetic at low and intermediate pressures. The atomic configuration of iron, $[\text{Ar}]3d^64s^2$, includes four unpaired $3d$ electrons in the free atom, and Hund's rule favors a spin arrangement that maximizes the total spin. In the metal at ambient conditions this leads to ferromagnetism, and in iron-bearing minerals it gives rise to local magnetic moments on the Fe ions whose magnitudes depend on the crystal field, the oxidation state of the iron, and the surrounding pressure and temperature. Whether spin polarization needs to be accounted for, and the form it takes when it does, depends on the system and the conditions. In ferropericlase, for example, the Fe^{2+} ions undergo a high-spin to low-spin transition at lower-mantle pressures that alters the calculated equation of state, electrical conductivity, and other properties of the mineral [6, 7]. At sufficiently high pressures, the magnetic moment on iron collapses entirely and a non-spin-polarized treatment becomes appropriate. The choice of whether to use spin-polarized or non-spin-polarized calculations is therefore made on a case-by-case basis in this work, depending on the system and the pressure-temperature conditions of interest.

2.15 Generalized gradient approximation

LDA's success suggests a natural route to improvement: include additional information about the local environment of each electron. The most obvious such information is the gradient of the density, $\nabla n(\mathbf{r})$, which characterizes how rapidly the density changes from point to point. Functionals of the form

$$E_{XC}^{\text{GGA}}[n] = \int n(\mathbf{r}) \epsilon_{xc}^{\text{GGA}}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) d\mathbf{r} \quad (2.35)$$

are known as generalized gradient approximations (GGAs). Unlike LDA, in which the exchange-correlation energy density at $\mathbf{r}$ depends only on the density at that point, GGAs are *semi-local*: the energy density depends on the density and its gradient in the immediate vicinity of $\mathbf{r}$.

The first systematic attempt to incorporate the density gradient was the gradient expansion

approximation (GEA), which expanded the exchange-correlation energy in powers of the gradient about the uniform-density limit. To leading order in $|\nabla n|$, this gives

$$E_{XC}^{\text{GEA}}[n] = \int n(\mathbf{r}) \epsilon_{xc}^{\text{LDA}}(n(\mathbf{r})) \left[1 + C \left(\frac{|\nabla n(\mathbf{r})|}{2k_F(\mathbf{r})n(\mathbf{r})} \right)^2 \right] d\mathbf{r} \quad (2.36)$$

where $k_F(\mathbf{r}) = (3\pi^2 n(\mathbf{r}))^{1/3}$ is the local Fermi wavevector. While this expression is exact for slowly varying densities, it performs worse than LDA for real systems. The reason is that GEA violates two physical constraints, or sum rules, that the exact exchange-correlation hole must satisfy: the integral of the correlation hole over space must vanish, and the exchange hole must be everywhere non-positive. The gradient correction in GEA improves the description of the hole near the electron but produces unphysical oscillations at larger distances, and these long-range artifacts are responsible for its poor performance.

GGAs were developed to retain the gradient information while restoring the sum rules. Many early GGAs accomplished this by truncating the GEA hole in real space at the distance where the sum rules are first satisfied. Modern GGAs are typically constructed by writing the exchange-correlation energy density as a product of the LDA result and an enhancement factor $F_{XC}(n, \nabla n)$, and choosing the form of the enhancement factor to satisfy a set of exact mathematical constraints on the exchange-correlation energy — such as scaling relations, limits at high and low density, and the sum rules. Functionals built in this way are called *non-empirical*, because their parameters are fixed by exact physical conditions rather than fitted to reproduce specific experimental or computational data.

The most widely used non-empirical GGA is the Perdew-Burke-Ernzerhof (PBE) functional [8], which writes the exchange energy as

$$E_X^{\text{PBE}}[n] = \int n(\mathbf{r}) \epsilon_x^{\text{unif}}(n(\mathbf{r})) F_X(s) d\mathbf{r} \quad (2.37)$$

where $s = |\nabla n|/(2k_F n)$ is a dimensionless reduced density gradient and $F_X(s)$ is a smooth enhancement factor that interpolates between the slowly varying limit at small s and a saturation value at large s . The correlation energy has an analogous structure, with the LDA correlation energy modified by a gradient-dependent additive term. The forms of these functions, and the values

of the small number of parameters they contain, are fixed by exact constraints including the LDA limit for slowly varying densities and known scaling behavior in various asymptotic regimes; the original publication gives explicit forms [8].

PBE is the default GGA in many DFT codes. Compared to LDA, it generally improves binding energies, atomization energies, and hydrogen-bonded interactions at similar computational cost. For dense condensed-phase systems, however, PBE overcorrects for LDA's overbinding, producing lattice constants that are typically too long and bulk moduli that are too small. The PBEsol functional [9] addresses this by retuning two parameters in the PBE exchange and correlation enhancement factors — one to restore the gradient expansion for slowly varying densities, the other to reproduce the exchange-correlation surface energy of the uniform electron gas — both better suited to the small density gradients and surface energetics characteristic of densely packed solids. PBEsol yields lattice constants, bulk moduli, and phonon frequencies in considerably better agreement with experiment than PBE at no additional cost. For ferropericlasite in particular, Holmström et al. [6] compared LDA, PBE, and PBEsol equations of state against 300 K experimental data and found PBEsol to give the best agreement. PBEsol is the exchange-correlation functional used throughout this dissertation.

2.16 DFT + U

The exchange-correlation approximations described above perform well for systems whose electrons are reasonably well delocalized, but they fail systematically for materials containing partially filled d or f shells. The most prominent failure is in the transition metal monoxides such as NiO, FeO, MnO, and CoO, which are experimentally Mott insulators with band gaps of several electronvolts but are predicted by LDA and GGAs to be either metallic or insulating with band gaps roughly an order of magnitude smaller than observed [10]. The underlying problem is that the semi-local functionals describe the localized d and f electrons as too delocalized, underestimating the on-site Coulomb repulsion that drives *strong correlation* and the energetic cost of fractional orbital occupation.

The DFT+U method addresses this by adding an explicit on-site Coulomb repulsion term to the energy functional, acting only on a chosen set of localized orbitals. The rotationally invariant

simplified scheme of Dudarev et al. [11], used in this work, introduces a single effective parameter $U_{\text{eff}} = U - J$ and an energy correction of the form

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \frac{U_{\text{eff}}}{2} \sum_{\sigma} \text{Tr} [\rho^{\sigma} - \rho^{\sigma} \rho^{\sigma}], \quad (2.38)$$

where ρ^{σ} is the density matrix of the chosen localized orbitals, typically the atomic-like d or f orbitals projected onto each transition metal or actinide site, for spin channel σ . The trace vanishes when each orbital is either fully occupied or fully empty and is maximized for fractional occupations, so the +U term penalizes partial occupation and favors states in which the localized electrons are integer-occupied.

The value of U_{eff} can in principle be computed from first principles, but it is more often treated as a system-specific parameter chosen to reproduce a known experimental observable. The value used throughout this work is $U_{\text{eff}} = 2.5$ eV [6], as the value that reproduces the experimentally observed high-spin to low-spin transition pressure in ferropericlase. With PBEsol alone, this transition is predicted at approximately 18 GPa, far below the experimental value of roughly 50 GPa, because the over-delocalization of the Fe $3d$ states destabilizes the high-spin (more localized) configuration too easily. The +U correction restores agreement with experiment by penalizing the fractional $3d$ occupations associated with hybridization. The same value is used for all iron-oxide-bearing systems studied in this dissertation, on the grounds that the local electronic environment of the Fe ions in these materials is similar to that in ferropericlase, and that consistency in the treatment of the Fe $3d$ states allows meaningful comparison across systems.

The +U correction has consequences beyond the spin transition. It widens the calculated band gap, consistent with the more general tendency of DFT+U to bring band gaps in transition metal compounds closer to their experimental values, and the more localized Fe $3d$ electrons are less mobile. Both effects act to reduce the calculated electrical conductivity relative to PBEsol alone, an effect observed in the calculations presented in this dissertation.

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CHAPTER 3

Background: Electron transport and Kubo-Greenwood Theory

3.1 Introduction

How heat and charge are transported within planetary interiors controls their thermal evolution, internal structure, and capacity to generate a global magnetic field, as discussed in Chapter 1. The electrical conductivity σ , the thermal conductivity k , and the Seebeck coefficient S are the key material properties that govern these processes. At the pressures and temperatures of deep planetary interiors ($10^2 - 10^3$ GPa and $10^3 - 10^4$ Kelvin) the materials of interest are metallic or semi-metallic, so that conduction electrons carry the bulk of both the charge and the heat. The electronic contribution therefore dominates each of these transport coefficients, and it is on this electronic contribution that we focus throughout this dissertation.

We calculate σ_{el} , k_{el} , and S using the Kubo–Greenwood formalism. The purpose of this chapter is to develop, from the ground up, the conceptual and mathematical framework needed to interpret these quantities and to motivate the Kubo–Greenwood formula as the natural tool for evaluating them within finite-temperature density-functional molecular dynamics. The presentation begins with band theory, proceeds through the Drude and Sommerfeld free-electron models, develops the semi-classical treatment of the kinetic coefficients, and finally builds up the linear-response theory that culminates in the Kubo-Greenwood formula for the optical and DC conductivities, and their generalizations to the thermal conductivity and Seebeck coefficient.

Much of the material in this chapter is standard solid-state physics, and is drawn from these references [1, 2]. Specific background and methods that go beyond this are cited individually as they appear.

3.2 Band theory

As we saw in the previous chapter, electrons in an isolated atom occupy discrete energy levels, or orbitals. When two or more atoms are brought closer together, the wavefunctions of electrons on neighboring atoms overlap and the Pauli exclusion principle forbids identical quantum states

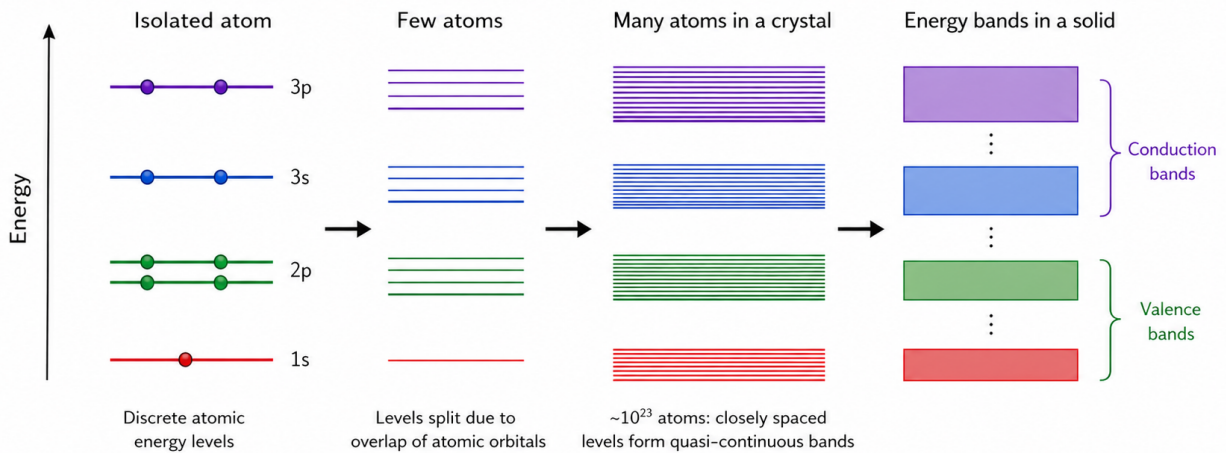


Figure 3.1: Schematic illustration of electronic band formation in solids.

from coexisting, forcing a split into closely spaced energy levels. In a crystalline solid, when these energy levels become so densely packed that they merge into continuous energy bands, separated by ranges of energy - band gaps - where no single-particle states exist. This evolution from discrete atomic levels to continuous bands in a solid is illustrated in Fig. 3.1

Electrons fill the available states from lowest to highest energy in accordance with the Pauli principle. The Fermi energy E_F is the highest occupied energy at $T = 0$. The valence band is the highest fully occupied band; its electrons are primarily involved in chemical bonding. The conduction band is the lowest unoccupied band; electrons promoted into it are weakly bound and propagate relatively freely through the solid. The unoccupied states left behind in the valence band, “holes”, also act as positively charged mobile carriers.

The way these bands are populated relative to E_F determines whether a material is a conductor, a semiconductor, or an insulator, as illustrated in Fig. 3.2. In a conductor (metal), the conduction band is partially filled, so that E_F lies within a band and a finite density of states is available at the Fermi level for electrons to scatter into under an applied field. In an insulator, E_F falls within a wide band gap separating a fully occupied valence band from an empty conduction band; thermal excitation across the gap is negligible and conduction is suppressed. A

semiconductor is the intermediate case: the gap is small enough ($\sim k_B T$ or smaller) that thermal excitation can populate the conduction band with a modest density of carriers, and small changes in temperature or doping can produce large changes in the carrier concentration.

Therefore, key to electron transport is the electron concentration n in the conduction band, and the hole concentration p in the valence band. These are related to the density of states, $g(E)$ via:

$$n = \int_{E_c}^{\infty} D(E) f(E) dE, \quad p = \int_{-\infty}^{E_v} D(E) [1 - f(E)] dE \quad (3.1)$$

where $D(E)$ is the electronic density of states, $f(E)$ is the Fermi–Dirac distribution, and E_c and E_v are respectively the bottom of the conduction band and the top of the valence band. Eq. (3.1) makes the central observation explicit: the density of mobile charge carriers is controlled by the position of the Fermi level relative to the band edges.

These ideas connect directly to the electrical conductivity σ . Ohm’s law identifies σ as the proportionality between the charge current density $\mathbf{J}_e$ and the electric field $\mathbf{E}$ that drives it,

$$\mathbf{J}_e = \sigma \mathbf{E} \quad (3.2)$$

so that σ measures the ease with which a material conducts charge. The conductivity therefore depends both on the density of mobile carriers and on how easily they move; a useful elementary decomposition is

$$\sigma = ne\mu_n + pe\mu_p \quad (3.3)$$

where μ_n and μ_p are the electron and hole mobilities. In the systems treated in this dissertation, hole mobility plays no significant role and we shall focus on the electronic contribution. The remainder of this chapter is concerned with developing successively more sophisticated theories of the electron mobility, and ultimately of the full transport tensor.

3.3 The Drude model

The classical theory of metallic conduction was formulated by Drude in 1900, who pictured a metal as a gas of free, classical electrons moving against a background of stationary, positively charged ionic cores. The basic assumptions of the model are:

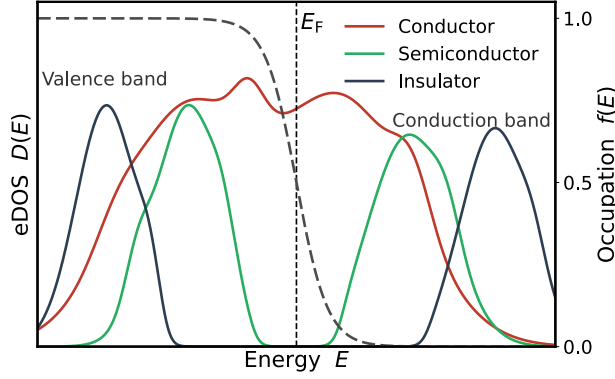


Figure 3.2: Schematic electronic density of states $g(E)$ for a conductor (red), semiconductor (green), and insulator (black). The Fermi energy E_F is indicated by vertical dashed line. The dashed gray curve shows the Fermi-Dirac occupation $f(E)$ of electrons at finite temperature (right axis).

1. Between collisions, an electron's interactions with other electrons (the *independent electron approximation*) and with the ions (the *free electron approximation*) are neglected.
2. Collisions are instantaneous events that abruptly change the electron's velocity.
3. In any infinitesimal time interval dt , an electron suffers a collision with probability dt/τ , where τ is the *relaxation time* (or mean free time between collisions).
4. Immediately after a collision, the velocity distribution of an electron is determined only by the local temperature and is independent of its velocity before the collision.

These assumptions are sufficient to derive expressions for all three transport coefficients of interest.

3.3.1 Electrical conductivity

A time t after its last collision, an electron has the (random) velocity $\mathbf{v}_0$ acquired in that collision plus the drift $-e\mathbf{E}t/m_e$ from the field. The post-collision velocity averages to zero, leaving, with $\langle t \rangle = \tau$,

$$\mathbf{v}_{\text{avg}} = -\frac{e\mathbf{E}\tau}{m_e}. \quad (3.4)$$

The current density $\mathbf{J}_e = -nev_{\text{avg}}$ then gives $\mathbf{J}_e = \sigma \mathbf{E}$ with the celebrated Drude result

$$\sigma = \frac{ne^2\tau}{m_e} \quad (3.5)$$

proportional to the carrier concentration and the time between scattering events. So robust is this expression that the more elaborate theories developed below all reduce to it in the appropriate limits.

3.3.2 Electronic thermal conductivity

The thermal current density $\mathbf{J}_q$, defined as the thermal energy crossing unit area per unit time, obeys Fourier's law for sufficiently small gradients,

$$\mathbf{J}_q = -k \nabla T \quad (3.6)$$

with $k > 0$ the thermal conductivity. Consider a 1D wire along which T varies slowly. By assumption 4, an electron at point x carries thermal energy $\varepsilon[T(x)]$. Half of the electrons at x arrived from the hot side, having had their last collision at $x - v\tau$; the other half came from $x + v\tau$. The net flux is therefore

$$\mathbf{J}_q = \frac{1}{2} nv \{ \varepsilon[T(x - v\tau)] - \varepsilon[T(x + v\tau)] \} \quad (3.7)$$

Expanding to first order in the mean free path $\ell = v\tau$, generalizing to three dimensions via $\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$, and identifying $n d\varepsilon/dT = c_v$ (the electronic specific heat per unit volume) gives

$$k = \frac{1}{3} v^2 \tau c_v \quad (3.8)$$

This derivation neglects any position dependence of the electron speed, an effect which does not significantly change the result. It does, however, induce a net drift toward the cold end and hence an electrical current; in an open-circuit measurement this current cannot flow, so charge accumulates at the cold end until the resulting field cancels it. That field is the Seebeck effect.

3.3.3 Seebeck effect

The thermoelectric field generated by a temperature gradient is

$$\mathbf{E} = S \nabla T \quad (3.9)$$

where S is the Seebeck coefficient. Applying the same 1D mean-velocity argument as above, but to the velocity itself rather than the energy, gives

$$\mathbf{v}_q = -\frac{\tau}{6} \frac{dv^2}{dT} \nabla T \quad (3.10)$$

The field-driven mean velocity is $\mathbf{v}_e = -e\mathbf{E}\tau/m_e$, and the open-circuit condition $\mathbf{v}_q + \mathbf{v}_e = 0$ yields

$$S = -\frac{1}{3e} \frac{d}{dT} \left(\frac{m_e v^2}{2} \right) = -\frac{c_v}{3ne} \quad (3.11)$$

The Drude Seebeck coefficient is thus proportional to the specific heat per carrier and is independent of the relaxation time.

3.3.4 Limitations of Drude model

The Drude model is far too simple to be quantitatively accurate: it is restricted to metals, misses the temperature dependence of σ , gives a Lorenz number ($L = k/(\sigma T)$) off by a factor of two, and overestimates the room-temperature Seebeck coefficient of simple metals by roughly two orders of magnitude. Nevertheless, it captures the essential microscopic ingredients of electronic transport:

- (i) electrons are responsible for electrical conduction, thermal conduction, and thermoelectricity;
- (ii) scattering of electrons gives rise to resistance.

3.4 The Sommerfeld model: applying Fermi-Dirac statistics

The Sommerfeld model retains Drude's free-electron formalism but replaces classical Maxwell-Boltzmann statistics with Fermi-Dirac statistics, thereby respecting the Pauli exclusion principle. The electrical conductivity (3.5) is unchanged, but the electronic specific heat c_v and mean-square velocity v^2 that enters (3.8) and (3.11) must be recomputed from the correct quantum statistics.

At temperatures of interest in metals, T is much smaller than the Fermi temperature $T_F = E_F/k_B$ (typically 10^4 – 10^5 K). The Fermi-Dirac distribution therefore differs from a step function only within a narrow window of width $\sim k_B T$ around the chemical potential μ , so any thermal average of the form $\int H(E) f(E) dE$ is dominated by states close to E_F . Expanding such an integral in powers of $k_B T/E_F$ (the Sommerfeld expansion) gives, to leading order,

$$\int_0^\infty H(E) f(E) dE = \int_0^\mu H(E) dE + \frac{\pi^2}{6} (k_B T)^2 H'(\mu) + \mathcal{O}[(k_B T/E_F)^4] \quad (3.12)$$

The Sommerfeld expansion of the relevant integrals gives an electronic heat capacity

$$c_v = \frac{\pi^2}{3} D(E_F) k_B^2 T \equiv \gamma T, \quad (3.13)$$

which is suppressed relative to the classical value $\frac{3}{2}nk_B$ by a factor of order T/T_F ($\sim 10^{-2}$ at room temperature). The same expansion shows that the relevant velocity is the Fermi velocity $v_F = \sqrt{2E_F/m}$, not a thermal velocity ($v = \sqrt{3k_B T/m}$). Inserting (3.13) into (3.8) yields the Wiedemann–Franz law

$$\frac{k}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 \equiv L_0 = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2} \quad (3.14)$$

in essentially exact agreement with experiment for simple metals at temperatures where elastic scattering dominates. The same Sommerfeld expansion applied to (3.11) reduces the predicted thermopower by the same factor T/T_F , bringing it into the microvolt-per-kelvin range characteristic of real metals.

Despite Sommerfeld's improvements, the free-electron model, whether classical or degenerate, retains a number of well-known shortcomings. Among them: the sign of the thermoelectric coefficient does not always match observation; the temperature dependence of the DC conductivity is not captured; and the Wiedemann–Franz law breaks down at intermediate temperatures, where $k/(\sigma T)$ is itself temperature-dependent. To address them we must abandon the picture of free, structureless electrons and acknowledge the presence of a periodic potential.

3.5 Semi-classical transport: applying Bloch theory

The free-electron model can be improved upon by recognizing that the conduction electrons in a solid move in the periodic potential of the ionic lattice. Instead of treating them as free particles, we treat them as Bloch electrons. The single-particle Hamiltonian

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e} \nabla^2 + V(\mathbf{r}), \quad V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r}), \quad (3.15)$$

yields eigenstates of the form

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad (3.16)$$

labeled by a band index n and a Bloch wavevector $\mathbf{k}$ in the first Brillouin zone (the primitive unit cell of the reciprocal lattice containing every physically distinct value $\mathbf{k}$), with eigenvalues $E_n(\mathbf{k})$.

The group velocity of a Bloch electron is

$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \nabla_{\mathbf{k}} E_n(\mathbf{k}) \quad (3.17)$$

The semi-classical model of transport rests on the following postulates. The band index n is a constant of the motion: so interband transitions are forbidden. The position and wavevector of an electron in band n evolve according to

$$\dot{\mathbf{r}} = \mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial E_n(\mathbf{k})}{\partial \mathbf{k}} \quad (3.18)$$

$$\hbar \dot{\mathbf{k}} = -e \left[\mathbf{E}(\mathbf{r}, t) + \frac{1}{c} \mathbf{v}_n(\mathbf{k}) \times \mathbf{H}(\mathbf{r}, t) \right] \quad (3.19)$$

The contribution of band n to the electron density from wavevectors in $d\mathbf{k}$ is given by the Fermi-Dirac distribution

$$f(E_n(\mathbf{k})) \frac{d\mathbf{k}}{4\pi^3} = \frac{d\mathbf{k}/4\pi^3}{\exp[(E_n(\mathbf{k}) - \mu)/k_B T] + 1} \quad (3.20)$$

A direct consequence is that conduction is contributed only by partially filled bands. A filled band has all of its states occupied up to the chemical potential; the Fermi–Dirac distribution describes the equilibrium occupation, and an applied field can perturb this distribution (“pushing” carriers to

slightly higher energies) only when accessible empty states exist nearby. If the band gap is much larger than $k_B T$, no such states are available and the band is inert.

3.5.1 Non-equilibrium distribution function

Computing transport coefficients requires knowledge of how the electrons are distributed across the available Bloch states when the system is driven out of equilibrium by an applied field or temperature gradient. This is captured by the non-equilibrium distribution function $g_n(\mathbf{r}, \mathbf{k}, t)$, which gives the probability of occupation of state $|n, \mathbf{k}\rangle$ at position $\mathbf{r}$ and time t . It reduces to the Fermi-Dirac distribution in the absence of fields and gradients. Within the relaxation-time approximation, g_n obeys

$$dg_n(\mathbf{r}, \mathbf{k}, t) = -\frac{dt}{\tau_n(\mathbf{r}, \mathbf{k})} [g_n(\mathbf{r}, \mathbf{k}, t) - g_n^0(\mathbf{r}, \mathbf{k})], \quad (3.21)$$

i.e., collisions drive the distribution back toward local equilibrium at a state-dependent rate. In the presence of static external fields and a temperature gradient, integration of the linearized Boltzmann equation gives, with an energy-dependent τ ,

$$g(\mathbf{k}, t) = g^0(\mathbf{k}) + \int_{-\infty}^t dt' e^{-(t-t')/\tau(E(\mathbf{k}))} \left(-\frac{\partial f}{\partial E} \right) \cdot \mathbf{v}(\mathbf{k}(t')) \left[-e\mathbf{E}(t') - \nabla\mu(t') - \frac{E(\mathbf{k}) - \mu}{T} \nabla T(t') \right] \quad (3.22)$$

3.5.2 D.C. electrical conductivity

In a static electric field with no temperature gradient or magnetic field, Eq. (3.22) reduces to

$$g(\mathbf{k}) = g^0(\mathbf{k}) - e\mathbf{E} \cdot \mathbf{v}(\mathbf{k}) \tau(E(\mathbf{k})) \left(-\frac{\partial f}{\partial E} \right). \quad (3.23)$$

Inserting this into the current density

$$\mathbf{J}_e = -e \int (d\mathbf{k}/4\pi^3) \mathbf{v}(\mathbf{k}) g \quad (3.24)$$

noting that the equilibrium term contributes nothing, and identifying $\mathbf{J}_e = \boldsymbol{\sigma} \mathbf{E}$ gives the band-resolved conductivity tensor

$$\boldsymbol{\sigma}^{(n)} = e^2 \int \frac{d\mathbf{k}}{4\pi^3} \tau_n(E(\mathbf{k})) \mathbf{v}_n(\mathbf{k}) \mathbf{v}_n(\mathbf{k}) \left(-\frac{\partial f}{\partial E} \right), \quad (3.25)$$

with $\boldsymbol{\sigma} = \sum_n \boldsymbol{\sigma}^{(n)}$. The factor $-\partial f / \partial E$ confirms again that filled bands do not conduct.

3.5.3 Kinetic coefficients

The thermal current density follows from the thermodynamic identity $dQ = T dS = dU - \mu dN$, so that

$$\mathbf{J}_q = \mathbf{J}_E - \mu \mathbf{J}_n, \quad (3.26)$$

where the energy and number current densities are obtained from g by weighting with $E_n(\mathbf{k})$ and unity, respectively. This yields

$$\mathbf{J}_q = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} [E_n(\mathbf{k}) - \mu] \mathbf{v}(\mathbf{k}) g_n(\mathbf{k}). \quad (3.27)$$

Reinstating the temperature gradient in the non-equilibrium distribution and assembling the charge and heat currents gives the canonical Onsager structure

$$\mathbf{J}_e = \mathbf{L}^{11} \left(\mathbf{E} + \frac{\nabla \mu}{e} \right) + \mathbf{L}^{12} (-\nabla T), \quad (3.28)$$

$$\mathbf{J}_q = \mathbf{L}^{21} \left(\mathbf{E} + \frac{\nabla \mu}{e} \right) + \mathbf{L}^{22} (-\nabla T), \quad (3.29)$$

with

$$\mathbf{L}^{11} = \mathcal{L}^{(0)}, \quad \mathbf{L}^{21} = T \mathbf{L}^{12} = -\frac{1}{e} \mathcal{L}^{(1)}, \quad \mathbf{L}^{22} = \frac{1}{e^2 T} \mathcal{L}^{(2)}, \quad (3.30)$$

and

$$\mathcal{L}^{(\alpha)} = e^2 \int \frac{d\mathbf{k}}{4\pi^3} \tau(E(\mathbf{k})) \mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k}) \left(-\frac{\partial f}{\partial E} \right) (E - \mu)^\alpha. \quad (3.31)$$

A more compact form is obtained by introducing the energy-resolved transport function

$$\boldsymbol{\sigma}(E) = e^2 \tau(E) \int \frac{d\mathbf{k}}{4\pi^3} \delta(E - E(\mathbf{k})) \mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k}), \quad (3.32)$$

in terms of which

$$\mathcal{L}^{(\alpha)} = \int dE \left(-\frac{\partial f}{\partial E} \right) (E - \mu)^\alpha \sigma(E). \quad (3.33)$$

Eq. (3.33) is the central result of the semi-classical theory: every linear transport coefficient is a moment of the transport function $\sigma(E)$ weighted by the Fermi window $-\partial f/\partial E$.

3.5.4 Electrical conductivity, thermal conductivity, Seebeck coefficient

The DC electrical conductivity is

$$\sigma = \mathbf{L}^{11} = \mathcal{L}^{(0)}, \quad (3.34)$$

recovering (3.25).

The electronic thermal conductivity is defined under the open-circuit condition $\mathbf{J}_e = 0$. Eq. (3.28) then gives

$$\mathbf{E} + \frac{\nabla \mu}{e} = -\frac{\mathbf{L}^{12}}{\mathbf{L}^{11}}(-\nabla T), \quad (3.35)$$

which on substitution into (3.29) yields

$$\mathbf{J}_q = \left(\mathbf{L}^{22} - \frac{\mathbf{L}^{21} \mathbf{L}^{12}}{\mathbf{L}^{11}} \right) (-\nabla T), \quad (3.36)$$

and therefore

$$k_{\text{el}} = \mathbf{L}^{22} - \frac{\mathbf{L}^{21} \mathbf{L}^{12}}{\mathbf{L}^{11}}. \quad (3.37)$$

The subtracted term is the back-action of the open-circuit Seebeck field on the heat current; for typical metals it is a small correction of order S^2/L_0 and is often neglected.

The Seebeck coefficient is obtained directly from the open-circuit condition. Defining the thermo-chemical potential $\mathcal{E} \equiv \mathbf{E} + \nabla \mu/e$ and the Seebeck relation $\mathcal{E} = S \nabla T$, we read off

$$S = \frac{\mathbf{L}^{12}}{\mathbf{L}^{11}}. \quad (3.38)$$

Eq. (3.38), combined with the moment expression (3.33), exposes the central principle of thermoelectricity at the semi-classical level: the thermopower is large when $\sigma(E)$ varies rapidly with energy near the Fermi level. That is, when there is a pronounced asymmetry between the conduc-

tivity of states just above and just below μ . This single observation underlies the entire search for thermoelectric materials with sharp features in the density of states near the chemical potential.

3.5.5 Why we go beyond the semi-classical model

The semi-classical Boltzmann picture is useful for building intuition, and Eqs. (3.28)–(3.38) will recur with reinterpreted ingredients, but it has two related limitations. First, it is not a fully quantum-mechanical theory: it uses quantum statistics and quantum band structure, but retains classical equations of motion between collisions. Second, the relaxation time $\tau(\mathbf{k})$ enters as an external input, which must be supplied from experiment or from a, generally difficult, microscopic calculation of each relevant scattering channel.

We therefore require a fully quantum-mechanical theory of transport, formulated directly in terms of the exact eigenstates of a possibly disordered single-particle Hamiltonian and free of any relaxation-time ansatz. A fully quantum treatment computes the response of the system to an applied field from the matrix elements of the current operator between exact eigenstates, with scattering arising automatically from the disordered potential rather than as a separate input. That formalism is linear-response theory, and its application to non-interacting electrons yields the Kubo–Greenwood formula derived in the next section.

3.6 The Kubo–Greenwood formula

The Kubo–Greenwood formula expresses the electrical conductivity, and its thermoelectric generalizations, directly in terms of matrix elements of the momentum operator between exact single-particle eigenstates of an arbitrary Hamiltonian. No relaxation time, no assumption of Bloch periodicity, and no distinction between coherent propagation and incoherent scattering need to be invoked: all of the physics is contained in the eigenstates and eigenvalues of $\hat{H}_0$, which in our calculations are the Kohn–Sham orbitals and energies obtained from density functional theory molecular dynamics at finite temperature. The derivation follows from reference [3]. It proceeds in four steps: (i) identify the macroscopic quantity to be computed (the average power absorbed by the system from an applied field); (ii) compute the same quantity microscopically using Fermi’s golden rule; (iii) equate the two and read off σ ; and (iv) generalize to thermoelectric coefficients by

replacing the charge current with the heat current.

3.6.1 Linear response

A system is dissipative if it absorbs energy when subjected to a time-periodic perturbation, and linear if the absorbed power is quadratic in the perturbation amplitude. For a linear electrical system driven by a sinusoidal voltage of amplitude V_0 and angular frequency ω , circuit theory gives the time-averaged absorbed power as

$$\langle P \rangle = \frac{1}{2} \frac{R}{|Z|^2} V_0^2 \quad (3.39)$$

where R is the resistance and Z the impedance. If we can compute the average rate of energy absorption quantum mechanically for the same applied voltage, and verify that it is indeed quadratic in V_0 , then comparison with (3.39) identifies the resistance and hence the conductivity.

3.6.2 Setting up the perturbation

Consider a single electron at position x inside a sample of length L , subjected to a sinusoidal voltage $V(t) = V_0 \sin(\omega t)$. The voltage produces a position-dependent potential energy $eV(t)x/L$, so the perturbation to the single-particle Hamiltonian is

$$\hat{V}(t) = \frac{eV_0}{L} \hat{x} \sin(\omega t) \quad (3.40)$$

We compute the rate at which this perturbation transfers energy to the electronic system using Fermi's golden rule.

3.6.3 Fermi's golden rule

Consider an unperturbed Hamiltonian $\hat{H}_0$ with eigenstates $|m\rangle$ and energies E_m , subjected to a time-periodic perturbation

$$\hat{V}(t) = \hat{V} e^{-i\omega t} + \hat{V}^\dagger e^{i\omega t} \quad (3.41)$$

Time-dependent perturbation theory, to first order in $\hat{V}$, gives the transition rate from initial state $|m\rangle$ to final state $|n\rangle$ as

$$W_{m \rightarrow n} = \frac{2\pi}{\hbar} |\langle n | \hat{V} | m \rangle|^2 \delta(E_n - E_m - \hbar\omega) \quad (3.42)$$

This is Fermi's golden rule. The matrix element $\langle n | \hat{V} | m \rangle$ encodes the coupling between initial and final states, while the δ -function enforces energy conservation: a single quantum $\hbar\omega$ from the perturbation is absorbed in the transition $|m\rangle \rightarrow |n\rangle$.

To convert the transition rate into a rate of energy absorption, we weight each transition by $\hbar\omega$ and sum over all initial and final states. The Pauli principle requires that the initial state be occupied and the final state empty, which adds a statistical factor $f(E_m) [1 - f(E_n)]$. The reverse process ($|n\rangle \rightarrow |m\rangle$), weighted by $f(E_n) [1 - f(E_m)]$ returns the same energy to the perturbation and must be subtracted. The net rate of energy absorption is therefore

$$\langle P \rangle = \hbar\omega \sum_{m,n} [f(E_m) [1 - f(E_n)] - f(E_n) [1 - f(E_m)]] W_{m \rightarrow n} \quad (3.43)$$

which simplifies, after expanding and relabeling, to

$$\langle P \rangle = \hbar\omega \sum_{m,n} [f(E_m) - f(E_n)] W_{m \rightarrow n} \quad (3.44)$$

3.6.4 The Kubo–Greenwood formula

Inserting the perturbation (3.40) into Fermi's golden rule (3.42) gives matrix elements of the form $\langle n | \hat{x} | m \rangle$, which are awkward to compute for extended states. They can be converted into momentum matrix elements via the operator identity

$$[\hat{x}, \hat{H}_0] = \frac{i\hbar}{m_e} \hat{p}_x \quad (3.45)$$

which between eigenstates of $\hat{H}_0$ implies

$$\langle n | \hat{x} | m \rangle = \frac{i\hbar}{m_e} \frac{\langle n | \hat{p}_x | m \rangle}{E_n - E_m} \quad (3.46)$$

Substituting (3.40) and (3.46) into (3.42), inserting the result into (3.44), and equating to (3.39) (with $V = V_0$, $R = L/\sigma A$, and the volume $\Omega = LA$) yields, after some algebra, the Kubo–Greenwood formula for the real part of the optical conductivity,

$$\sigma(\omega) = \frac{2\pi e^2 \hbar}{m_e^2 \omega \Omega} \sum_{n,m} [f(E_n) - f(E_m)] |\langle m | \hat{p}_\alpha | n \rangle|^2 \delta(E_m - E_n - \hbar\omega) \quad (3.47)$$

Here Ω is the volume of the simulation cell, the sum runs over all single-particle eigenstates, α is a Cartesian direction, and an isotropic system has been assumed for notational simplicity. The formula has a transparent physical interpretation: the conductivity at frequency ω is built up from electronic transitions $|n\rangle \rightarrow |m\rangle$ that absorb a quantum $\hbar\omega$, weighted by (i) the probability that state $|n\rangle$ is occupied and $|m\rangle$ is empty, and (ii) the squared momentum matrix element coupling the two states.

The momentum operator $\hat{p} = -i\hbar\nabla$ can be replaced by the gradient operator. Also, for the isotropic systems considered here, the scalar conductivity is obtained by averaging the diagonal elements of the conductivity tensor, $\sigma(\omega) = \frac{1}{3} \sum_\alpha \sigma_{\alpha\alpha}(\omega)$, which converts the single-component $|\langle m | \nabla_\alpha | n \rangle|^2$ into the squared magnitude of the full gradient $|\langle m | \nabla | n \rangle|^2$ together with an overall factor of 1/3. With these two conversions (3.47) reads equivalently

$$\sigma(\omega) = \frac{2\pi e^2 \hbar^3}{3 m_e^2 \omega \Omega} \sum_{n,m} [f(E_n) - f(E_m)] |\langle m | \nabla | n \rangle|^2 \delta(E_m - E_n - \hbar\omega) \quad (3.48)$$

which is the form output directly by most ab initio Kubo–Greenwood implementations and the form to which the rest of this dissertation refers.

The DC conductivity is the static limit

$$\sigma_{\text{DC}} = \lim_{\omega \rightarrow 0} \sigma(\omega) \quad (3.49)$$

Three features make (3.47) the natural workhorse for first-principles transport in disordered systems. First, no assumption of Bloch periodicity is required: the labels n, m index any complete set of single-particle eigenstates, including those of a glassy, liquid, or amorphous Hamiltonian. Second, all physical input — band velocities, scattering, Fermi-surface geometry — is encoded in

the momentum matrix elements between exact eigenstates; no relaxation-time ansatz is invoked. Third, the formula is naturally frequency-resolved, providing access to the optical conductivity in addition to the DC limit.

3.6.5 Generalization to heat transport

The same chain of arguments, applied to the heat current rather than the charge current, yields the full set of frequency-dependent kinetic coefficients. The heat current carried in a transition $|n\rangle \rightarrow |m\rangle$ differs from the charge current by a weighting in the energies of the participating states relative to the chemical potential μ . Repeating the derivation of (3.48) for charge-charge, charge-heat, and heat-heat correlations gives

$$\begin{aligned} \mathcal{L}^{(\alpha\beta)}(\omega) = & \frac{2\pi e^2 \hbar^2}{3 m_e^2 \omega \Omega} \sum_{n,m} [f(E_n) - f(E_m)] |\langle m | \nabla | n \rangle|^2 \\ & \times (-1)^{\alpha+\beta} (E_n - \mu)^{\alpha-1} (E_m - \mu)^{\beta-1} \delta(E_m - E_n - \hbar\omega) \end{aligned} \quad (3.50)$$

where the indices $\alpha, \beta = 1, 2$ label the charge (1) and heat (2) currents respectively. The $(\alpha\beta) = (1, 1)$ component describes charge-charge correlations, $(\alpha\beta) = (1, 2) = (2, 1)$ the thermoelectric cross-coupling (equal by Onsager reciprocity), and $(\alpha\beta) = (2, 2)$ heat-heat correlations. The conductivity formula (3.48) is recovered as the special case $\sigma(\omega) = \mathcal{L}^{(11)}(\omega)$.

The transport coefficients are obtained from the static limit $\omega \rightarrow 0$ of these correlation functions, in the same Onsager combination derived in the semi-classical theory:

$$\sigma = \mathcal{L}^{(11)}, \quad k_{\text{el}} = \frac{1}{e^2 T} \left[\mathcal{L}^{(22)} - \frac{(\mathcal{L}^{(12)})^2}{\mathcal{L}^{(11)}} \right], \quad S = \frac{1}{eT} \frac{\mathcal{L}^{(12)}}{\mathcal{L}^{(11)}} \quad (3.51)$$

Eqs. (3.50) and (3.51) are the central computational result of this chapter and the working formulae used throughout the rest of this dissertation. They express every electronic transport coefficient as a static moment of a frequency-dependent correlation function, evaluated entirely from Kohn–Sham eigenstates with no adjustable relaxation time.

3.6.6 Practical evaluation in DFT-MD

In an ab initio molecular-dynamics simulation (Chapter 4), (3.47) and (3.50) are evaluated for a sequence of statistically uncorrelated ionic snapshots. For each snapshot one (i) solves the Kohn–Sham equations to obtain the eigenvalues E_n and orbitals $|n\rangle$, (ii) computes the momentum matrix elements $\langle n | \hat{p}_\alpha | m \rangle$, and (iii) assembles $\sigma(\omega)$ and $\mathcal{L}^{(\alpha)}(\omega)$ as broadened sums over transitions. The frequency-resolved results are then averaged over snapshots, and over the (typically small) discrete $\mathbf{k}$ -point set used to sample the supercell Brillouin zone, yielding a smooth optical conductivity from which the d.c. limit is extracted by extrapolation $\omega \rightarrow 0$.

The energy-conserving δ -function in (3.47) cannot be evaluated exactly with a finite, discrete set of Kohn–Sham eigenvalues, and must be replaced by a finite-width Gaussian of broadening η . A broadening that is too small produces spurious oscillations as individual transitions fail to overlap, while too large a value washes out genuine spectral features. In practice η is chosen to be equal to, or a few times, the average level spacing, and the DC limit is verified to be stable under variations of this choice [4, 5].

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CHAPTER 4

Methodology & simulation: implementation of DFT

4.1 Introduction

In Chapter 2, we saw how density functional theory recasts the intractable many-electron problem into a set of single-particle Kohn-Sham equations,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (4.1)$$

to be solved self-consistently for the Kohn-Sham orbitals $\psi_i(\mathbf{r})$ and electron density $n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$, where f_i are occupation numbers. While this formulation is exact in principle, turning it into a practical computational scheme for a periodic solid at the high temperatures of the Earth's interior requires several additional ingredients. We must (i) choose a basis set in which to expand the Kohn-Sham orbitals, (ii) sample the Brillouin zone, (iii) handle the rapid oscillations of the valence orbitals near the atomic cores, (iv) extend the Kohn-Sham formalism to finite electronic temperature, (v) iterate the equations to self-consistency, and (vi) compute the forces on the ions for use in molecular dynamics. In this section, we describe how each of these steps is implemented in the Vienna *Ab initio* Simulation Package (VASP) [1, 2], which we use throughout this work. Also, much of the background is drawn from references [3, 4]

4.2 Plane-Wave Basis Sets and Bloch's Theorem

To solve Eq. 4.1 numerically, the Kohn-Sham orbitals must be represented in some chosen basis. For a periodic solid, the natural choice is a basis of plane waves, as justified by Bloch's theorem. Bloch's theorem states that for a system with a periodic potential, $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$, where $\mathbf{R}$ is any lattice translation vector, the eigenstates of the Hamiltonian can be written as a plane wave modulated by a function with the same periodicity as the lattice:

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (4.2)$$

where $\mathbf{k}$ is a wavevector lying in the first Brillouin zone, and $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$ has the periodicity of the lattice. Because $u_{\mathbf{k}}$ is periodic, it can be expanded as a Fourier series over the reciprocal lattice vectors $\mathbf{G}$:

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}. \quad (4.3)$$

Substituting into Eq. 4.2, we see that any Bloch state is a linear combination of plane waves:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (4.4)$$

The Kohn-Sham problem at each $\mathbf{k}$ has thus been reduced from finding a continuous function $\psi_{\mathbf{k}}(\mathbf{r})$ to finding the discrete set of coefficients $c_{\mathbf{k},\mathbf{G}}$.

In principle the sum in Eq. 4.4 runs over an infinite number of reciprocal lattice vectors, but in practice it is truncated by retaining only those plane waves whose kinetic energy lies below a chosen cutoff:

$$\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}}. \quad (4.5)$$

Higher-frequency plane waves describe more rapid spatial oscillations of $\psi_{\mathbf{k}}$, so E_{cut} controls the resolution with which the orbitals are represented. The cutoff energy is a convergence parameter that must be tested for each system: E_{cut} is increased until the quantities of interest (total energy, forces, and stresses) are converged.

4.3 k -point Sampling

Although Bloch's theorem allows us to label states by a wavevector $\mathbf{k}$ in the first Brillouin zone, computing the electron density and total energy requires integrals of these states over the Brillouin zone. For example, the electron density is

$$n(\mathbf{r}) = \sum_n \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} f_{n,\mathbf{k}} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2, \quad (4.6)$$

where n is a band index. In practice this integral is replaced by a weighted sum over a discrete mesh of $\mathbf{k}$ -points. The most widely used scheme, and the one we adopt, is the Monkhorst-Pack mesh [5], which generates a uniformly spaced grid of $\mathbf{k}$ -points in the Brillouin zone. The fineness

of this grid is another convergence parameter: a denser mesh provides a more accurate representation of the integral but increases the cost of each self-consistent cycle linearly with the number of k -points.

The required density of k -points depends on the size of the simulation cell. The Brillouin zone is the reciprocal of the real-space cell, so a larger supercell has a correspondingly smaller Brillouin zone, which can be sampled accurately with fewer k -points. For the large supercells used in our molecular dynamics simulations (80-160 atoms), Brillouin zone sampling is well converged at the Γ -point alone (the single point $k = 0$), and we use this choice throughout for molecular dynamics. For static calculations, such as those used to generate the orbitals that feed into the Kubo-Greenwood equation (Section 3.6), a finer mesh is required; specific values are reported with the relevant calculations.

4.4 Pseudopotentials and the Projector Augmented Wave Method

A naive plane-wave expansion of the Kohn-Sham orbitals is impractical because of the behavior of these orbitals near the atomic nuclei. Close to a nucleus, the bare Coulomb potential diverges, and the all-electron wavefunctions oscillate rapidly: core states are tightly bound and localized, while the valence states must oscillate to remain orthogonal to the core states. Representing these oscillations directly in a plane-wave basis would require an enormous cutoff energy, making the calculation intractable.

The fundamental observation that allows us to circumvent this problem is that the core electrons are essentially inert. They sit deep within the atom, do not participate in chemical bonding, and respond only weakly to changes in the external environment. Only the valence electrons need to be treated explicitly. This motivates the introduction of pseudopotentials, in which the all-electron potential of the bare nucleus plus the core electrons is replaced by an effective potential that acts only on the valence electrons. Outside a chosen core radius the pseudopotential reproduces the all-electron potential exactly; inside the core radius it is constructed to be smooth, so that the resulting valence pseudo-wavefunctions are nodeless and can be described with a modest plane-wave cutoff. The trade-off is a loss of information about the wavefunction inside the core region, which limits the accuracy with which certain properties (such as hyperfine parameters) can

be computed.

The specific scheme used by VASP, and adopted in this work, is the projector augmented wave (PAW) method of Blöchl [6], which retains the formal accuracy of an all-electron calculation while keeping the computational efficiency of pseudopotentials. The central idea is that the true, all-electron orbitals and a set of smooth pseudo-orbitals are related by a linear transformation that differs from the identity only inside a sphere centered on each nucleus, called the augmentation region. Inside these spheres, the smooth pseudo-orbital is decomposed onto a set of atomic pseudo-partial-waves obtained from a reference calculation on the isolated atom; the corresponding all-electron partial waves are then substituted back in to reconstruct the true orbital with all of its rapid core-region oscillations. Outside the augmentation spheres, the pseudo-orbitals and the all-electron orbitals coincide.

4.5 Finite-Temperature DFT and the Mermin Functional

The plane-wave basis, k-point sampling, and PAW method described above provide a tractable framework for solving the Kohn-Sham equations for a periodic solid, but they do so within a strictly zero-temperature formulation. For calculations at the conditions of the planetary interiors, we need an extension to finite temperature. Mermin [7] extended the Hohenberg-Kohn theorems to finite temperature by replacing the energy functional with the grand-canonical free-energy functional

$$\Omega[n] = E[n] - T_{\text{el}} S[n] - \mu \int n(\mathbf{r}) d\mathbf{r}, \quad (4.7)$$

where T_{el} is the electronic temperature, μ is the chemical potential, and $S_{\text{el}}[n]$ is the electronic entropy. Mermin showed that the equilibrium density at temperature T_{el} is the one that minimizes $\Omega[n]$, and that all equilibrium thermodynamic properties are unique functionals of this density. The Kohn-Sham equations retain their form, but the orbital occupations are now given by the Fermi-Dirac distribution at T_{el} ,

$$f_i = \frac{1}{e^{(\epsilon_i - \mu)/k_B T_{\text{el}}} + 1}, \quad (4.8)$$

which determines the electronic entropy:

$$S_{\text{el}} = -k_B \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)] \quad (4.9)$$

The Mermin formulation has two practical consequences for our calculations. First, it provides the rigorous justification for using a finite electronic smearing in metallic systems: the Fermi-Dirac smearing of width $\sigma = k_B T_{\text{el}}$ used in the Brillouin zone integration is not just a numerical convenience, but a physically meaningful representation of the system at temperature T_{el} . Second, in molecular dynamics simulations, the relevant thermodynamic potential governing the ionic dynamics is no longer the internal energy but the electronic free energy $F = E - T_{\text{el}} S_{\text{el}}$. Forces on the ions must therefore be derived from F rather than from E . We set the electronic temperature equal to the ionic temperature throughout, treating the electronic and ionic subsystems as being in thermal equilibrium.

4.6 Self-Consistent Solution

The Kohn-Sham equations are nonlinear: the effective potential $v_{\text{eff}}[n]$ depends on the density n , which in turn is built from the orbitals that are eigenstates of v_{eff} . They must therefore be solved self-consistently, by iteration. The standard procedure is

1. Generate an initial guess for the density $n_{\text{in}}(\mathbf{r})$, typically by superposing the densities of isolated atoms.
2. Construct the effective potential $v_{\text{eff}}[n_{\text{in}}]$.
3. Diagonalize the Kohn-Sham Hamiltonian to obtain orbitals $\{\psi_i\}$ and eigenvalues $\{\epsilon_i\}$.
4. Compute the chemical potential μ that gives the correct number of electrons under the chosen smearing, and assign occupations f_i .
5. Construct the output density, $n_{\text{out}} = \sum_i f_i |\psi_i|^2$.
6. Compare n_{out} with n_{in} . If they agree to within a chosen tolerance, the calculation has converged. Otherwise, mix n_{in} and n_{out} to produce a new input density and return to step 2.

In our calculations, we consider the cycle converged when the change in the total free energy between successive iterations falls below 10^{-5} or 10^{-6} eV.

4.7 Forces from the Hellmann-Feynman Theorem

The Kohn-Sham scheme described so far gives us the electronic free energy for a fixed configuration of nuclei. To run molecular dynamics, however, we also need the forces on those nuclei. Computing the force on each ion by finite differences of the energy would require a separate self-consistent calculation for each displacement and would quickly become prohibitive. The Hellmann-Feynman theorem provides a far more efficient alternative.

Consider a Hamiltonian $\hat{H}(\lambda)$ that depends on a parameter λ (here, an ionic coordinate), with normalized eigenstate $|\Psi(\lambda)\rangle$ and eigenvalue $E(\lambda)$. Differentiating $E(\lambda) = \langle \Psi(\lambda) | \hat{H}(\lambda) | \Psi(\lambda) \rangle$ with respect to λ gives

$$\frac{\partial E}{\partial \lambda} = \langle \Psi | \frac{\partial \hat{H}}{\partial \lambda} | \Psi \rangle + \langle \frac{\partial \Psi}{\partial \lambda} | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H} | \frac{\partial \Psi}{\partial \lambda} \rangle \quad (4.10)$$

For an exact eigenstate the last two terms combine to $E \partial \langle \Psi | \Psi \rangle / \partial \lambda$, which vanishes because $|\Psi\rangle$ is normalized. We are left with the Hellmann-Feynman theorem:

$$\frac{\partial E}{\partial \lambda} = \langle \Psi | \frac{\partial \hat{H}}{\partial \lambda} | \Psi \rangle. \quad (4.11)$$

The force on ion α is therefore given by

$$\mathbf{F}_\alpha = -\frac{\partial E}{\partial \mathbf{R}_\alpha} = -\langle \Psi | \frac{\partial \hat{H}}{\partial \mathbf{R}_\alpha} | \Psi \rangle \quad (4.12)$$

which can be evaluated as a single integral over the converged electronic state, with no need for additional self-consistency cycles. The forces obtained from Eq. 4.12 are then handed to the molecular dynamics integrator, as described in Section 4.8.

4.8 Molecular Dynamics

The methods of the previous section give us, for any chosen configuration of nuclei, the electronic free energy and the forces on each ion. We now need to evolve the ions through time under those

forces. This is the role of molecular dynamics (MD). In an MD simulation, the nuclei are treated as classical point particles whose trajectories are obtained by numerically integrating Newton's equations of motion, with the forces supplied at each step by, in our work, a first-principles electronic structure calculation.

Treating the nuclei classically while the electrons are described quantum-mechanically rests on the same Born-Oppenheimer approximation introduced in the previous chapter. Because the nuclei are several thousand times heavier than the electrons, they move on much slower timescales, and to a good approximation the electrons relax instantaneously to their ground state for any given nuclear configuration. This separation of timescales has two consequences for molecular dynamics. First, the electronic problem can be solved at each MD step assuming the nuclei are fixed, producing an electronic free-energy surface that depends parametrically on the nuclear positions. Second, this electronic free energy plays the role of the potential energy that drives the classical motion of the nuclei. The forces on the ions, computed via the Hellmann-Feynman theorem of Section 4.7, are simply the negative gradients of this surface. Treating the nuclei themselves classically is a separate approximation, and one that becomes questionable at low temperatures, where nuclear quantum effects (zero-point motion and tunneling) can be important. At the temperatures relevant to studies of planetary deep interiors, however, a classical treatment of the nuclei is appropriate.

To integrate the equations of motion forward in time, we discretize time into steps of size Δt and update the positions and velocities at each step, using the velocity Verlet algorithm. At each step, the new positions are computed from the current positions, velocities, and accelerations, the forces are then re-evaluated at the new positions, and the velocities are updated using the average of the old and new accelerations:

$$\mathbf{r}_\alpha(t + \Delta t) = \mathbf{r}_\alpha(t) + \mathbf{v}_\alpha(t)\Delta t + \frac{1}{2}\mathbf{a}_\alpha(t)\Delta t^2 \quad (4.13)$$

$$\mathbf{v}_\alpha(t + \Delta t) = \mathbf{v}_\alpha(t) + \frac{1}{2}[\mathbf{a}_\alpha(t) + \mathbf{a}_\alpha(t + \Delta t)]\Delta t \quad (4.14)$$

where $\mathbf{a}_\alpha = \mathbf{F}_\alpha/m_\alpha$. For the systems studied in our work, we use a timestep of $\Delta t = 0.5 - 1$ fs, which we find conserves energy/configurations and is consistent with values used in the literature for similar systems.

Beyond the choice of integrator and ensemble, setting up an MD simulation involves several further practical choices. The simulation cell is constructed as a periodic supercell of the underlying crystal structure, or primitive cell, large enough to suppress spurious interactions between an ion and its own periodic images. For our studies, we obtain converged results with supercells between 80 and 160 atoms in size. For liquid simulations, we overheat and melt the crystalline structure prior to performing a production run.

Because the initial configuration is rarely in equilibrium with the chosen thermodynamic state, each simulation begins with an equilibration phase, typically several picoseconds long, during which the system relaxes toward equilibrium and during which any time-averaged quantities are discarded. Production data are collected only after the running averages of the temperature, pressure, and total energy have stabilized. The total simulation time required depends on the quantity being computed, but ranges from 5 to 20 ps for our studies.

4.9 Thermodynamic Ensembles and Thermostats

Direct integration of Newton's equations as described above conserves the total energy and generates trajectories in the microcanonical ensemble (NVE): fixed number of particles, fixed volume, fixed total energy. This is rarely the ensemble of physical interest. Experiments and natural systems are more naturally described by ensembles at fixed temperature, or fixed temperature and pressure. To sample these ensembles, the Newtonian dynamics must be modified to allow energy to be exchanged with a heat bath (for the canonical ensemble, NVT) or with both a heat bath and a pressure reservoir (for the isothermal-isobaric ensemble, NPT). Throughout, we perform MD in the NVT ensemble.

The device that mediates the exchange of energy with a heat bath is called a thermostat. A simple but crude thermostat is velocity rescaling, in which the ionic velocities are periodically multiplied by a factor chosen to return the instantaneous kinetic temperature

$$T_{\text{ion}}(t) = \frac{1}{3Nk_B} \sum_{\alpha} m_{\alpha} |\mathbf{v}_{\alpha}(t)|^2 \quad (4.15)$$

to its target value. While this enforces the correct average temperature, it does not generate a true canonical distribution. We instead use the Nosé-Hoover thermostat, which introduces an

additional dynamical variable representing the heat bath and couples it to the ionic motion through an extended Hamiltonian. The resulting equations of motion can be shown to sample the canonical distribution exactly, in the limit of long simulation times.

4.10 Thermodynamic Integration

The molecular dynamics simulations described above give us direct access to mechanical and dynamical quantities (positions, velocities, forces, stresses), and to time-averaged thermodynamic quantities such as the internal energy and pressure. There is, however, a class of problems central to this work that lies beyond the reach of straightforward MD: the calculation of free energies, and of free energy differences between two systems. The Helmholtz free energy $F = U - TS$ depends explicitly on the entropy, which is not the time-average of any mechanical observable and therefore cannot be read off from a single trajectory. Yet it is precisely free energies, and free energy differences, that determine which of two phases is stable, and element partitioning between two phases. To compute these quantities we must turn to a separate technique: thermodynamic integration.

The basic idea of thermodynamic integration is to construct a continuous path in some parameter space that connects a reference system whose free energy is known to the target system whose free energy we wish to determine. Along this path, the rate of change of the free energy is the thermal average of an observable that can be computed from MD, and the total free energy difference is recovered by integrating along the path. Concretely, suppose we introduce a coupling parameter λ that smoothly interpolates between two Hamiltonians,

$$\hat{H}(\lambda) = (1 - \lambda)\hat{H}_0 + \lambda\hat{H}_1 \quad (4.16)$$

so that $\lambda = 0$ corresponds to the reference system and $\lambda = 1$ to the target system. The free energy at coupling λ is

$$F(\lambda) = -k_B T \ln Z(\lambda), \quad Z(\lambda) = \int e^{-\hat{H}(\lambda)/k_B T} d\Gamma, \quad (4.17)$$

and differentiating with respect to λ yields the central identity of thermodynamic integration:

$$\frac{\partial F}{\partial \lambda} = \left\langle \frac{\partial \hat{H}}{\partial \lambda} \right\rangle_{\lambda} = \langle \hat{H}_1 - \hat{H}_0 \rangle_{\lambda}, \quad (4.18)$$

where $\langle \cdot \rangle_{\lambda}$ denotes a thermal average taken in the ensemble generated by $\hat{H}(\lambda)$. The free energy difference between the two systems is then obtained by integrating Eq. 4.18 from $\lambda = 0$ to $\lambda = 1$:

$$\Delta F = F(1) - F(0) = \int_0^1 \langle \hat{H}_1 - \hat{H}_0 \rangle_{\lambda} d\lambda. \quad (4.19)$$

In practice, the integral is evaluated by running MD simulations at several values of λ between zero and one, computing the average energy difference at each, and approximating the integral by quadrature. The information lost by “not knowing the entropy” is recovered by sampling the configurations that the system actually visits at each intermediate λ .

In its most familiar use, thermodynamic integration is applied to absolute free energy calculations: one of the two endpoints is chosen to be a reference system whose free energy is already known analytically (the ideal gas, the harmonic crystal, or an Einstein solid) and the integration delivers the absolute free energy of the target system by adding a computed ΔF to the known reference value. This is the approach used, for example, to compute melting curves or absolute defect formation free energies.

Our application is different (see Chapter 5). Because we are ultimately interested in a ratio of concentrations - the distribution coefficient K_D between crystalline solid and silicate liquid - only differences of free energies enter the final answer, and the absolute free energies of the two endpoints drop out. We therefore do not need to anchor either endpoint to an analytically tractable reference system. Instead, the two endpoints of our integration are themselves both fully interacting, first-principles systems: one in which a chosen atom is treated as Mg, and another in which the same atom is treated as Fe. The integration delivers the free energy of transmuted Mg into Fe directly, with no reference state required.

Concretely, in our study of iron partitioning between bridgmanite and (Mg,Fe)SiO₃ liquid [8], we follow the approach of Alfè *et al.* [9] and Frenkel and Smit [3]: we identify $\lambda = 0$ with an MD trajectory in which the chosen atom is treated as Mg, and $\lambda = 1$ with the corresponding trajectory

in which that same atom is treated as Fe. The free energy of transmutation is then

$$\Delta F = \int_0^1 \langle \Delta U \rangle_\lambda d\lambda \approx \frac{\langle \Delta U \rangle_{\lambda=0} + \langle \Delta U \rangle_{\lambda=1}}{2}, \quad (4.20)$$

where ΔU is the difference in total energy between the iron-bearing and iron-free states evaluated on the same configuration. The total energy in this expression includes not only the internal energy E , but also the electronic and magnetic entropy contributions: $U = E - TS_{\text{el}} - TS_{\text{mag}}$, with the magnetic entropy given by $S_{\text{mag}} = Nk_B \ln(m + 1)$, where N is the number of iron atoms and m is the mean magnetic moment on the iron atoms in units of Bohr magnetons.

The two-point trapezoidal approximation in Eq. 4.20 is justified because the fluctuations in ΔU are small compared with both $\langle \Delta U \rangle$ and $k_B T$ [10], so the integrand is nearly linear in λ , and a single MD trajectory at each endpoint is sufficient. Once ΔF is in hand for each phase, the chemical potential difference driving the cation-exchange reaction, and the distribution coefficient K_D , are recovered through the relation

$$K_D = \exp \left(-\frac{\Delta \tilde{\mu}_R}{k_B T} \right), \quad (4.21)$$

as described in more detail in Chapter 5.

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CHAPTER 5

Results: Partitioning of iron between (Mg,Fe)SiO₃ liquid and Bridgmanite

This chapter is reproduced from Dragulet & Stixrude (2024) [1].

5.1 Introduction

The early Earth was extensively molten due to several large-scale heat sources, including radioactive decay, gravitational differentiation, and giant impacts [2], with the moon-forming impact likely melting the entire mantle [3]. The evolution and present-day structure of the mantle derives from how this molten mantle, or magma ocean, crystallized. An emerging view of this crystallization process suggests the formation of a basal magma ocean: a layer of silicate melt sandwiched between the outer core and solid mantle [4]. A basal magma ocean might explain the anomalous seismic properties of large low shear wave velocity provinces (LLSVPs) and ultra-low velocity zones (ULVZs), geochemical anomalies in mantle-derived rocks [5], and it could have powered the Earth's early magnetic field due to its high electrical conductivity [6].

The basal magma ocean is stabilized by crystal buoyancy, requiring crystal assemblages to have a lower density than silicate liquid at lower mantle conditions [7, 8]. While silicate crystals have higher densities than iso-chemical liquids throughout the mantle, the density of silicate liquid approaches that of the crystals as the depth increases [9]. In the lower mantle, the partitioning of heavy elements, including iron, into the liquid phase can cause its density to exceed that of crystals, inducing crystal flotation [10].

The degree of iron partitioning between the crystalline and liquid phases of the lower mantle is key to determining the gravitational stability of a basal magma ocean, and it is quantified by the Fe-Mg distribution coefficient, K_D . While there is a consensus that iron is incompatible ($K_D < 1$) in the dominant solid phase of the lower mantle (bridgmanite), the value of K_D is not well constrained experimentally. Reported values of K_D range from 0.06 to 0.6 [11, 12]. Values of the distribution coefficients on the lower end of this range are compatible with gravitational stability of a magma

ocean, while values at the higher end of this range imply bridgmanite crystals sink, and that a basal magma ocean cannot exist. Another important uncertainty is how the value of K_D varies with $X_{\text{Fe}} = \text{Fe}/(\text{Mg} + \text{Fe})$, which increases as the magma ocean crystallizes.

Here, we investigate the degree of ferrous iron partitioning between bridgmanite and liquid phases of $(\text{Mg,Fe})\text{SiO}_3$. We focus on bridgmanite because it is the most abundant mineral in the mantle and it is likely the first phase to crystallize out from the magma ocean at lower mantle conditions [13], so its buoyancy lays the foundation for the rest of the crystallization process. By applying a theoretical approach based on first principles, we seek to better constrain K_D for bridgmanite over the entire range of mantle pressures, and to test the gravitational stability of a putative basal magma ocean.

5.2 Methods

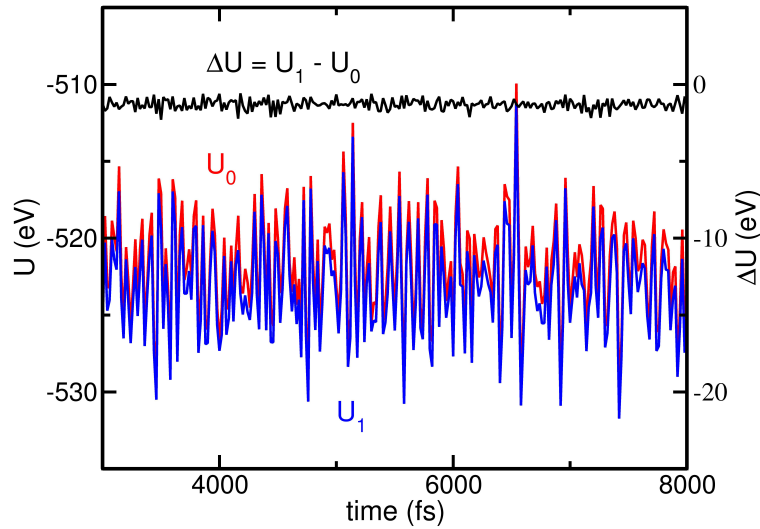


Figure 5.1: Internal energy of the bridgmanite phase along the iron-bearing trajectory ($\lambda = 1$) for iron-bearing (U_1) and iron-free (U_0) crystals at 4000 K and $V = 570 \text{ \AA}^3/\text{cell}$. The internal energy difference $\Delta U = U_1 - U_0$ is also shown (black, right axis).

Our techniques are similar to those recently applied to study Hf partitioning between bridgmanite and silicate liquid [5], and iron partitioning between solid and liquid $(\text{Mg,Fe})\text{O}$ [14]. An important generalization of these earlier studies, which focused on dilute solutions, is that here we explore

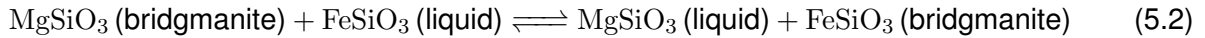
the entire range: $0 < X_{\text{Fe}} < 1$. First, we briefly review the theoretical basis for computing K_D from first principles molecular dynamics simulations and thermodynamic integration, a technique to compute the free energy difference between two states of a system that are coupled by some parameter. In our study, this coupling parameter is the iron content of the crystalline or liquid phases. Then, we provide further details of our simulations.

5.2.1 Iron Crystal-Liquid Partitioning and Thermodynamic Integration

The Fe/Mg distribution coefficient between bridgmanite and (Mg,Fe)SiO₃ liquid, K_D is defined by

$$K_D = \frac{X_{\text{Fe}}^{\text{bdg}} X_{\text{Mg}}^{\text{liq}}}{X_{\text{Fe}}^{\text{liq}} X_{\text{Mg}}^{\text{bdg}}} = \exp \left(-\frac{\Delta \tilde{\mu}_R}{k_B T} \right) \quad (5.1)$$

where X_i^j is the concentration of species i in phase j , k_B is the Boltzmann constant, T is the temperature, and $\Delta \tilde{\mu}_R$ is related to the chemical potential difference of the cation-exchange reaction



The chemical potential is

$$\mu_i^j = \tilde{\mu}_i^j + k_B T \ln X_i^j \quad (5.3)$$

with

$$\tilde{\mu}_i^j = \mu_{i0}^j + k_B T \ln \gamma_i^j \quad (5.4)$$

where $\tilde{\mu}_{i0}^j$ is the chemical potential at the end-member composition and γ_i^j is the activity coefficient. In Fig. 5.6 of the Supporting Information (Section 5.6), we show that the activity coefficients vary minimally with iron concentration. We can decompose the chemical potential of the reaction into contributions from the individual phases: $\Delta \tilde{\mu}_R = \Delta \tilde{\mu}_{\text{bdg}} - \Delta \tilde{\mu}_{\text{liq}}$ with $\Delta \tilde{\mu}_{\text{bdg}} = \tilde{\mu}_{\text{Fe}}^{\text{bdg}} - \tilde{\mu}_{\text{Mg}}^{\text{bdg}}$ and $\Delta \tilde{\mu}_{\text{liq}} = \tilde{\mu}_{\text{Fe}}^{\text{liq}} - \tilde{\mu}_{\text{Mg}}^{\text{liq}}$. To compute the chemical potentials, we make use of the thermodynamic identities: $\mu_i^j = (\partial F^j / \partial N_i)_{V,T,N_{k \neq i}} = (\partial G^j / \partial N_i)_{P,T,N_{k \neq i}}$ where F is the Helmholtz free energy, and find the free energy of transmutation of an Mg atom into an Fe atom via [15, 16]

$$\Delta F = \int_0^1 \langle \Delta U \rangle_\lambda d\lambda \approx \frac{\langle \Delta U \rangle_{\lambda=0} + \langle \Delta U \rangle_{\lambda=1}}{2} \quad (5.5)$$

where λ is a coupling parameter that connects our two systems of interest and determines the Hamiltonian that produces the molecular dynamics trajectory: $\lambda = 0$ corresponds to the iron-free trajectory while $\lambda = 1$ specifies the iron-bearing trajectory. $\langle \Delta U \rangle$ is the time-averaged difference in the total energy between the iron-bearing and iron-free states. The total energy $U = E - TS_{\text{el}} - TS_{\text{mag}}$, where E is the internal energy, T is the temperature, S_{el} is the electronic entropy and S_{mag} is the magnetic entropy. The latter is given by $S_{\text{mag}} = Nk_B \ln(m + 1)$ with N being the number of iron atoms, and m being the (mean) magnetic moment on the iron atom(s) in units of Bohr magnetons. We only require the two endpoints to compute the integral in Eq. 5.5 because the fluctuations in ΔU are small compared with $\langle \Delta U \rangle$ and $k_B T$ [17], as shown in Fig. 5.1.

The difference in pressure between crystalline and liquid phases is significant, and must be considered to compute $\Delta \tilde{\mu}_R$ at the pressure P_m :

$$\Delta \tilde{\mu}_R(P_m) = \frac{\Delta G_{\text{bdg}}(V, T, P_{\text{bdg}})}{\Delta N_{\text{Fe}}} - \frac{\Delta G_{\text{liq}}(V, T, P_{\text{liq}})}{\Delta N_{\text{Fe}}} \quad (5.6)$$

with

$$\Delta G_j(V, T, P_j) \cong \Delta F_j(V, T, P_j) - V \Delta P_j^2 / 2\kappa_j \quad (5.7)$$

where j represents the phase, and ΔP_j is the pressure difference between iron-free and iron-bearing compositions [17]. ΔP_j is insignificant because we transmute only one Mg atom into an Fe atom ($\Delta N_{\text{Fe}} = 1$). Therefore, P_j is taken as the pressure of the iron-free systems, and P_m is [18]:

$$P_m = \frac{P_{\text{bdg}} \sqrt{\kappa_{\text{bdg}}} + P_{\text{liq}} \sqrt{\kappa_{\text{liq}}}}{\sqrt{\kappa_{\text{bdg}}} + \sqrt{\kappa_{\text{liq}}}} \quad (5.8)$$

Here, κ_j represents the isothermal compressibility, determined from a third-order Birch-Murnaghan equation of state fit to our results (Fig. 5.2). We find that our equation of state for MgSiO_3 bridgmanite is in excellent agreement with experimental measurements [19]. Similarly, our MgSiO_3 liquid results are consistent with X-ray absorption measurements on MgSiO_3 glass [20], which acts as a structural analog to the melt. We find the substitution of Mg by Fe expands the volume of liquid and bridgmanite phases, as found experimentally [21, 22], and that the substitution makes both phases less compressible as also found experimentally for bridgmanite [21].

5.2.2 Simulation Details

Our first principles molecular dynamics simulations are based on density functional theory in the PBEsol approximation [23], using the projector augmented plane wave method as implemented in VASP [24, 25]. We perform Born-Oppenheimer molecular dynamics simulations in the canonical ensemble with periodic boundary conditions, a Nosé-Hoover thermostat, and a duration of 8–20 ps with 1 fs time step. We assume thermal equilibrium between the ions and electrons via the Mermin functional [26]. Sampling the Brillouin zone at the Gamma point and a basis-set energy cutoff of 500 eV converges the energy and pressure to within 4 meV/atom and 0.2 GPa, respectively. Prior to running simulations of the crystal, we adjust the lattice parameters of the orthorhombic cell at constant volume to ensure that the stress is hydrostatic [27]. For liquid simulations, we first melt the crystalline structure at 8000 K, and then cool to the temperature of interest.

Our system contains 16 MgSiO_3 units, with or without a single Fe^{2+} atom substituted for one Mg^{2+} atom, corresponding to $X_{\text{Fe}} = 6.25\%$. The outermost core radii, in Bohr, and number of electrons treated as valence are: Fe (2.2, 14), Mg (2, 8), Si (1.9, 4), and O (1.52, 6). To account for the Fe atom, our calculations are spin-polarized and utilize the $+U$ method [28], with $U - J = 2.5$ eV. The magnetic moment of the Fe^{2+} atom is fixed to $m = 4$ for high-spin (HS) calculations, and to $m = 0$ for low-spin (LS) simulations. We compute the equilibrium HS fraction via

$$f = \left\{ 1 + \exp \left[\frac{\Delta F_{\text{HS}} - \Delta F_{\text{LS}}}{k_{\text{B}}T} \right] \right\}^{-1} \quad (5.9)$$

which produces a value near unity (pure high-spin) at all but the smallest volume investigated ($520 \text{ \AA}^3$ per cell), where $f = 0.89 \pm 0.01$ for bridgmanite at 6000 K (135 GPa), $f = 0.83 \pm 0.04$ for the liquid phase at 6000 K (159 GPa), and $f = 0.92 \pm 0.03$ for the liquid phase at 4000 K (140 GPa) (Fig. 5.3).

We also investigate the dependence of the distribution coefficient on composition by calculating how ΔF varies with X_{Fe} . To do this, we increase the number of iron atoms in the simulation cell. For instance, at $X_{\text{Fe}} = 0.5$, $\lambda = 0$ and $\lambda = 1$ correspond to trajectories of $(\text{Mg}_7\text{Fe}_9)\text{Si}_{16}\text{O}_{48}$ and $(\text{Mg}_8\text{Fe}_8)\text{Si}_{16}\text{O}_{48}$, respectively. For simulations of bridgmanite with multiple iron atoms, we found that the distribution of iron atoms throughout the cell, whether clustered or evenly dispersed, does

not significantly affect ΔF . Our values of ΔF show minimal variation with X_{Fe} in both phases, at high and low pressures (Fig. 5.6). Hence, we find that K_D does not vary significantly with X_{Fe} . In the following, we therefore focus on our results near the Mg end-member as representative of the entire Mg-Fe join.

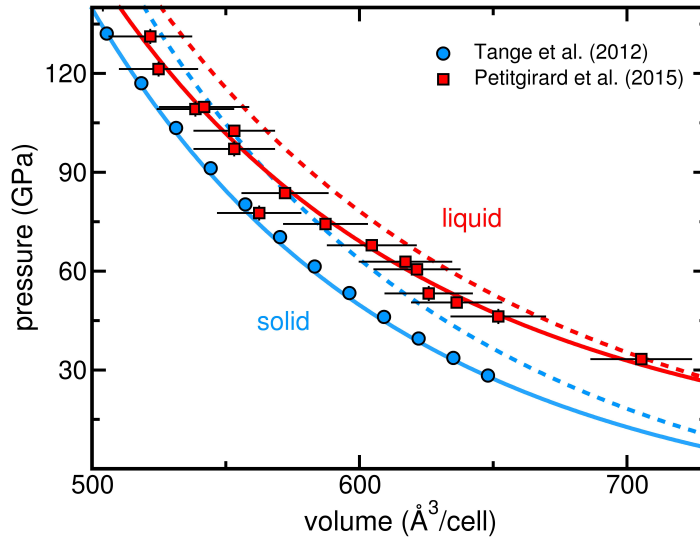


Figure 5.2: Equation of state of the bridgmanite (blue) and liquid (red) phases at 4000 K. The lines are third-order Birch-Murnaghan equation of state fits to our simulation results for MgSiO_3 (solid lines) and FeSiO_3 (dashed lines). The blue circles represent the 4000 K experimental isotherm of MgSiO_3 bridgmanite [19] while the red squares are X-ray absorption measurements on MgSiO_3 glass at 300 K that have been extrapolated to 4000 K [20].

5.3 Results

Fig. 5.3 shows the free energy difference of iron substitution, ΔF , as determined by Eq. 5.5. The key contributions to ΔF are the changes in internal energy and electronic entropy, while the contribution of magnetic entropy is minor (Fig. 5.7). Iron substitution is more favorable when the free energy change is more negative. At each temperature examined and over the entire range of volumes explored, we find that iron prefers the liquid phase. Additionally, ΔF increases as the volume decreases, and increases more rapidly for the solid than the liquid, indicating that iron becomes increasingly incompatible on compression.

The distribution coefficient between bridgmanite and silicate liquid, K_D , is less than unity as

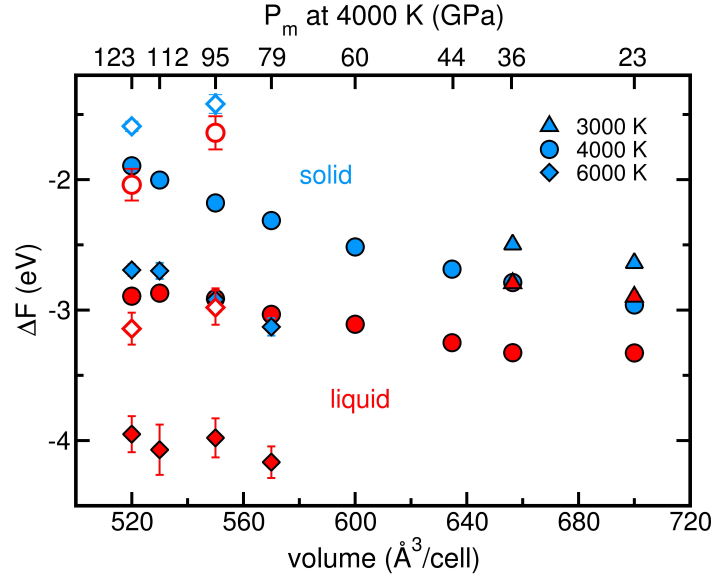


Figure 5.3: Free energy change of iron substitution, ΔF , versus volume of our simulation cell for bridgmanite (blue) and liquid (red) phases, with temperature denoted by the different symbol types. The pressure P_m (Eq. 5.8), is provided on the top axis. Closed and open symbols are calculations with high-spin and low-spin iron, respectively.

expected: iron is incompatible and partitions into the liquid phase (Fig. 5.4). At lower pressures, our ab-initio results are within uncertainty of multi-anvil experiments with peridotite bulk compositions [29, 30]. The distribution coefficient decreases with increasing pressure, reaching $K_D \leq 0.1$ at pressures characteristic of a putative basal magma ocean (>100 GPa). At these pressures, iron is strongly incompatible in the solid. We find a weak dependence of K_D on temperature. At higher pressure, our values for K_D fall within the range of many previous experimental results on a variety of starting materials, including olivine [12], pyrolite [31], and MORB [32] compositions.

We use our results to examine the possibility of crystal flotation (Fig. 5.5 top). First, we use our K_D results to calculate the densities of bridgmanite and silicate liquid at 4000 K, considering the effect of iron partitioning. We rearrange the definition of the distribution coefficient to obtain the bridgmanite iron content:

$$x_{\text{bdg}} = \left(\frac{1 - x_{\text{liq}}}{K_D x_{\text{liq}}} + 1 \right)^{-1} \quad (5.10)$$

where K_D is taken as the red curve in Fig. 5.4, x_{liq} is the iron fraction of the liquid, and x_{bdg} is the resulting pressure-dependent iron fraction in the crystals. We examine cases with $x_{\text{liq}} = 0.1$, char-

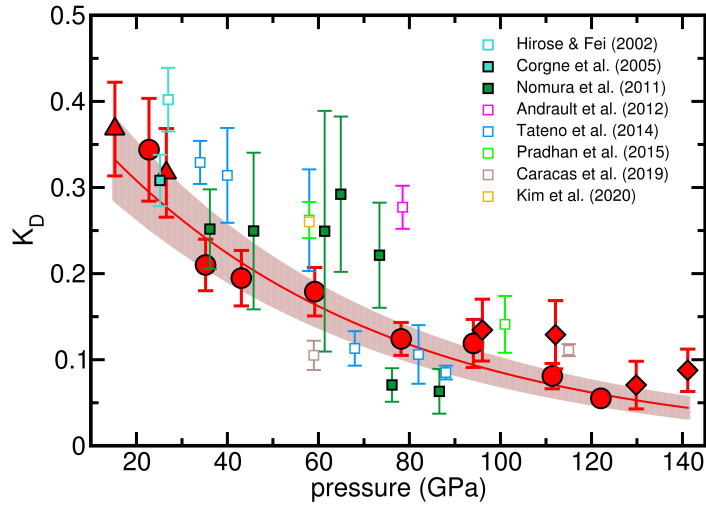


Figure 5.4: Fe/Mg distribution between bridgmanite and silicate liquid K_D versus pressure. The larger red symbols are our results, with symbol type indicating temperature as in Fig. 5.3 (triangles—3000 K; circles—4000 K; diamonds—6000 K). We fit our results to $K_D = \exp[-(\Delta H - T\Delta S + P\Delta V)/k_B T]$ and find $\Delta H = -19.66 \pm 10.90$ kJ/mol, $\Delta S = -12.04 \pm 3.28$ J/mol/K and $\Delta V = 0.53 \pm 0.05$ cm³/mol. The red line and shading is this exponential fit plotted with $T = 4000$ K. The smaller squares are results from experiments on aluminum-bearing starting materials (open squares) and aluminum-free starting materials (closed squares).

acteristic of a magma ocean with a bulk silicate Earth composition, and $x_{\text{liq}} = 0.2$, representative of an iron-enriched magma ocean.

Then, we compute the density of phase j by assuming the volume V varies linearly with iron content [21],

$$\rho_j = \frac{m^{\text{FeSiO}_3} x_j + m^{\text{MgSiO}_3} (1 - x_j)}{V_j^{\text{FeSiO}_3} x_j + V_j^{\text{MgSiO}_3} (1 - x_j)} \quad (5.11)$$

where m^i is the molar mass of component i and V_j^i is the volume of component i in phase j along the 4000 K isotherm. With no iron present (solid lines), there is no density crossover. The crossover pressure is at the core-mantle boundary (136 GPa) for $x_{\text{liq}} = 0.083$. For $x_{\text{liq}} = 0.1$, there is a density crossover around 120 GPa, meaning that the first bridgmanite crystal formed is neutrally buoyant at 120 GPa. For $x_{\text{liq}} = 0.2$, the first bridgmanite crystal floats at pressures greater than 75 GPa.

Next, we show how crystal buoyancy varies as the magma ocean freezes and becomes increasingly enriched in iron. We consider two end-member models of crystallization: fractional crystallization and batch crystallization. In the fractional crystallization model, infinitesimally small crystals are continuously removed from the melt as they form, and the evolution of the liquid (magma ocean) composition is described by the differential equation

$$\frac{dx_{\text{liq}}}{d\phi} = (D_{\text{Fe}} - 1) \frac{x_{\text{liq}}}{\phi} \quad (5.12)$$

where ϕ is the melt fraction, and $D_{\text{Fe}} = K_{\text{D}}(X_{\text{Mg}}^{\text{bdg}}/X_{\text{Mg}}^{\text{liq}})$ is the iron partition coefficient (Fig. 5.8). Starting with $x_{\text{liq}}^0 = 0.1$, we determine the iron fraction of the liquid and bridgmanite phases as the magma ocean is crystallizing. The density difference between the two phases is then obtained via Eq. 5.10. We also considered batch crystallization, where chemical equilibrium is maintained until the melt has completely solidified, and mass balance between the two phases yields the iron fraction:

$$x_{\text{liq}} = \frac{x_{\text{liq}}^0}{\phi(1 - D_{\text{Fe}}) + D_{\text{Fe}}} \quad (5.13)$$

At all pressures, the density of the liquid increases relative to the crystals as the magma ocean solidifies (Fig. 5.5 bottom). This increase becomes more prominent at higher pressures, due to smaller values of K_{D} and because the isochemical density contrast is smaller at higher pressures

(Fig. 5.2). Furthermore, the pressure of neutral buoyancy decreases with increasing crystallization, and is similar for fractional and batch crystallization. Thus, bridgmanite flotation occurs at the onset of crystallization and throughout the solidification process. We expect this conclusion to hold for the range of temperatures relevant for a basal magma ocean (Fig. 5.9). For extremely iron-rich compositions ($x_{\text{liq}} \rightarrow 1$), the density difference between the two phases diminishes as they both approach nearly Mg-free compositions.

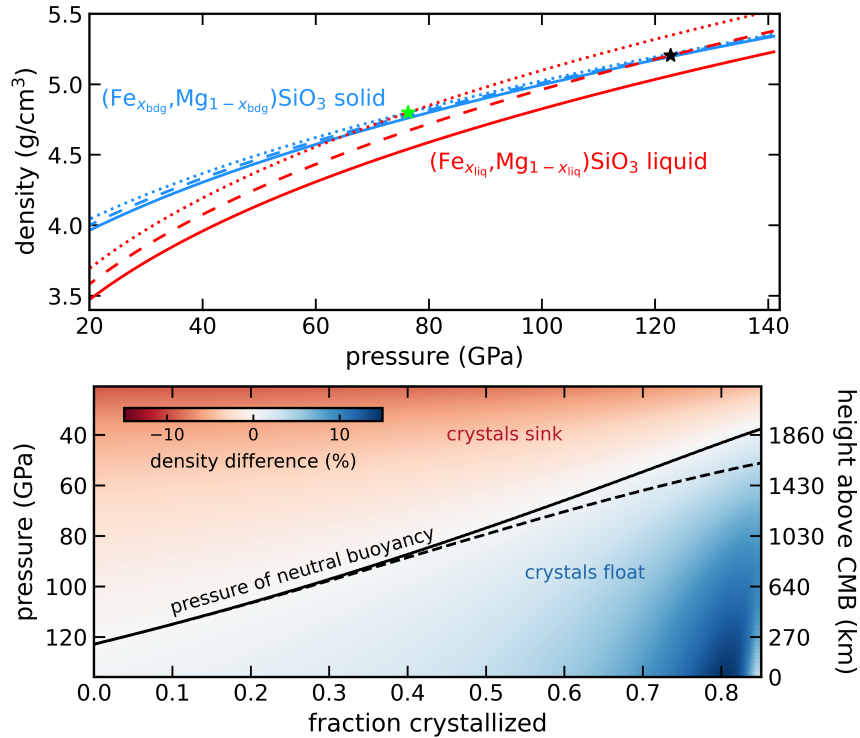


Figure 5.5: Top: density of the bridgmanite (blue) and liquid (red) phases versus pressure. The solid lines represent the densities of MgSiO_3 , while the dashed and dotted lines show the densities of both phases for $x_{\text{liq}} = 0.1$ and $x_{\text{liq}} = 0.2$, respectively, when taking iron partitioning effects into account via Eqs. 5.10 and 5.11. The black ($x_{\text{liq}} = 0.1$) and green ($x_{\text{liq}} = 0.2$) stars mark the density crossovers. Bottom: pressure versus the fraction of the magma ocean that has crystallized, starting with $x_{\text{liq}}^0 = 0.1$. Color indicates the density difference between bridgmanite and $(\text{Mg}, \text{Fe})\text{SiO}_3$ liquid computed via fractional crystallization (Eq. 5.12). Positive density differences (blue) correspond to the liquid being denser. The black lines denote the pressure at which the densities of both phases are equal for fractional (solid) and batch (dashed) crystallization.

5.4 Discussion

We predict that K_D decreases gradually with increasing pressure, with no abrupt changes. This trend is at odds with two experimental studies that find an abrupt decrease in K_D at pressures of 60–70 GPa [12, 31], which the authors attribute to a high-spin to low-spin transition in the liquid. We find no sharp spin transition in our results; in fact, liquid and solid phases are almost entirely high spin over the entire range of our study. A sharp spin transition also disagrees with experimental findings that the spin transition in silicate glasses occurs gradually with increasing pressure [33, 34]. Another explanation that has been advanced for the rapid pressure-induced change seen in K_D experimentally is a sudden change in Al-Fe incorporation mechanisms in bridgmanite [31]. This hypothesis could be tested with further ab initio simulations in Al-bearing systems, although we note that existing experimental results show no clear trend in K_D as a function of Al concentration (Fig. 5.4). We have focused on metasilicate stoichiometry, whereas the bulk silicate Earth has $(\text{Mg} + \text{Fe})/\text{Si} > 1$. An experimental study concluded that the range of perovskite flotation expands with increasing $(\text{Mg} + \text{Fe})/\text{Si}$ [35], strengthening our conclusions.

The small value of K_D that we find at lower mantle pressure makes the basal magma ocean gravitationally stable. We find that the first bridgmanite crystal formed in a magma ocean is neutrally buoyant at 120 GPa (270 km above the core-mantle boundary). For comparison, we note that if the value of K_D were much larger than what we find ($K_D > 0.2$), this first crystal would instead sink at all mantle pressures. As crystallization proceeds, the liquid is enriched in iron and crystals become buoyant over a larger range of pressure. For example, the pressure of neutral buoyancy is 101 GPa after 30% crystallization, and 62 GPa after 70% crystallization. Thus, the basal magma ocean becomes even more gravitationally stable with respect to crystals as crystallization proceeds. Our results suggest that the basal magma ocean may initially grow with time as the depth of neutral buoyancy rises further above the core-mantle boundary. In detail, the thickness of the magma ocean will also depend on other factors, including the variation of the geotherm with time, and the precise location of liquidus and solidus. Future dynamical studies of basal magma ocean evolution should include the effects of crystal buoyancy.

5.5 Conclusions

We have demonstrated how the Fe-Mg distribution coefficient, K_D , between bridgmanite and (Mg, Fe)SiO₃ liquid can be calculated using ab-initio molecular dynamics simulations and thermodynamic integration. K_D is much less than unity and decreases with increasing pressure, indicating that iron is incompatible in bridgmanite and becomes more incompatible at higher pressures. The magma ocean therefore becomes enriched in iron as it crystallizes, causing bridgmanite crystals to float at lower mantle conditions. We find this conclusion is unaffected by either temperature nor iron concentration; in fact the pressure of neutral buoyancy diminishes upon iron enrichment, so that the basal magma ocean may increase in thickness as it crystallizes. Ultimately, iron's preference for the liquid phase allows for a gravitationally stable basal magma ocean, which could have powered Earth's early magnetic field, and might explain some of the geochemical and seismic anomalies of today's mantle.

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5.6 Supplementary Information

Fig. 5.6 shows the free energy of iron substitution as a function of the iron concentration, to demonstrate that the Fe-Mg distribution coefficient between bridgmanite and silicate liquid does not vary significantly with iron content. Fig. 5.7 shows the electronic and magnetic contributions to the free energy of iron substitution. Fig. 5.8 shows how the iron content of silicate liquid and bridgmanite change as the liquid undergoes fractional crystallization. Fig. 5.9 shows how the volume difference between solid and liquid phases changes with temperature.

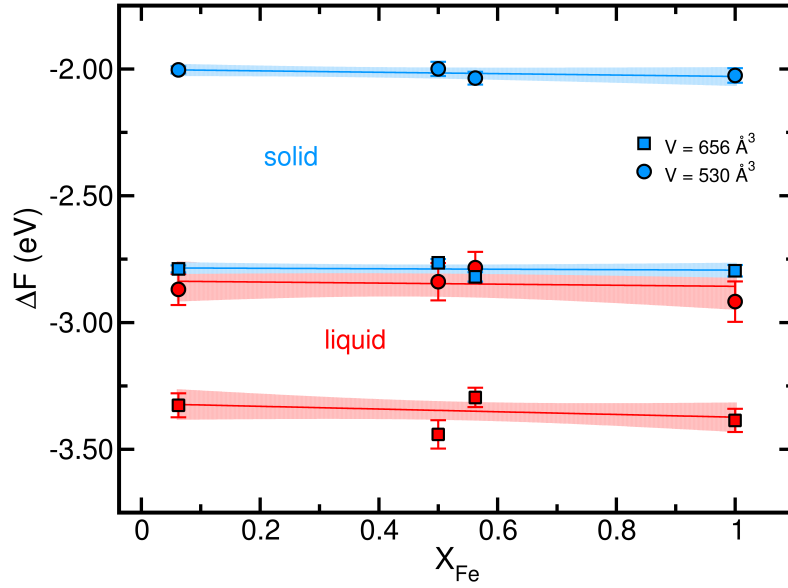


Figure 5.6: Free energy change of iron substitution, ΔF , versus the iron fraction, X_{Fe} , for the bridgmanite (blue) and liquid (red) phases at 4000 K and two different volumes. We see that ΔF does not vary significantly with iron content. The interaction parameters resulting from fits (lines with shaded uncertainty) to a symmetric regular solution model are $W^{\text{bdg}} = -0.44 \pm 1.70 \text{ kJ/mol}$ at $V = 656 \text{ \AA}^3$, $W^{\text{bdg}} = -1.33 \pm 1.99 \text{ kJ/mol}$ at $V = 530 \text{ \AA}^3$, $W^{\text{liq}} = -2.59 \pm 4.47 \text{ kJ/mol}$ at $V = 656 \text{ \AA}^3$ and $W^{\text{liq}} = -1.03 \pm 6.71 \text{ kJ/mol}$ at $V = 530 \text{ \AA}^3$. Therefore, the activity coefficients in Eq. 5.4 are near unity for all iron fractions, and K_{D} varies by less than 1% when W^{bdg} and W^{liq} are included in the calculation.

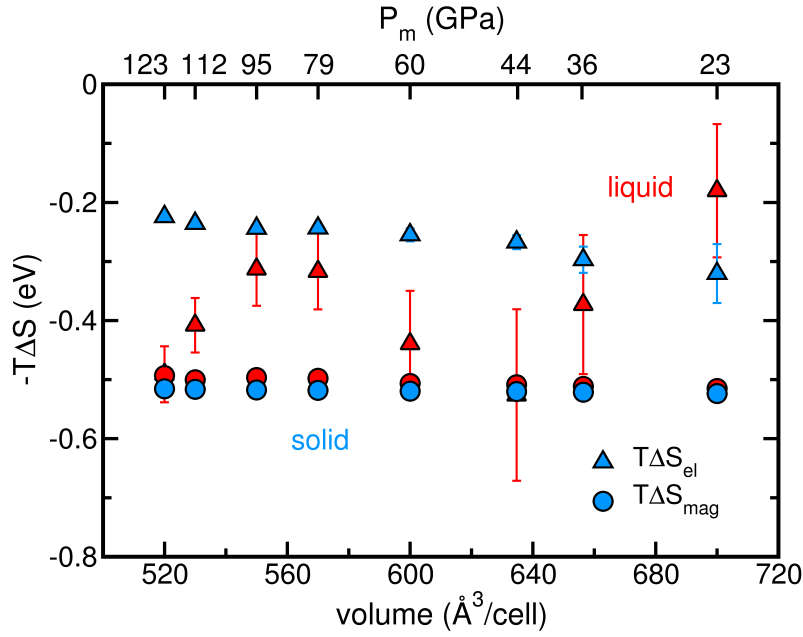


Figure 5.7: Contributions to free energy change of iron substitution, ΔF , from magnetic entropy S_{mag} and electronic entropy S_{el} for the bridgmanite (blue) and liquid (red) phases at 4000 K. More negative values indicate iron substitution is more favorable. The magnetic and electronic entropy make up 20–40% of the total free energy change ΔF in Fig. 5.3 of the main text. The magnetic entropy is very similar in both phases, while the electronic entropy favors iron partitioning into the liquid phase.

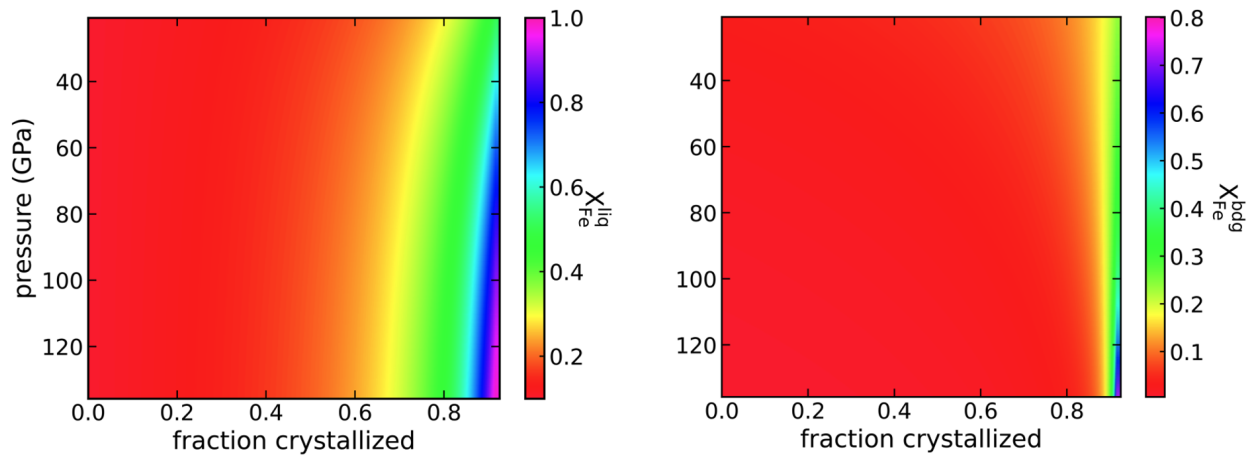


Figure 5.8: Fe/Mg iron fraction in the liquid ($X_{\text{Fe}}^{\text{liq}}$, left) and bridgmanite ($X_{\text{Fe}}^{\text{bdg}}$, right) as the magma ocean is undergoing fractional crystallization, as determined by Eqs. 5.10 and 5.12 in the main text.

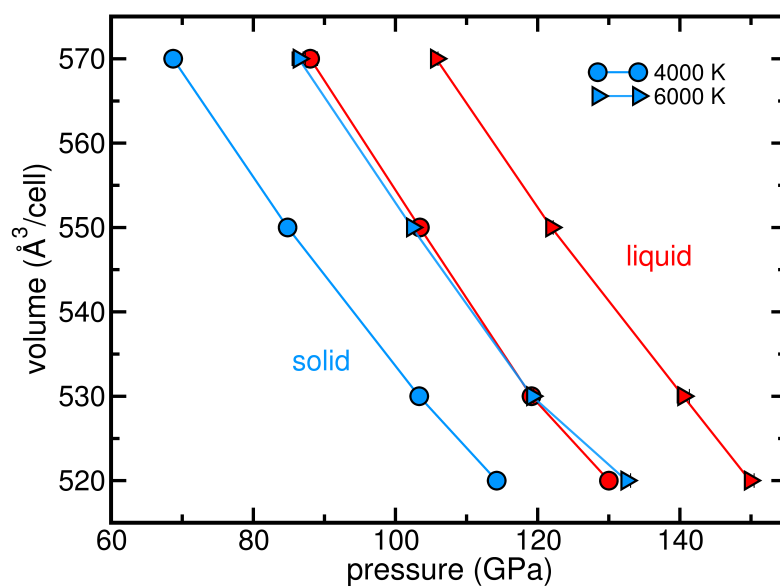


Figure 5.9: Volume vs pressure of solid (blue) and liquid (red) MgSiO_3 phases at 4000 K (circles) and 6000 K (triangles). The difference in volume between the two phases is not strongly affected by temperature, for the pressures and temperatures relevant for a basal magma ocean.

CHAPTER 6

Results: Electrical and thermal conductivity of Earth’s iron-enriched basal magma ocean

This chapter is reproduced from Dragulet & Stixrude (2025) [1].

6.1 Introduction

The Earth’s magnetic field has been active for at least 3.4 billion years, potentially playing a crucial role in making the planet habitable by shielding the surface from stellar irradiation and preventing atmospheric loss [2, 3]. Today, the magnetic field is sustained by a dynamo process, driven by the convection of liquid iron in the outer core. Given the core’s high thermal conductivity, this convection is likely thermochemical, powered by latent heat release and the expulsion of light elements during inner core solidification [4–6]. Consequently, the age of the core-powered dynamo is closely tied to the inner core’s formation, which is estimated to be relatively recent (< 1 Gyr) [7, 8]. Alternative methods of driving convection in the core, such as magnesium precipitation or radioactive heating, may be insufficient to drive a dynamo before inner core nucleation [9]. This suggests that another mechanism powered the early magnetic field.

The Earth’s early dynamo may have been operating in an electrically conducting basal magma ocean (BMO) [10, 11]. This layer of silicate melt, located between the core and solid mantle, likely persisted for billions of years, due to the insulating effect of the overlying mantle [12, 13]. As the BMO slowly crystallized from the top down, its chemical composition evolved through element partitioning between the melt and the overlying solid mantle. Over time, the BMO became significantly enriched in iron, as iron is incompatible with the mineral assemblages of the lower mantle [14–17]. This enrichment contributed to its gravitational stability and lowered its melting temperature.

Iron enrichment in the BMO likely influenced its ability to generate a dynamo by increasing electrical conductivity, which suggests a boost in the magnetic Reynolds number, R_m , and by modifying the conditions for convective motion through changes in thermal conductivity. The magnetic Reynolds number, a dimensionless quantity describing the ratio of magnetic induction to

magnetic diffusion, is defined as $R_m = \mu_0 v l \sigma$, where μ_0 is the magnetic permeability, v is the flow velocity, l is the thickness of the layer, and σ is the electrical conductivity. Magnetohydrodynamic simulations suggest that a minimum R_m of 40 is required for a self-sustaining dynamo [18]. However, R_m and, in particular, the electrical conductivity of the BMO are poorly constrained. No experiments have measured the electrical conductivity of iron-enriched silicate liquids at BMO conditions. High-pressure experiments on iron-bearing mantle minerals show that Fe enrichment can markedly increase electrical conductivity in solids [19–21], hinting a similar trend might occur in the liquid state despite different conduction mechanisms. Furthermore, previous calculations on liquids have focused on simplified systems - such as MgO, MgSiO₃, SiO₂, and bulk silicate Earth liquid [11, 22–24] - that do not capture the iron enrichment expected in a crystallizing BMO.

A silicate dynamo also requires the BMO to be convecting. Thermal convection occurs when the total heat flux out of the BMO, Q_{total} , exceeds the conductive heat flux $Q_{\text{cond}} = 4\pi r^2 k \nabla T_{\text{ad}}$, where r is the radius, k is the thermal conductivity, and ∇T_{ad} is the adiabatic temperature gradient. If thermal conductivity increases excessively with iron enrichment, heat transport becomes predominantly conductive, which can either completely suppress dynamo action or restrict it to compositional convection alone [25]. However, the thermal conductivity of the basal magma ocean, and its dependence on iron content, is unknown.

To better constrain the BMO’s potential to power a dynamo, we investigate how iron enrichment affects its electrical and thermal conductivity. We perform molecular dynamics simulations of silicate liquid with varying degrees of iron enrichment, quantified by the Fe-Mg fraction: $X_{\text{Fe}} = \text{Fe}/(\text{Fe} + \text{Mg})$. Our simulations are then combined with Kubo-Greenwood linear response theory to calculate the electronic contributions to electrical and thermal conductivity, following techniques from previous work [11, 22] - see Methods. We integrate our electrical conductivity results into a thermal evolution model to estimate the time evolution of the magnetic Reynolds number. We find that the electrical conductivity increases significantly with iron content, allowing R_m to exceed the threshold for dynamo action in Earth’s early history. Although thermal conductivity also rises with iron enrichment, it remains low enough to permit convective motion, suggesting that a silicate dynamo in the BMO was a viable mechanism for powering Earth’s early magnetic field.

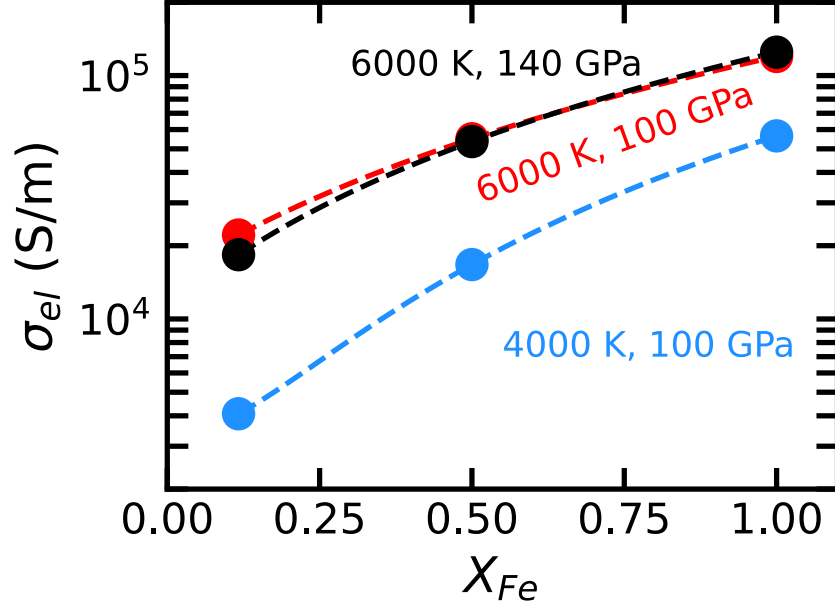


Figure 6.1: Electronic contribution to electrical conductivity σ_{el} of silicate liquid versus iron fraction $X_{Fe} = Fe/(Fe+Mg)$. Colors indicate different temperature and pressure conditions representative of Earth’s basal magma ocean. Circles denote our conductivity results at equilibrium high spin fraction at three iron fractions, with error bars smaller than the symbol size, while dashed lines represent quadratic fits to these data points.

6.2 Results

6.2.1 Electrical Conductivity

Fig. 6.1 shows the electronic contribution to the electrical conductivity, σ_{el} , for silicate liquid in its equilibrium spin state (see Methods). The silicate liquid composition approximates a pyrolitic mantle [26] (Table 6.1). To assess the impact of iron enrichment, we consider three iron fractions: $X_{Fe} = Fe/(Fe + Mg) = 0.12$ (pyrolitic), 0.5, and 1, with the latter two more representative of a crystallizing basal magma ocean. We find that σ_{el} is significantly greater than the ionic contribution σ_{ion} (Fig. 6.6). At $X_{Fe} = 0.12$, σ_{el} accounts for 70-80% of the total electrical conductivity $\sigma_{total} = \sigma_{el} + \sigma_{ion}$, depending on temperature. At $X_{Fe} = 1$, σ_{el} contributes more than 90 % of σ_{total} . This indicates that electrons are the dominant charge carriers in iron-bearing silicate liquid for the pressure-temperature-composition conditions examined.

At the pressures relevant for a basal magma ocean on Earth (100-140 GPa), σ_{el} increases with temperature (Fig. 6.1). Along the 6000 K isotherm, σ_{el} decreases slightly with increasing pressure

at $X_{\text{Fe}} = 0.12$. As X_{Fe} increases, the small effect of pressure is further reduced. Conductivity increases significantly with X_{Fe} : σ_{el} exceeds 10^5 S/m as X_{Fe} approaches 1, which is roughly an order of magnitude greater than σ_{el} at $X_{\text{Fe}} = 0.12$, yet still below typical metallic conductivities ($\sim 10^6$ S/m).

We find the origin of the strong dependence of σ_{el} on iron concentration in the electronic density of states. Fig. 6.2 compares the electronic density of states for iron-rich and iron-poor liquids when iron is high-spin, which is the dominant spin state (Fig. 6.7). The conductivity tracks the density of states at the Fermi level, $g(E_F)$, which is non-zero but lower than typical metals. As X_{Fe} increases, $g(E_F)$ rises due to the broad energy bands formed by the 3d electrons of the Fe ions and their hybridization with O 2p states. We find that the increase in $g(E_F)$ is linear in X_{Fe} for the pressures, temperatures and magnetic states explored (Fig. 6.8).

The dependence of σ_{el} on X_{Fe} is well described by a quadratic function (dotted lines in Fig. 6.1). This scaling is consistent with Mott-Ziman theory [27], which predicts that conductivity is proportional to the square of $g(E_F)$, which we observe to increase linearly with iron concentration (Fig. 6.8).

6.2.2 Thermal Conductivity

The electronic contribution to the thermal conductivity, k_{el} , in the equilibrium spin state is shown in Fig. 6.3. While the ionic thermal conductivity, k_{ion} , of iron-enriched silicate liquid is unknown, k_{ion} of MgSiO_3 liquid is 4-5 W/m/K at similar pressures and temperatures [28]. At low X_{Fe} , the electronic thermal conductivity of silicate liquid is comparable to both the ionic contribution in MgSiO_3 liquid [28] and the radiative contribution in iron-bearing silicate glasses [29]. However, at the higher iron concentrations characteristic of the basal magma ocean, the electronic component is expected to dominate.

The electronic contribution to the thermal conductivity k_{el} follows similar trends to σ_{el} : it is largely insensitive to pressure, increases with temperature, and rises significantly with iron content. As iron concentration increases, k_{el} remains substantially less than the range calculated for Earth's liquid outer core ($k_{\text{el}} > 100$ W/m/K) [4, 5, 30].

We explore the relationship between the electronic electrical conductivity and thermal conductivity and find that our results do not obey the Wiedemann-Franz law (Fig. 6.9). This semi-empirical

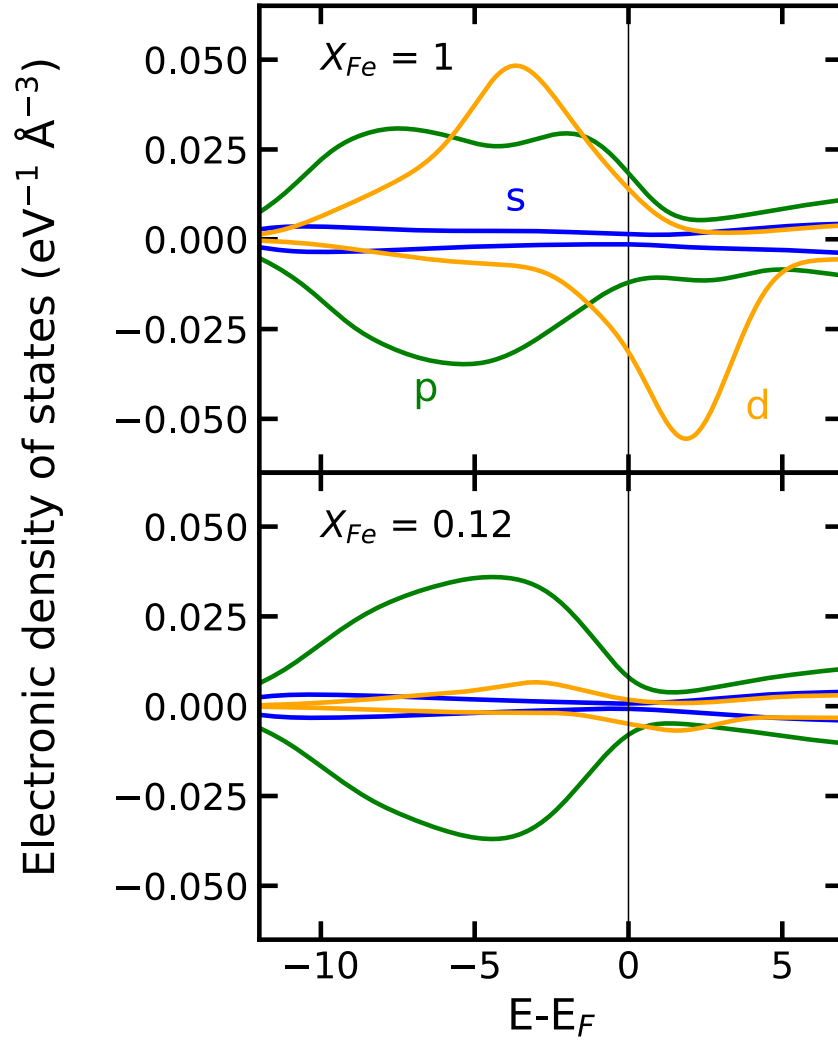


Figure 6.2: Electronic density of states in the high-spin iron bearing silicate liquid at 6000 K and 100 ± 10 GPa, shown for an iron-rich (top) and iron-poor (bottom) composition. Contributions from s (blue), p (green) and d (orange) states are shown separately, with up-spin and down-spin plotted as positive and negative, respectively. The black vertical line indicates the Fermi energy, E_F .

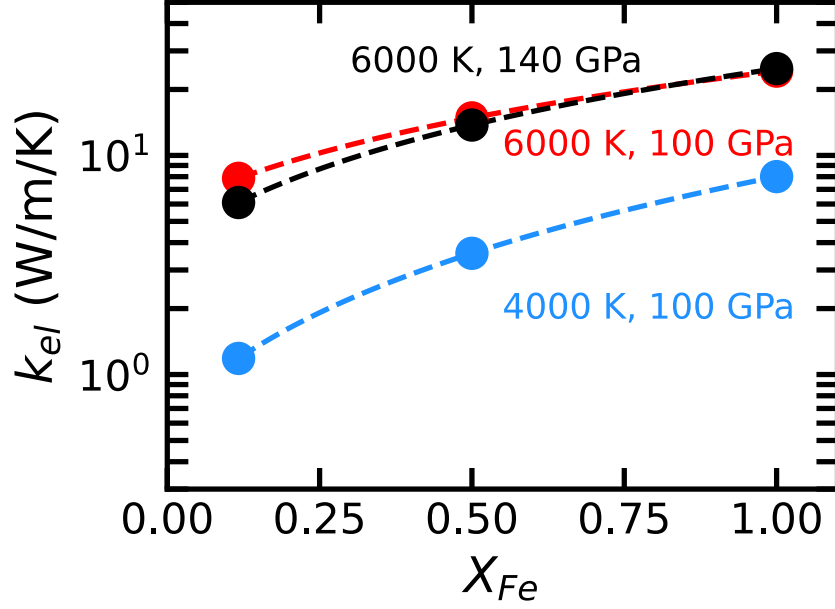


Figure 6.3: Electronic contribution to thermal conductivity k_{el} of silicate liquid versus iron fraction $X_{Fe} = Fe/(Fe+Mg)$. As in Fig. 6.1, colors indicate temperatures and pressures, while dashed lines represent quadratic fits to our conductivity results at the equilibrium spin state (circles). The errors in k_{el} are smaller than the symbol size.

result predicts a linear relationship according to the Lorenz number: $\lambda_0 = k_{el} (\sigma_{el} T)^{-1} = 2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$. However, this value of the Lorenz number is derived for metals, and we find the Lorenz number in our system to be significantly larger and dependent on pressure, temperature, and composition. Applying the Wiedemann-Franz law to estimate k_{el} from σ_{el} would lead to an underestimation. As iron concentration increases, the computed Lorenz number approaches the theoretical value, reflecting a trend toward metallic behavior (Fig. 6.9).

Although k_{el} increases substantially with iron content, it is not high enough to inhibit convection in the magma ocean. Even at the highest calculated values of k_{el} , the conductive heat flux remains less than the total outward heat flux from the basal magma ocean. For example, taking $k < 30 \text{ W/m/K}$, an adiabatic temperature gradient ∇T_{ad} of 0.6 K/km [31], and a BMO thickness of 400 km, yields a conductive heat flux, $Q_{cond} = 4\pi r^2 k \nabla T_{ad} < 4 \text{ TW}$. This is significantly less than the total heat flux out of the basal magma ocean estimated by our thermal evolution model (Fig. 6.10) and by other models [12, 32].

6.2.3 Thermal and Magnetic Evolution

To assess the potential for a silicate dynamo in Earth's past, we combine our results with a thermal evolution model of the basal magma ocean (Methods). This model tracks the BMO thickness, temperature, and iron content over time, all of which determine the time evolution of conductivity per Eqs. 6.10 and 6.8, along with a quadratic dependence of σ_{el} on X_{Fe} . The model also predicts the heat flux from the BMO, which, together with the conductivity, allows us to calculate the time evolution of the magnetic Reynolds number R_m .

Fig. 6.4 shows the time dependence of the magnetic Reynolds number, assuming a mixing length scaling for flow velocity [33] - see Methods. As the basal magma ocean crystallizes and shrinks over time (Fig. 6.10), the magnetic Reynolds number decreases. If the BMO maintains a constant pyrolytic composition (no iron enrichment), R_m surpasses the dynamo threshold of ($R_m = 40$) for the first 1.4 billion years of Earth's history. However, accounting for iron enrichment significantly increases the magnetic Reynolds number and the lifetime of the silicate dynamo (black line in Fig. 6.4). In this case, R_m remains above the dynamo threshold for 3.3 billion years, i.e. until 1.2 billion years ago. If the threshold value were doubled ($R_m = 80$), our model predicts a BMO dynamo for the first 2.5 Gyr of Earth's history. Using Coriolis-inertial-Archimedean balance scaling for the flow velocity instead reduces the silicate dynamo lifetime by 1.3 billion years (Fig. 6.11).

Also in Fig. 6.4, we show the dependence of the magnetic Reynolds number on the BMO thickness and X_{Fe} . X_{Fe} determines the liquidus temperature, T_{liq} , which, along with BMO thickness, controls total heat flowing out of the BMO, and, consequently, the flow velocity (Methods). Increases in X_{Fe} and BMO thickness both raise R_m . The minimum BMO thickness required to sustain a dynamo ($R_m = 40$) decreases from 200 km to less than 100 km, as X_{Fe} increases from 0.12 to 1.

6.3 Discussion

The basal magma ocean is significantly enriched in iron for most of its lifetime, which has a major impact on its electron transport properties. As the BMO cools, electrical and thermal conductivity tend to decrease with decreasing temperature. However, this trend is more than compensated by

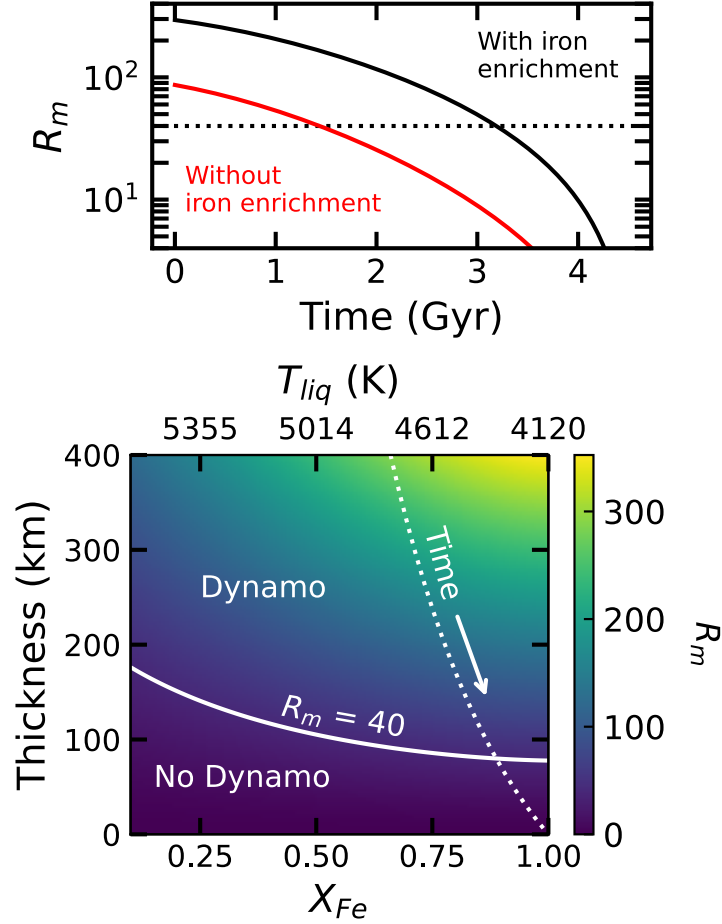


Figure 6.4: **Top:** Time evolution of the magnetic Reynolds number, R_m , as calculated by our thermal evolution model. The red line represents a constant pyrolite composition ($X_{Fe} = 0.12$), while the black line accounts for the effect of iron enrichment on electrical conductivity. The dotted line marks the threshold for a self-sustaining dynamo ($R_m > 40$). **Bottom:** Parameter space illustrating the effect of basal magma ocean thickness and Fe-Mg fraction X_{Fe} on the magnetic Reynolds number. The white contour ($R_m = 40$) represents the minimum BMO thickness required to sustain a dynamo for a given iron fraction. The dotted white line traces the thickness- X_{Fe} relationship predicted by our thermal evolution model. The top axis indicates the corresponding liquidus temperature, T_{liq} , defined by X_{Fe} (Eq. 6.15). R_m is calculated using a mixing length velocity scaling.

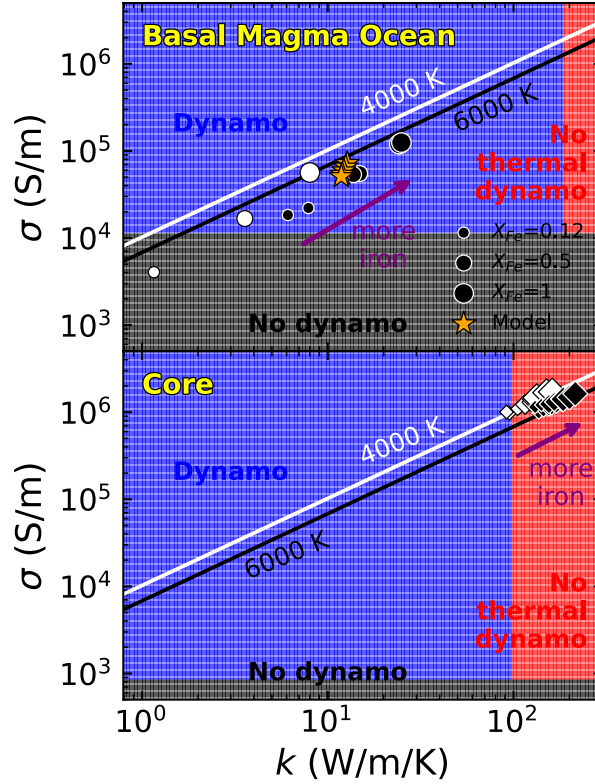


Figure 6.5: Regime diagram illustrating the effect of electrical conductivity σ and thermal conductivity k on dynamo production. The boundary between the "dynamo" and "no dynamo" regimes is defined by the magnetic Reynolds number $R_m = \mu_0 v l \sigma = 40$, while no thermal dynamo will occur if $Q_{\text{cond}} = 4\pi r^2 k \nabla T_{\text{ad}} > Q_{\text{total}}$. The solid lines correspond to the Wiedemann-Franz law relation, $k_{\text{el}}/\sigma_{\text{el}} = \lambda_0 T$, at 4000 K (white) and 6000 K (black). **Top:** basal magma ocean with a thickness of 300 km, total outward heat flux of $Q_{\text{total}} = 20$ TW, and adiabatic temperature gradient $\nabla T_{\text{ad}} = 0.6$ K/km [31]. Circles are electronic conductivity values at 4000 K (white) and 6000 K (black) from Figs. 6.1 and 6.3 of this study. Orange stars represent the time evolution of conductivity predicted by our thermal evolution model. **Bottom:** liquid core with thickness of 2260 km, $Q_{\text{total}} = 15$ TW, and $\nabla T_{\text{ad}} = 1$ K/km. Diamonds represent calculations of σ_{el} and k_{el} for Fe, Fe₇O, Fe₃O, Fe₇Si, and Fe₃Si liquid from reference [5]. These calculations are also along 4000 K (white) and 6000 K (black) isotherms, with larger symbols again corresponding to higher iron content (or lower fraction of light elements).

the significant increase in conductivity with increasing iron content, X_{Fe} , as the BMO crystallizes.

The iron-driven increase in conductivity is crucial for sustaining a silicate dynamo. Accounting for iron enrichment raises the magnetic Reynolds number above the threshold required for dynamo action for a much longer portion of Earth's history. At the same time, the increase in thermal conductivity with iron enrichment is not sufficient to make conduction the dominant heat transfer mechanism.

The compositional evolution of the basal magma ocean cannot be solely described by changes in X_{Fe} . In a crystallizing magma ocean, the silica content is expected to diminish with time since the liquidus phase at basal magma ocean conditions is bridgmanite [34–36]. Silica depletion is likely to further enhance σ_{el} [22], potentially allowing the BMO to sustain a dynamo until inner core nucleation, less than 1 billion years ago [7, 8].

Furthermore, we have not accounted for compositional convection. Similar to how compositional convection in the core is driven by the accumulation of light elements at the inner core boundary, compositional convection in a BMO can be driven by the descent of iron-enriched liquid during crystallization. This would further enhance the silicate dynamo.

Although the simultaneous increase in electrical and thermal conductivity raises the possibility of reaching a regime where a dynamo driven by thermal convection is not possible [25], a silicate dynamo does not reach this limit. This is illustrated in Fig. 6.5, which shows the effect of σ and k on dynamo generation for both the BMO and the core. While the core's thermal conductivity is too high to host a thermal dynamo, the iron-enriched basal magma ocean lies well within the thermal dynamo regime.

The implications of our findings extend beyond Earth. Other rocky extrasolar planets likely host, or have hosted, basal magma oceans [24, 37]. This suggests that silicate dynamos may be a widespread phenomenon, potentially playing a critical role in maintaining habitable conditions on rocky planets where a core dynamo is absent. Future work should investigate electrical and thermal conductivities at the more extreme pressures and temperatures of super-Earth interiors.

6.4 Methods

6.4.1 Molecular Dynamics Simulations

Our molecular dynamics simulations are based on density functional theory in the PBEsol approximation [38] augmented by the "+ U " method [39], with $U - J = 2.5$ eV as in our previous work [11, 22, 40, 41]. We utilize the projector augmented plane wave method, as implemented in VASP [42, 43]. We perform Born-Oppenheimer molecular dynamics simulations in the NVT ensemble with periodic boundary conditions, a Nosé-Hoover thermostat, and a duration of 10–15 ps with 1 fs time step. We assume thermal equilibrium between the ions and electrons via the Mermin functional [44]. Sampling the Brillouin zone at the Gamma point and a basis-set energy cutoff of 500 eV converges the energy and pressure to within 3 meV/atom and 0.2 GPa, respectively. We also perform spin-polarized molecular dynamics simulations; for the high-spin simulations, the difference between the number of up-spin and down-spin electrons is set equal to 4 times the number of iron atoms.

Our system contains 149 atoms of six different elements (Mg, Fe, Si, O, Ca and Al), with the relative proportions at $X_{\text{Fe}} = 0.12$ chosen to closely match a pyrolite model [26] - see Table 6.1. Our results at $X_{\text{Fe}} = 0.12$ with 149 atoms agree with simulations conducted with 1129 atoms [11]. At higher values of X_{Fe} , Mg is replaced by Fe.

We find that our results are little affected by the value of U - J or the exchange correlation functional. For example, setting U - J =0, instead of 2.5 eV increases the electrical conductivity by 20% (Fig. 6.12). Adopting the PBE exchange-correlation functional instead of PBEsol decreases the electrical conductivity by 10% (Fig. 6.12). We have neglected electron-electron scattering because the evaluation of this term is prohibitively expensive for our simulations and because previous studies have found that the effect on the electrical conductivity is less than 20% in thermally disordered systems such as ours [45].

6.4.2 Electrical and Thermal Conductivity

The electronic contributions to the electrical and thermal conductivity are computed by the Chester-Thellung formulation of the Kubo-Greenwood method:

$$\sigma_{\text{el}}(\omega) = L_{11}(\omega) \quad (6.1)$$

$$k_{\text{el}}(\omega) = \frac{1}{e^2 T} \left(L_{22}(\omega) - \frac{L_{12}(\omega)L_{21}(\omega)}{L_{11}(\omega)} \right) \quad (6.2)$$

The kinetic coefficients $L_{\alpha\beta}(\omega)$ at the electric field frequency ω are defined as

$$L_{\alpha\beta}(\omega) = \frac{2\pi e^2 \hbar^2}{3m_e^2 \omega \Omega} \sum_{i,j} (f_i - f_j) \delta(\epsilon_i - \epsilon_j - \hbar\omega) |\langle \psi_i | \nabla | \psi_j \rangle|^2 \times (-1)^{\alpha+\beta} (\epsilon_i - \mu)^{\alpha-1} (\epsilon_j - \mu)^{\beta-1} \quad (6.3)$$

where the summation is over pairs of states i, j , f is the Fermi occupation, ψ is the wavefunction, ϵ is the corresponding single-electron eigenvalue, Ω is the simulation volume, m_e is the electron mass, and μ is the chemical potential. The values of α and β denote whether the electrons are transporting charge or heat. In practice, the δ function is replaced by a Gaussian with a width given by the average spacing between eigenvalues weighted by the corresponding change in the Fermi function. To obtain the DC conductivity, the frequency dependent conductivity is extrapolated to zero frequency using a linear fit at small ω .

We compute σ_{el} , k_{el} and the electronic density of states by averaging over 10 uncorrelated molecular dynamics simulation snapshots. We found both σ_{el} and k_{el} to be well converged with a $1 \times 1 \times 1$ k-point mesh and 2500 electronic bands.

σ_{el} and k_{el} for high-spin and low-spin states are shown in Fig. 6.13. As X_{Fe} rises, the difference between high-spin and low-spin conductivities becomes pronounced, with the low-spin state exhibiting larger conductivity. For example, at $X_{\text{Fe}} = 1$ and a temperature of 6000 K, low-spin σ_{el} is at least double that of high-spin σ_{el} .

To obtain the total electrical conductivity $\sigma_{\text{total}} = \sigma_{\text{el}} + \sigma_{\text{ion}}$, we calculate the ionic contribution in the DC limit from the electric current auto correlation function $J(t)$ by

$$\sigma_{\text{ion}} = \frac{e^2}{3k_B T \Omega} \int J(t) dt \quad (6.4)$$

where

$$J(t) = \sum_{i,j} z_i z_j \langle \vec{u}_i(t+t_0) \cdot \vec{u}_j(t_0) \rangle \quad (6.5)$$

The angle brackets indicate an average over time origins t_0 , and the sum over ions i and j contains the Bader charge z and ion velocity $\vec{u}$. For the total thermal conductivity $k_{\text{total}} = k_{\text{el}} + k_{\text{ion}}$, we use the ionic thermal conductivity computed for MgSiO_3 liquid, 4 W/m/K at BMO conditions [28]. We neglect the radiative contribution to thermal conductivity, k_{rad} , as it is less than 1 W/m/K at the relevant pressures and temperatures [29].

6.4.3 Spin Transition

Eqs. 6.1, 6.2 and 6.3 specify the electronic conductivities from the molecular dynamics simulations, which treat iron as either high-spin or low-spin. The conductivity at the equilibrium spin state depends on the fraction of iron atoms that are high-spin, f_{eq} , which we calculate as

$$f_{\text{eq}} = \left[1 + \exp \left(\frac{\Delta F_{\text{HS-LS}}}{k_B T} \right) \right]^{-1} \quad (6.6)$$

Following our previous work [14, 17], we compute the free energy difference between liquids with high-spin iron and low-spin iron, $\Delta F_{\text{HS-LS}}$, via thermodynamic integration:

$$\Delta F_{\text{HS-LS}} = \int_0^1 \langle \Delta U \rangle_\lambda d\lambda \approx \frac{\langle \Delta U \rangle_{\lambda=0} + \langle \Delta U \rangle_{\lambda=1}}{2} \quad (6.7)$$

where λ determines the Hamiltonian that produces the molecular dynamics trajectory: $\lambda = 0$ corresponds to the high-spin iron simulation trajectory while $\lambda = 1$ specifies the low-spin trajectory. $\langle \Delta U \rangle$ is the time-averaged difference in the total energy between high-spin and low-spin simulations, calculated by transmuting a low-spin iron atom into a high-spin iron atom. The total energy is $U = E - T(S_{\text{el}} + S_{\text{mag}})$, where E is the internal energy, T is the temperature, S_{el} is the electronic entropy, and S_{mag} is the magnetic entropy. The magnetic entropy is $S_{\text{mag}} = N k_B \ln(\mu_m + 1)$, with N being the number of iron atoms and μ_m being the magnetic moment averaged over time and number of Fe atoms, in units of Bohr magnetons. Fig. 6.7 shows f_{eq} and its dependence on pressure, temperature and iron content.

We find that the high spin is the preferred spin state at lower pressures ($f_{\text{eq}} > 0.8$ at 100 GPa), consistent with other ab-initio studies on liquid silicates and oxides [41], and recent x-ray measurements on shock compressed $(\text{Mg}_{0.88}\text{Fe}_{0.12})_2\text{SiO}_4$ liquid [46]. As pressure increases, the

preferred spin state gradually shifts from high-spin to low-spin. The spin crossover, where $f_{\text{eq}} = 0.5$, depends on X_{Fe} , and occurs within the pressure range of 200-350 GPa for the silicate liquid. Notably, the concentration of low-spin iron atoms increases with the iron content, contrasting with the behavior observed in crystalline solids [21].

6.4.4 Electrical and Thermal Conductivity in Equilibrium

The high-spin conductivity $\sigma_{\text{el}}^{\text{HS}}$, low-spin conductivity $\sigma_{\text{el}}^{\text{LS}}$, and equilibrium high spin fraction f_{eq} are used to obtain the equilibrium electrical conductivity $\sigma_{\text{el}}^{\text{eq}}$ via [22]

$$\frac{1}{\sigma_{\text{el}}^{\text{eq}}} = \frac{f_{\text{eq}}}{\sigma_{\text{el}}^{\text{HS}}} + \frac{1 - f_{\text{eq}}}{\sigma_{\text{el}}^{\text{LS}}} \quad (6.8)$$

and likewise for the equilibrium electronic thermal conductivity:

$$\frac{1}{k_{\text{el}}^{\text{eq}}} = \frac{f_{\text{eq}}}{k_{\text{el}}^{\text{HS}}} + \frac{1 - f_{\text{eq}}}{k_{\text{el}}^{\text{LS}}} \quad (6.9)$$

To capture the pressure and temperature dependence of the electrical conductivity, we fit our results to the function

$$\sigma_{\text{el}}(P, T) = \sigma_s \exp\left(-\frac{\Delta E_s + P\Delta V_s}{RT}\right) \quad (6.10)$$

where P is the pressure, T is the temperature, and R is the gas constant. Similarly, we fit thermal conductivity data points to

$$k_{\text{el}}(P, T) = \sigma_k \lambda_0 T \exp\left(-\frac{\Delta E_k + P\Delta V_k}{RT}\right) \quad (6.11)$$

where $\lambda_0 = 2.44 \times 10^{-8} \text{W}\Omega/\text{K}^2$ is the theoretical Lorenz number. We assume the fit parameters σ_s , ΔE_s , ΔV_s , σ_k , ΔE_k , and ΔV_k are independent of pressure and temperature. We perform this fit at each X_{Fe} , with the resulting parameters displayed in Table 6.2. Furthermore, we fit our conductivity values to all variables to capture the multivariate dependence via a single function:

$$\sigma_{\text{el}}(X_{\text{Fe}}, P, T) = (\sigma'_u + \sigma''_u X_{\text{Fe}} + \sigma'''_u X_{\text{Fe}}^2) \exp\left(-\frac{\Delta E_u + P\Delta V_u}{RT}\right) \quad (6.12)$$

and

$$k_{\text{el}}(X_{\text{Fe}}, P, T) = (\sigma'_g + \sigma''_g X_{\text{Fe}} + \sigma'''_g X_{\text{Fe}}^2) \lambda_0 T \exp\left(-\frac{\Delta E_g + P\Delta V_g}{RT}\right) \quad (6.13)$$

finding $\sigma'_u = 49208.578$ S/m, $\sigma''_u = 474823.882$ S/m, $\sigma'''_u = 290152.338$ S/m, $\Delta E_u = 100.321$ kJ/mol, and $\Delta V_u = -0.026$ cm³/mol, $\sigma'_g = 141788.293$ S/m, $\sigma''_g = 588452.203$ S/m, $\sigma'''_g = 122128.270$ S/m, $\Delta E_g = 76.072$ kJ/mol, and $\Delta V_g = 0.035$ cm³/mol.

6.4.5 Thermal and Magnetic Evolution

We model the thermal and magnetic evolution of the basal magma ocean by solving the coupled system of equations:

$$4\pi a^2 k_m \frac{T_{\text{liq}} - T_m}{\delta} = -(M_m c_m + M_c c_c) \frac{dT_{\text{liq}}}{dt} + Q_{\text{radio}}(t) - 4\pi a^2 \rho \Delta S T_{\text{liq}} \frac{da}{dt} \quad (6.14)$$

$$T_{\text{liq}} = (T_A - T_B) \left(1 - \frac{\ln(1 - X_{\text{liq}}(1 - K_D))}{\ln(K_D)}\right) + T_B \quad (6.15)$$

$$\frac{dX_{\text{liq}}}{dt} = -\frac{3a^2(1 - D_{\text{Fe}})X_{\text{liq}}}{a^3 - b^3} \frac{da}{dt} \quad (6.16)$$

Eq. 6.14 describes the heat balance at the top boundary of the BMO, where the left-hand side is the total heat flux out of the BMO. The right-hand side includes contributions from, respectively, BMO secular cooling, core secular cooling, radioactive heat production, and latent heat of freezing. Here, a is the BMO outer radius, k_m is the thermal conductivity of the overlying mantle, T_{liq} is the liquidus temperature, and T_m is the mantle temperature, or the temperature atop the thermal boundary layer above the BMO. This thermal boundary layer has a thickness δ , which is held constant in our model. In reality, δ will change with time as it depends on viscosity and temperature; a recent study [47] explores such effects and finds scenarios with BMO thickness and lifetimes consistent with our assumptions. M and c are, respectively, the mass and specific heat of the BMO (subscript m) and core (subscript c), ρ is the BMO density, ΔS is the entropy change on freezing, and Q_{radio} is the radioactive heat production. Future studies should examine the partitioning of

radioactive elements between the BMO and solid mantle at relevant conditions, and its effect on the time evolution of Q_{radio} .

While previous models have assumed a linear phase diagram for T_{liq} as a function of BMO iron fraction X_{liq} [10–12], we adopt a nonlinear phase diagram, whose curvature depends on the Fe-Mg distribution coefficient, K_D [48]. This is Eq. 6.15, where the T_{liq} also depends on the melting temperature of MgSiO_3 , T_A , and the melting temperature of FeSiO_3 , T_B .

Eq. 6.16 governs the time evolution of X_{liq} , assuming fractional crystallization. The iron partition coefficient D_{Fe} is related to the distribution coefficient K_D by $D_{\text{Fe}} = K_D (1 - X_{\text{sol}}) / (1 - X_{\text{liq}})$, where X_{sol} is the iron fraction in the solid phase. Finally, b is the radius of the core (3480 km).

We solve these three equations numerically using a fourth-order Runge-Kutta method, yielding the time evolution of the BMO thickness, temperature and iron content (Fig. 6.10), which in turn allows us to track the time evolution of σ_{total} and k_{total} . We adopt most of the parameters from previous studies [11, 12] - see Table 6.3. Exceptions include T_A and ΔS , both of which we take from reference [49], and T_B , which we estimate as $T_B = \Delta H / \Delta S$, taking the enthalpy of melting ΔH from our previous simulations of solid and liquid FeSiO_3 [14], and assuming that the entropy of melting ΔS is the same as that of the MgSiO_3 system.

The final component needed to compute the time evolution of the magnetic Reynolds number is the flow velocity. We consider two different velocity scalings [33]. The first is mixing length theory (MLT):

$$v_{\text{MLT}} = \left(\frac{lq}{\rho H_T} \right)^{1/3} \quad (6.17)$$

and the second is based on a balance of Coriolis, inertial and Archimedean forces (CIA):

$$v_{\text{CIA}} = \left(\frac{q}{\rho H_T} \right)^{2/5} \left(\frac{l}{\Omega} \right)^{1/5} \quad (6.18)$$

where q is the total heat flow out of the basal magma ocean, l is the BMO thickness, ρ is the BMO density, H_T is the thermal scale height [31], and Ω is the rotation rate.

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6.5 Supplementary Information

Table 6.1: Composition of simulated system

Element	Number of atoms ($X_{\text{Fe}} = 0.117 / 0.5 / 1$)	Oxides wt. % ($X_{\text{Fe}} = 0.117 / 0.5 / 1$)	Pyrolite wt. % [26]
Mg	30 / 17 / 0	38.37 / 19.24 / 0	37.80
Fe	4 / 17 / 34	9.12 / 34.29 / 59.61	8.05
Si	24	45.72 / 40.46 / 35.16	45.00
Ca	2	3.56 / 3.15 / 2.74	3.55
Al	2	3.23 / 2.86 / 2.49	4.45
O	87		

Table 6.2: Conductivity Fit Parameters

X_{Fe}	σ_s (S/m)	ΔE_s (kJ/mol)	ΔV_s (cm ³ /mol)	σ_k (S/m)	ΔE_k (kJ/mol)	ΔV_k (cm ³ /mol)
0.12	715436.899	145.342	0.263	1038523.985	117.293	0.310
0.5	515811.595	111.415	0.020	753264.805	91.485	0.089
1	310290.887	67.819	-0.122	560784.939	67.154	-0.047

Table 6.3: Parameters of thermal evolution model

Parameter	Symbol	Value
Mantle thermal conductivity	k_m	8 W/m/K
Thermal boundary layer thickness	δ	95 km
Mantle temperature	T_m	2730 K
Basal magma ocean specific heat	c_m	1000 J/kg/K
Core specific heat	c_c	860 J/kg/K
Core mass	M_c	2×10^{24} kg
Entropy of melting	ΔS	580 J/kg/K
Melting temperature at $X_{\text{Fe}} = 0$	T_A	5650 K
Melting temperature at $X_{\text{Fe}} = 1$	T_B	4120 K
Fe-Mg distribution coefficient	K_D	0.5
Core radius	b	3480 km
Rotation rate	Ω	24 hours ⁻¹
Basal magma ocean adiabatic temperature gradient	∇T_{ad}	0.6 K/km
Basal magma ocean initial thickness	a_0	400 km
Basal magma ocean initial Fe-Mg fraction	$X_{\text{liq},0}$	0.65

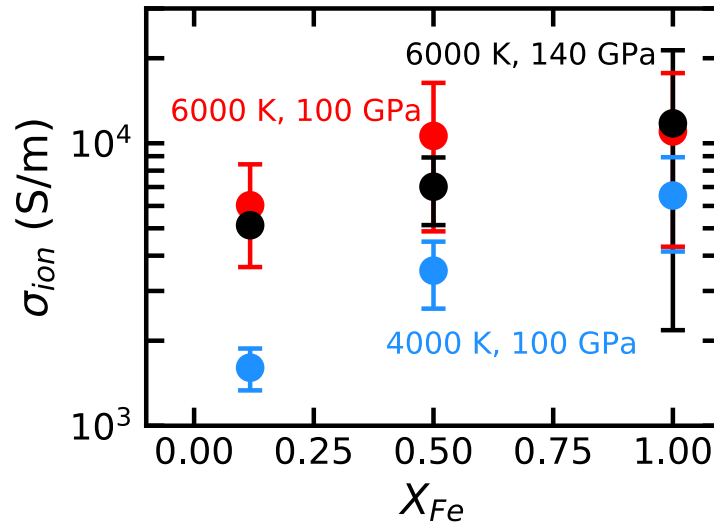


Figure 6.6: Ionic conductivity σ_{ion} of silicate liquid versus iron fraction $X_{Fe} = \text{Fe}/(\text{Fe}+\text{Mg})$. Colors indicate different temperature and pressure conditions representative of Earth's basal magma ocean. We show results from low-spin simulations, which do not differ significantly from high-spin results.

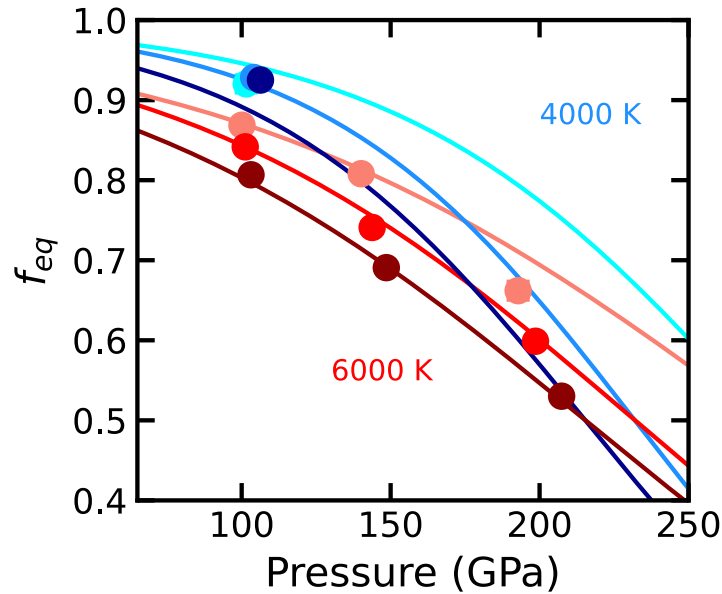


Figure 6.7: Equilibrium high-spin fraction f_{eq} versus pressure, at 4000 K (blue) and 6000 K (red). Symbol darkness represents the iron fraction $X_{Fe} = \text{Fe}/(\text{Fe}+\text{Mg})$: light blue/red for $X_{Fe} = 0.12$, medium blue/red $X_{Fe} = 0.5$, and darker blue/red for $X_{Fe} = 1$. Lines are fits of isochemical data to: $f_{eq} = \left[1 + \exp\left(-\frac{E^* + PV^*}{RT}\right)\right]^{-1}$.

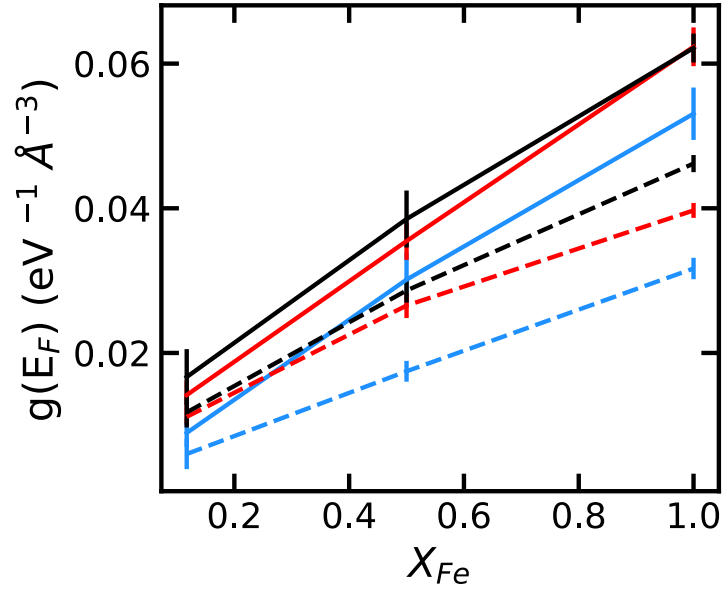


Figure 6.8: Density of states at the Fermi energy, $g(E_F)$ versus iron fraction X_{Fe} . Solid lines indicate low-spin results while dashed lines represent high-spin results. Colors represent pressure and temperature conditions (blue: 4000 K and ~ 100 GPa, red: 6000 K and ~ 100 GPa, black: 6000 K and ~ 200 GPa.)

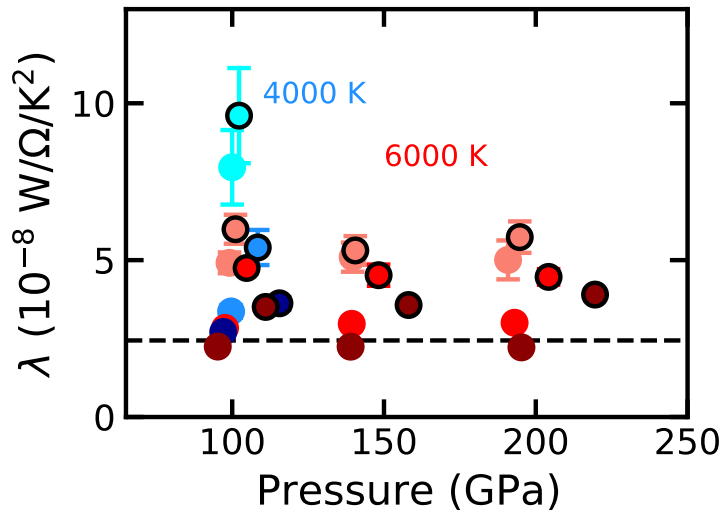


Figure 6.9: Lorenz number calculated as $\lambda = k_{el}/(\sigma_{el}T)$, as a function of pressure, at 4000 K (blue) and 6000 K (red). Symbol darkness represents the iron fraction X_{Fe} : light blue/red for $X_{Fe} = 0.12$, medium blue/red for $X_{Fe} = 0.5$, and dark blue/red for $X_{Fe} = 1$. Symbols outlined in black denote high-spin results, while symbols without an outline represent low-spin results. The black dashed line represents the theoretical Lorenz number ($\lambda = 2.44 \times 10^{-8} \text{ W}/\Omega/\text{K}^2$) typically used in applications of the Wiedemann-Franz law, determined by the free electron Sommerfeld model.

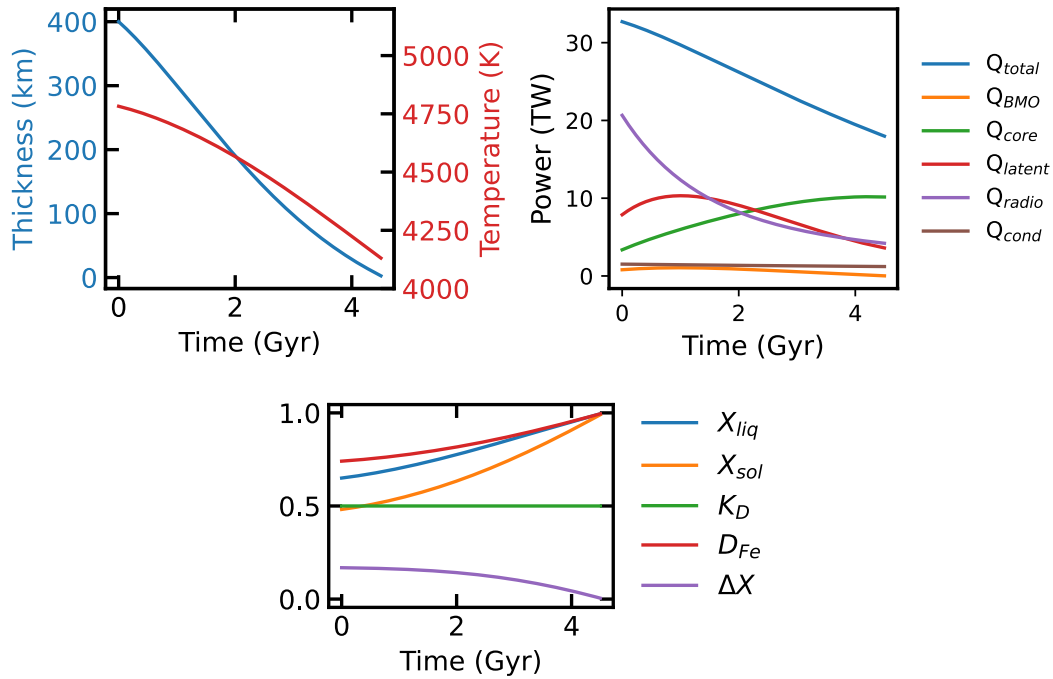


Figure 6.10: Thermal evolution of the basal magma ocean. **Top Left:** thickness of the basal magma ocean (blue) and liquidus temperature (red). **Top Right:** Heat flow over time, including total outward heat flux (blue), secular cooling of the core (green) and basal magma ocean (orange), radiogenic heat (purple), latent heat of freezing (red), and conductive heat flux (brown). **Bottom:** time evolution of iron fraction in the liquid (X_{liq}) and solid (X_{sol}), Fe-Mg distribution coefficient (K_D), iron partition coefficient (D_{Fe}), and difference in iron fractions between solid and liquid (ΔX).

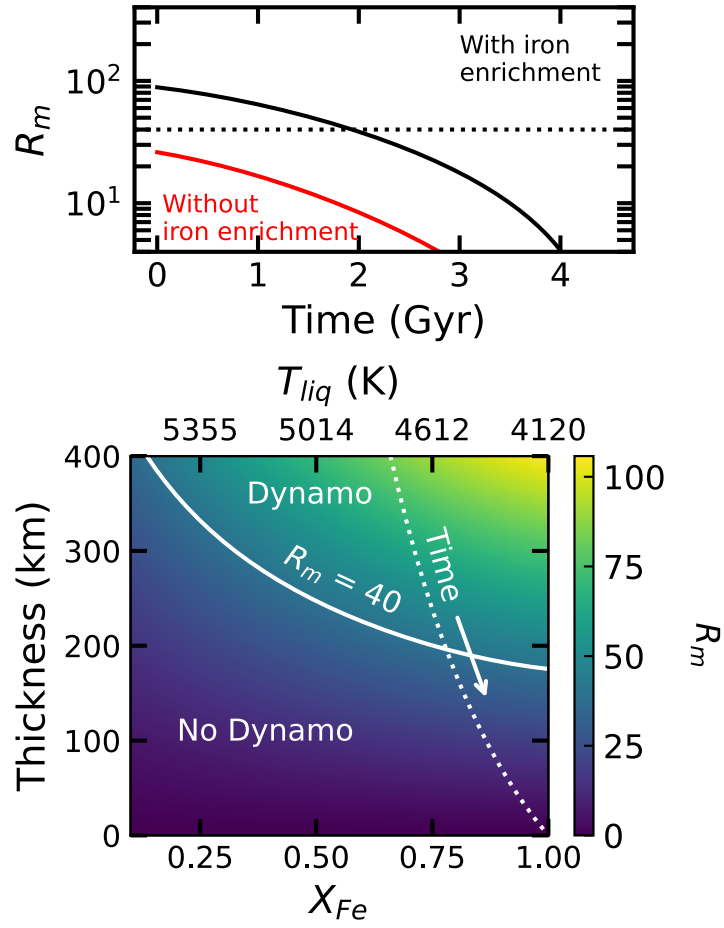


Figure 6.11: Same as Fig. 6.4, but now with Coriolis-inertial-Archimedean balance scaling for the flow velocity (Eq. 6.18).

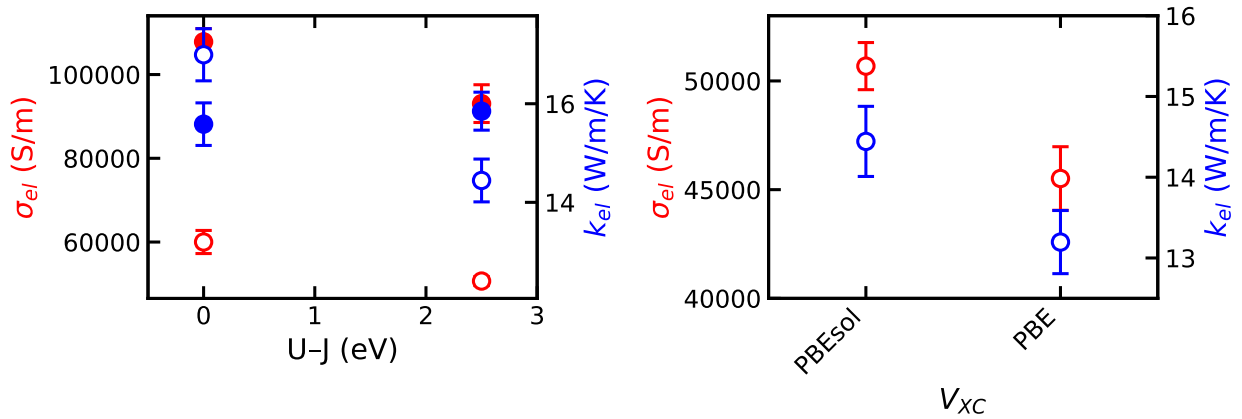


Figure 6.12: Effect of $U-J$ value (left) and exchange correlation potential V_{XC} (right) on electrical conductivity σ_{el} (red) and electronic thermal conductivity k_{el} (blue) at 6000 K, 100 GPa and $X_{Fe} = 0.5$. Open circles are simulations with high-spin iron, while closed circles are with low-spin iron.

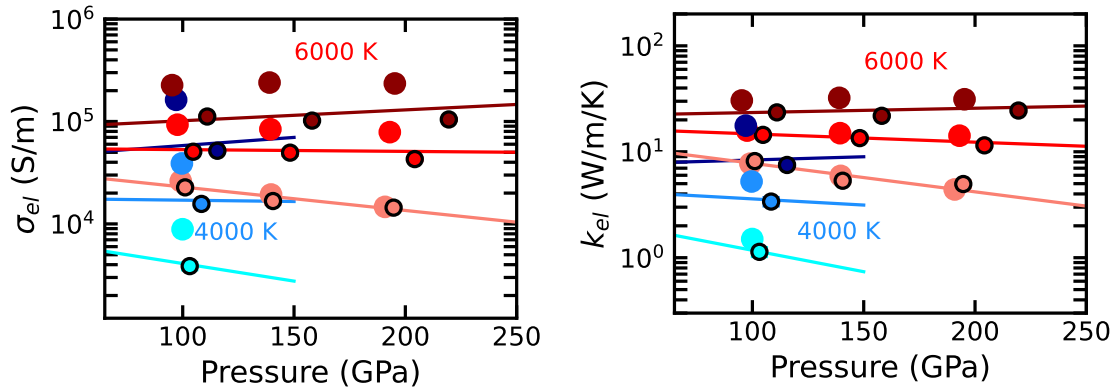


Figure 6.13: Electronic contribution to electrical conductivity, σ_{el} (**left**), and thermal conductivity, k_{el} (**right**), versus pressure at 4000 K (blue) and 6000 K (red). Symbol darkness represents the iron fraction X_{Fe} : light blue/red for $X_{Fe} = 0.12$, medium blue/red for $X_{Fe} = 0.5$, and dark blue/red for $X_{Fe} = 1$. Larger symbols denote low-spin results, while smaller symbols outlined in black denote high-spin results. Lines are fits of data at constant X_{Fe} and spin state to Eqs. 6.10 and 6.11.

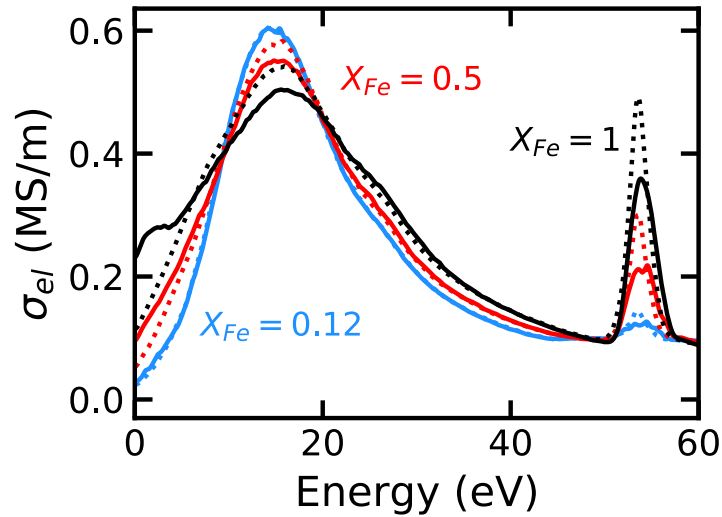


Figure 6.14: Electronic electrical conductivity as a function of energy at 6000 K and 100 ± 10 GPa for various iron fractions (colors), and spin states (solid: low-spin, dotted: high-spin).

CHAPTER 7

Results: Conductivity and thermoelectricity of iron up to super-Earth core conditions

7.1 Introduction

Exoplanet surveys, led by NASA's *Kepler* mission, have discovered thousands of exoplanets. Many of these planets have masses $1\text{--}10\ M_{\oplus}$ and bulk densities consistent with Earth-like compositions, so-called super-Earths, suggesting iron-silicate interiors broadly similar in structure to Earth [1]. A central question is whether, and how, these worlds generate global magnetic fields. Magnetic fields offer a potential probe of deep planetary interiors, as their existence requires a large, electrically conducting fluid layer undergoing convective motion [2]. They are also thought to be important for habitability, shielding planetary surfaces from stellar wind erosion and reducing atmospheric loss [3, 4]. Magnetic field generation and internal structure are therefore inseparable problems that jointly determine a planet's long-term evolution and habitability.

One pathway to magnetic field generation in rocky planets is a core-powered dynamo, as operates in the present-day Earth [5]. Earth's magnetic field is sustained by convection of liquid iron in the outer core, driven primarily by the solidification of the inner core: as the inner core freezes, it releases latent heat and expels light elements into the overlying liquid, generating the compositional buoyancy that powers convection [6]. Thermal convection, driven by the secular cooling of the core, could in principle also sustain a dynamo, but first-principles calculations of iron's thermal conductivity at core conditions ($\sim 135\text{--}360$ GPa, $\sim 4000\text{--}6000$ K) indicate that the heat conducted down the adiabat can exceed the heat extracted through the core-mantle boundary [7, 8], so that without inner core growth the core would not undergo the requisite convection to sustain a dynamo [9, 10]. Whether the cores of super-Earths face the same predicament, or whether their different pressure and temperature conditions shift the balance in favor of thermal convection, remains an open question.

A second, less-explored pathway for magnetic field generation is the thermoelectric (Seebeck) effect, which produces electric currents wherever a temperature gradient spans an interface be-

tween two conductors with different Seebeck coefficients. In planets, lateral temperature gradients at a bumpy core-mantle boundary can generate thermoelectric currents that produce a toroidal magnetic field, which can in turn be converted to a poloidal field via convective helicity in the core [11, 12]. Recent magnetohydrodynamic experiments support the plausibility of this mechanism: at both solid-liquid [13] and liquid-liquid [14] metal interfaces, Seebeck contrasts of order $\sim 10 \mu\text{V/K}$ are sufficient to drive dynamically significant flows and generate non-negligible induced magnetic fields. For such currents to flow at a planetary core-mantle boundary, both sides of the interface must be electrically conductive. This condition may be met in super-Earths, where the extreme pressures and temperatures at the base of the mantle raise silicate electrical conductivity to semi-metallic values [15, 16], allowing thermoelectric currents to close through the mantle side of the boundary. Evaluating this mechanism quantitatively requires the Seebeck coefficients of both iron and silicate phases at conditions far beyond existing experimental and theoretical data.

Both mechanisms depend fundamentally on iron’s transport properties: electrical conductivity σ_{el} sets the magnetic Reynolds number and hence the viability of dynamo action, electronic thermal conductivity k_{el} controls the adiabatic heat flux that must be exceeded for thermal convection to occur, and the Seebeck coefficient S determines the magnitude of thermoelectric currents at core interfaces. Super-Earth cores may reach pressures of several thousand GPa and temperatures on the order of 10^4 K [17]. For example, at the core-mantle boundary of a $10 M_{\oplus}$ planet with an Earth-like core mass fraction, pressures of 1600-1800 GPa and temperatures of 18,000 - 20,000 K are expected for a just-molten core. Under such conditions, σ_{el} , k_{el} , and S are largely unconstrained. In this study, we use density functional theory molecular dynamics simulations combined with Kubo-Greenwood linear response theory to compute σ_{el} , k_{el} and S at pressures ranging from 2.5 to 4000 GPa, and temperatures ranging from 900 to 25,000 K. We incorporate the thermal conductivity into self-consistent super-Earth interior structure models to determine, as a function of planet mass and core mass fraction (CMF), whether thermally driven dynamos are thermodynamically permitted. We also estimate inner core solidification timescales across the same range of planet masses and CMF. The Seebeck coefficient results provide the first-principles core-side input required for future evaluation of thermoelectric currents at core-mantle interfaces.

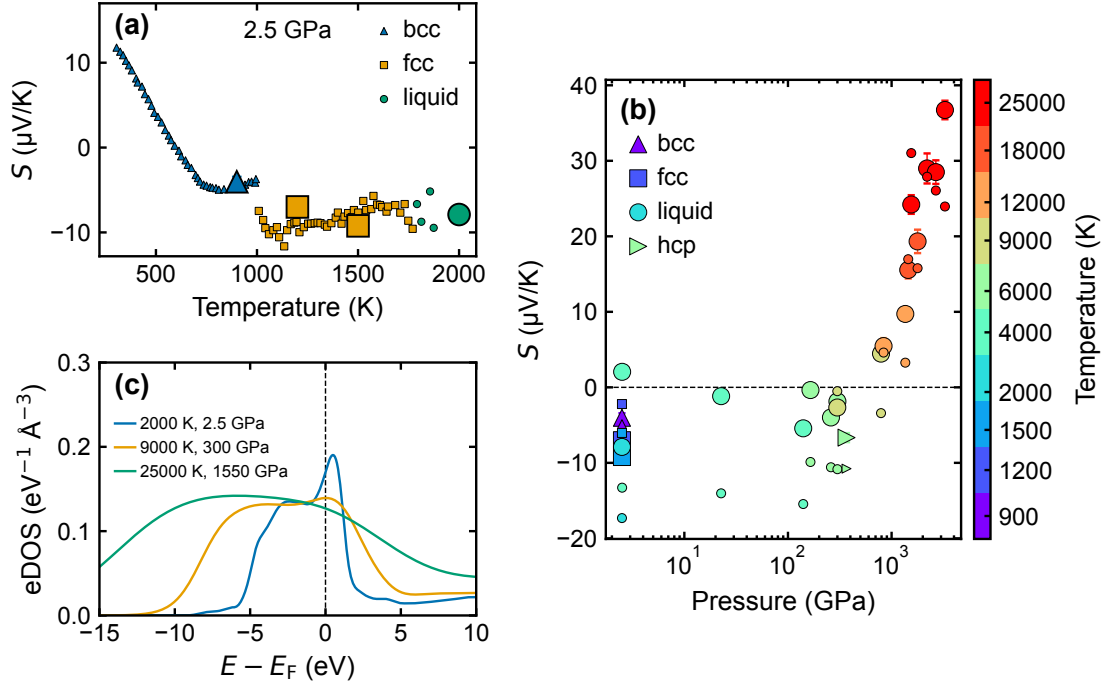


Figure 7.1: Seebeck coefficient and electronic density of states of iron. **(a)** Seebeck coefficient at 2.5 GPa as a function of temperature. Small symbols are experimental measurements from reference [18]; large symbols are DFT Kubo-Greenwood calculations. Colors denote the bcc (triangle), fcc (square), and liquid (circle) phases. **(b)** Seebeck coefficient across all simulated pressures and temperatures. Large symbols: full Kubo-Greenwood result; small symbols: Mott-formula estimate from the logarithmic slope of the DOS at E_F (see text). Marker shapes denote crystal structure as in (a), with hcp shown as right-pointing triangles. The color scale indicates temperature. **(c)** Snapshot-averaged electronic density of states (eDOS), normalized by simulation-cell volume, for three representative conditions.

7.2 Results

7.2.1 Seebeck Coefficient

Fig. 7.1 shows the Seebeck coefficient of iron across a wide range of thermodynamic conditions, from low pressure solid phases to the deep planetary interior regime, alongside the electronic density of states (DOS) that underlies the transport behavior. Panel (a) compares experimental measurements at 2.5 GPa obtained with a thermocouple in a cubic-anvil press [18], with our DFT Kubo-Greenwood calculations at the same pressure. The experimental data capture the continuous evolution of S through the bcc, fcc, and liquid stability fields as temperature increases. At these pressures, the Seebeck coefficient is small in magnitude and weakly dependent on temper-

ature. Our *ab initio* calculations reproduce the sign and order of magnitude of S across all three phases, with agreement to within $2 \mu\text{V}/\text{K}$ throughout, lending confidence to our approach as we explore conditions inaccessible to laboratory measurements.

Across the full range of pressure and temperature conditions (panel b), S undergoes a sign change from negative to positive with increasing temperature and pressure, exceeding $30 \mu\text{V}/\text{K}$ at 4000 GPa and 25,000 K. The sign and magnitude of S can be understood, to first approximation, from the slope of the electronic density of states, $N(E)$, at the Fermi level, E_F . The Mott formula makes this dependence explicit:

$$S_{\text{mott}} = \frac{-\pi^2 k_B^2 T}{3e} \left[\frac{d \ln N}{dE} \right]_{E_F} \quad (7.1)$$

The small symbols in panel (b) show S_{mott} evaluated from our *ab initio* $N(E)$. The Mott estimate captures the overall trend of S across the full pressure-temperature range, including the sign change, but can differ from the full Kubo-Greenwood result by up to $15 \mu\text{V}/\text{K}$ at individual conditions, reflecting electronic-structure contributions beyond the $N(E)$ slope at E_F that the Mott approximation neglects.

Panel (c) illustrates how $N(E)$ near E_F for iron liquid evolves with compression and heating. At 2.5 GPa and 2000 K, a sharp d -band peak sits just above E_F , producing a steep positive slope in $N(E)$ and the negative S observed at low pressure. Increasing pressure broadens the d -band; at 300 GPa and 9000 K, $N(E)$ near E_F flattens, reducing S to near zero. At 1550 GPa and 25,000 K, $N(E)$ becomes nearly free-electron-like; although the slope is shallow, the large thermal prefactor ($k_B T \approx 2.15 \text{ eV}$) amplifies this small asymmetry into the larger positive S seen at the most extreme conditions.

The Seebeck coefficients of iron here span -10 to $+35 \mu\text{V}/\text{K}$ across the full pressure-temperature range, reaching magnitudes comparable to or exceeding $\sim 10 \mu\text{V}/\text{K}$ contrast shown experimentally to drive significant thermoelectric flows. However, a complete assessment of the thermoelectric mechanism in super-Earth interiors additionally requires the Seebeck coefficients of candidate mantle phases at core-mantle boundary conditions, which remain to be determined.

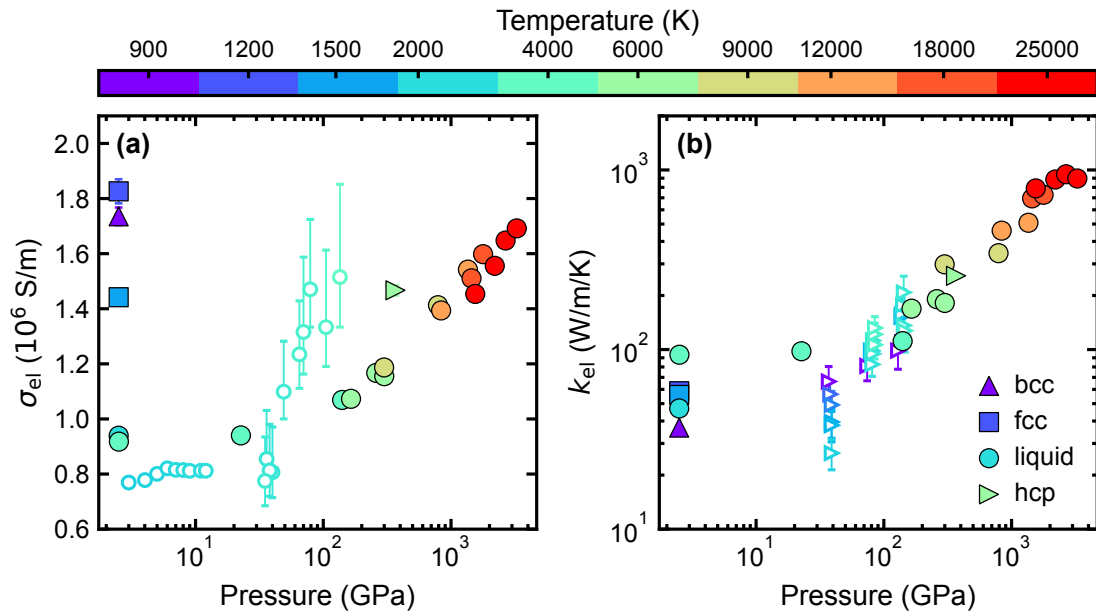


Figure 7.2: Electrical and thermal conductivity of iron. **(a)** Electrical conductivity σ_{el} versus pressure. **(b)** Electronic contribution to thermal conductivity k_{el} versus pressure. In both panels, marker shapes denote crystal structure: bcc (triangle), fcc (square), liquid (circle), and hcp (right-pointing triangle). Colors indicate temperature, and error bars, where not visible, are smaller than the symbol size. Open symbols are experimental results, including measurements of liquid iron electrical conductivity at low pressure ($P \leq 12$ GPa) [19] and higher pressure ($P > 30$ GPa) via diamond-anvil cell experiments [20]. Also included are direct measurements of thermal conductivity of iron in the hcp phase [21].

7.2.2 Electrical and Thermal Conductivity

Fig. 7.2 shows the electrical conductivity σ_{el} and electronic thermal conductivity k_{el} of iron across all simulated conditions. The electrical conductivity (panel a) varies modestly with pressure and temperature, remaining within the range $0.9\text{--}1.8 \times 10^6$ S/m throughout. At low pressures, the solid bcc and fcc phases exhibit the highest conductivities ($\sim 1.4\text{--}1.8 \times 10^6$ S/m), reflecting the long-range crystalline order. Upon melting, σ_{el} drops to $\sim 0.9 \times 10^6$ S/m at 4000 K and 2.5 GPa. Along the liquid branch, σ_{el} rises gradually with pressure, with the temperature dependence along isobars being weak. Our calculated electrical conductivities agree well with the low-pressure liquid iron measurements [19] and with the higher-pressure diamond-anvil cell measurements [20], with slight differences in the dependence on pressure. Deviations from experiments at lower pressure may be explained by the lack of spin polarization in our calculations [22].

These conductivity values are sufficient to sustain dynamo action in planetary cores. Taking a characteristic electrical conductivity of $\sigma \approx 1.2 \times 10^6$ S/m, a convective length scale of $l = 1000$ km, and a core flow velocity of $v \sim 10^{-3}$ m/s [2, 5], the magnetic Reynolds number, or the ratio of magnetic induction to magnetic diffusion, is $R_m = \mu_0 v l \sigma \approx 1500$. This is well above the critical value of ~ 40 required for self-sustaining dynamo action [23].

The thermal conductivity (panel b) rises more steeply than the electrical conductivity, increasing by more than an order of magnitude across the range of simulated conditions, from 30-100 W/m/K at low pressure to ~ 1000 W/m/K at the highest conditions explored. At Earth's core conditions, our values of $\sim 110\text{--}200$ W/m/K are consistent with previous *ab initio* calculations [7, 8]. Although direct experimental measurement of thermal conductivity at these high pressures is on the solid hcp phase [21], they are largely consistent with our results.

The thermal conductivity of liquid iron is key to governing the thermal and magnetic evolution of super-Earth cores, by controlling the heat conducted down the adiabat. To evaluate k_{el} at arbitrary core conditions in the interiors of super-Earths, we fit the 16 liquid data points spanning 4000-25,000 K to a two-term model:

$$k(P, T) = k_0 \left(\frac{P}{P_{\text{ref}}} \right)^a + k_1 \frac{T}{T_{\text{ref}}} \left(\frac{P}{P_{\text{ref}}} \right)^b \quad (7.2)$$

with $k_0 = 20.4 \text{ W/m/K}$, $k_1 = 147.5 \text{ W/m/K}$, $a = 1.04$, $b = 0.015$, $P_{\text{ref}} = 164.8 \text{ GPa}$, and $T_{\text{ref}} = 6000 \text{ K}$. The thermal conductivity in super-Earth cores, and therefore the viability of thermal convection, depends on their interior structure and thermal state, which we evaluate in the next section.

These trends in electrical and thermal conductivity are tied together by the Wiedemann-Franz relation $k_{\text{el}} = \lambda \sigma_{\text{el}} T$: σ_{el} varies only weakly across the full pressure-temperature range; the Lorenz number $\lambda = k_{\text{el}}/(\sigma_{\text{el}} T)$ remains close to (within 20% of) the Sommerfeld value $\lambda_0 = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ throughout (Fig. 7.5); and k_{el} grows approximately linearly with temperature along isobars.

7.2.3 Thermal Dynamos in super-Earth cores

A thermally driven dynamo requires that the heat flux extracted from the core, Q_{CMB} , exceed the heat conducted down the core adiabat, $Q_{\text{ad}}(r) = 4\pi r^2 k_{\text{el}}(r) \nabla T_{\text{ad}}$, evaluated at the core–mantle boundary. Both quantities depend on a planet’s interior structure: Q_{ad} on the thermal conductivity and adiabatic temperature gradient, ∇T_{ad} , at the CMB, and Q_{CMB} on the heat extracted from the core through the overlying mantle. To evaluate them across the rocky exoplanet population, we construct self-consistent two-layer (mantle and core) interior structure models for planets of 1–10 $M_{\oplus}$ at three core mass fractions: CMF = 0.20 (Mars-like), 0.32 (Earth-like), and 0.68 (Mercury-like). The models solve the equations of hydrostatic equilibrium assuming adiabatic temperature profiles in both layers. We treat the mantle as solid; basal magma oceans would alter the heat extraction at the CMB and its treatment is deferred to future work. For each planet, we obtain radial profiles of pressure, density, and temperature (Fig. 7.6), which are used to evaluate k_{el} using Eq. 7.2. We estimate Q_{CMB} from a thermal boundary layer model calibrated to reproduce Earth’s present-day core heat flux of $\sim 15 \text{ TW}$. We consider two thermal states for the core: a hotter, fully molten core representing the core just before inner core nucleation, and a cooler completely solid core representing the end of core crystallization. Full details of the interior structure model and boundary conditions are given in *Methods*.

Fig. 7.3 summarizes the results across the three core mass fractions. In the top and middle rows, solid lines correspond to the hotter, fully molten core profile (just before inner core nucleation), dashed lines to the cooler profile (end of inner core crystallization), and shading spans intermediate states in which the core is partially crystallized. The thermal conductivity at the CMB

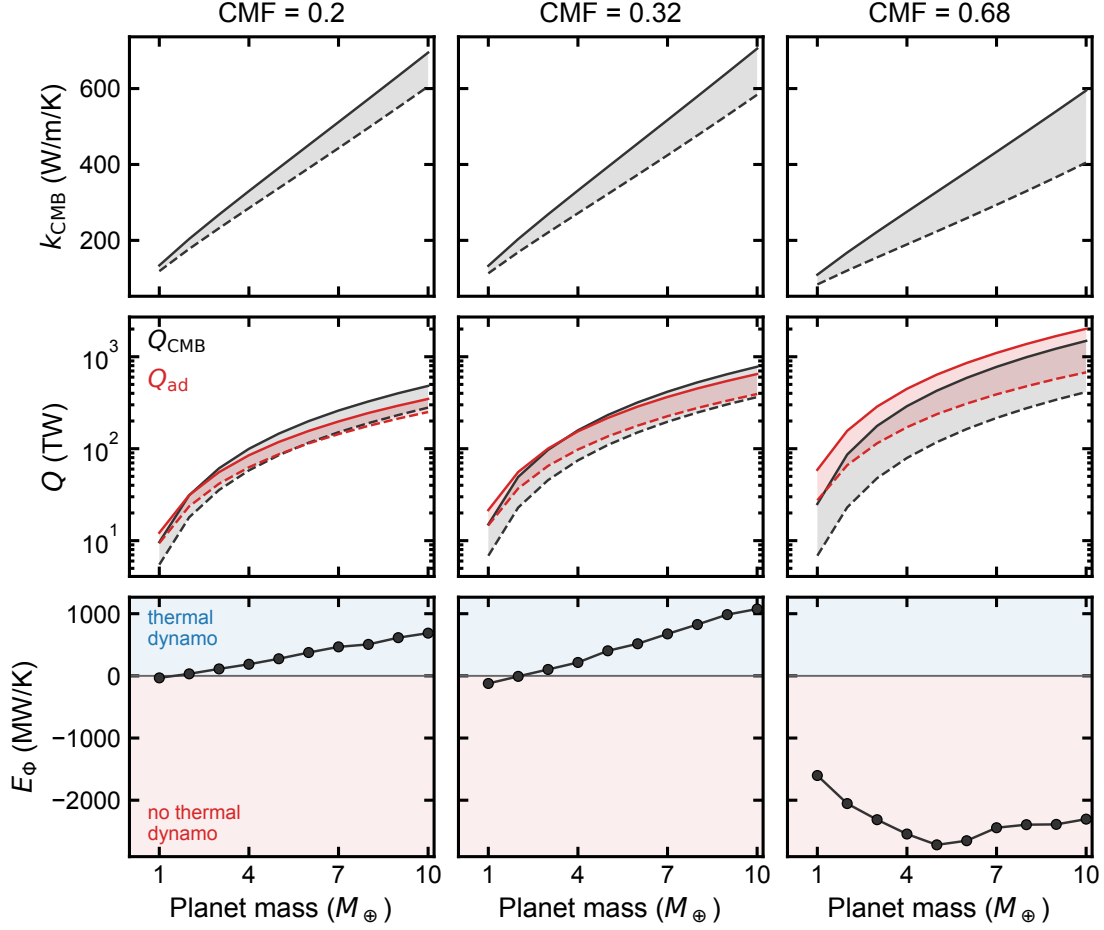


Figure 7.3: Thermal conductivity, heat flow, and entropy budget for super-Earth cores as a function of planet mass, for three core mass fractions (CMF = 0.20, 0.32, 0.68). **Top row:** Thermal conductivity at the core–mantle boundary, k_{CMB} , evaluated from Eq. 7.2 using the pressure and temperature at each planet’s CMB. **Middle row:** Total heat flux at the CMB, Q_{CMB} (black), compared to the adiabatic conductive heat flux, Q_{ad} (red). A thermal dynamo requires $Q_{\text{CMB}} > Q_{\text{ad}}$. In the top two rows, solid lines correspond to the hotter, fully molten core profile (just before inner core nucleation), dashed lines to the cooler profile (completely solid core), and shading spans intermediate states of partial crystallization. **Bottom row:** Dissipative entropy, $E_{\Phi} = E_S - E_k$, available for ohmic dissipation, computed for the fully molten core profile only. Positive values (blue region) indicate that a thermally driven dynamo is thermodynamically permitted; negative values (red region) indicate that conductive losses exceed the entropy produced by secular cooling.

(top row) increases with planet mass, from ~ 100 W/m/K at $1 M_{\oplus}$ for Earth-like CMF to $\sim 600 - 700$ W/m/K at $10 M_{\oplus}$, driven by the rise in CMB pressure and temperature with increasing planet size.

The middle row compares Q_{CMB} and Q_{ad} . For all three core mass fractions, both quantities grow with planet mass and remain comparable in magnitude. At Mars-like (CMF = 0.20) and Earth-like (CMF = 0.32) compositions, Q_{CMB} exceeds Q_{ad} around $2 M_{\oplus}$, opening a window in which thermal convection can drive a dynamo. For planets with larger cores (CMF = 0.68), Q_{CMB} remains below Q_{ad} at every mass considered, suggesting that thermal convection is suppressed in these planets. This is true despite the lower thermal conductivity at the top of these larger cores: the much greater core surface area at fixed planet mass makes Q_{ad} rise faster than Q_{CMB} across the full range.

These trends are also reflected in the dissipative entropy $E_{\Phi} = E_S - E_k$ (the bottom row of Fig. 7.3), or entropy available for dynamo production. E_S is the entropy produced by secular cooling and E_k is the entropy consumed by thermal conduction along the adiabat (*Methods*). This calculation focuses on the hotter, fully molten core profile, isolating the contribution of thermal driving alone before inner core nucleation introduces additional compositional and latent heat sources. For Earth-like CMF (0.32), E_{Φ} is slightly negative at $1 M_{\oplus}$, consistent with the well-established result that the Earth's present day dynamo requires compositional convection from inner core solidification to supplement secular cooling [6]. E_{Φ} crosses zero near $1-2 M_{\oplus}$ and rises to ~ 1000 MW/K at $10 M_{\oplus}$, reiterating the point that larger planets may be better suited for thermal core dynamos. For CMF = 0.2, the transition occurs near $2 M_{\oplus}$. For Mercury-like CMF, E_{Φ} is strongly negative at all masses (-1600 to -2300 MW/K), confirming the heat-flow result: thermal dynamos are thermodynamically forbidden in iron-rich super-Earths regardless of planet mass.

7.2.4 Core Solidification Timescale

Following Kraus *et al.* [24], we compute this timescale τ as the ratio of the total heat that must be extracted from the core to completely solidify it (cooling along the iron melting curve plus latent heat of freezing), to the heat extracted at the CMB. We use Q_{ad} as the heat flux in the denominator, because it is better constrained than Q_{CMB} by our thermal conductivity calculations, and it provides an estimate for an upper bound on τ , and therefore dynamo lifetime, assuming a dynamo is active.

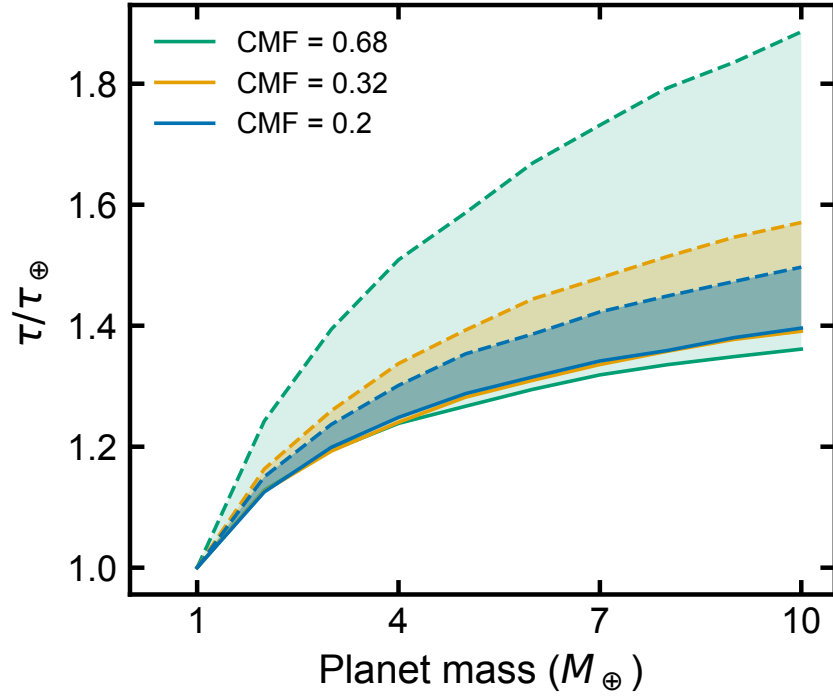


Figure 7.4: Inner core solidification timescale τ , normalized to the calculated Earth value $\tau_{\oplus}$, as a function of planet mass for three core mass fractions (CMF = 0.20, 0.32, 0.68). Solid lines use the heat flux, core radii, and core pressures from the fully molten core just before inner core nucleation ($\tau_{\oplus} = 4.5$ Gyr); dashed lines use the corresponding quantities from the end-of-crystallization profile ($\tau_{\oplus} = 3.1$ Gyr). Shading spans intermediate states of partial crystallization.

Fig. 7.4 shows $\tau/\tau_{\oplus}$ as a function of planet mass for the three core mass fractions. For all CMF values, τ increases monotonically with planet mass, reaching 1.4–1.8 $\tau_{\oplus}$ at 10 $M_{\oplus}$, implying that super-Earths will have longer-lived dynamos than Earth. The increase arises because the mass-averaged core temperature and the entropy of cooling both grow with planet mass, while the core surface area through which heat escapes, and outward heat flow at the CMB, grow more slowly. CMF = 0.68 shows the steepest increase and the largest spread between the two end-member profiles, reflecting the wider pressure range and the greater sensitivity of these large cores to the assumed thermal state.

7.3 Discussion

Our calculations provide the first determination of iron’s Seebeck coefficient across the full pressure-temperature range relevant to rocky exoplanet cores, identifying a sign change at high temperature that reflects a fundamental restructuring of iron’s electronic structure under compression. The relevant quantity for planetary magnetic field generation, however, is the contrast in Seebeck coefficient across a conducting interface, such as the core-mantle boundary. Our results constrain only the core side of this contrast; the mantle-side Seebeck coefficients of phases like bridgmanite, post-perovskite, and silicate melts at the relevant conditions remain unknown. The contrast may nonetheless be substantial: in many metallic and semiconducting systems, $|S|$ scales inversely with electrical conductivity, and the lower conductivity of mantle silicates relative to iron may translate to a Seebeck contrast at the CMB that is dominated by the mantle side. If so, the contrast would readily exceed the $\sim 10 \mu\text{V/K}$ shown in laboratory experiments to be sufficient for thermoelectric Lorentz forces to drive dynamically significant flows [13, 14], given that iron’s Seebeck coefficient alone reaches up to $\sim 35 \mu\text{V/K}$ at super-Earth core conditions. Whether this expectation holds depends on the detailed electronic structure of candidate mantle phases at deep super-Earth conditions and must be tested by future first-principles calculations.

The thermal conductivity of iron rises steeply with pressure and temperature across the super-Earth core regime, and the resulting growth of the adiabatic heat flux Q_{ad} is the central obstacle to thermal dynamo generation in larger planets. Our entropy budget analysis reveals that the outcome depends sensitively on core mass fraction. For low-to-moderate CMF (Mars-like and

Earth-like), Q_{CMB} and Q_{ad} remain within a factor of two of each other across the full mass range, making dynamo viability marginal and sensitive to the details of the interior model: small changes in the treatment of mantle heat extraction, the iron equation of state, or the assumed core thermal state can shift the transition mass at which a thermal dynamo becomes viable. The Earth-mass case is itself slightly subcritical in our model, consistent with the well-established conclusion that Earth’s present-day dynamo requires compositional convection from inner core solidification to supplement thermal driving [6]; for larger Earth-like planets, however, the entropy produced by secular cooling outpaces the conductive entropy cost, and a purely thermal dynamo becomes viable above $\sim 2 M_{\oplus}$. The Mercury-like (CMF = 0.68) case sits in a different regime: Q_{ad} exceeds Q_{CMB} by a wide margin at all masses, suggesting that thermal dynamos are forbidden in iron-rich super-Earths.

Compositional convection following inner core nucleation provides a more robust pathway to magnetic field generation across all core mass fractions. Because the inner core solidification timescale lengthens with planet mass, larger super-Earths host longer-lived compositional dynamos. For iron-rich super-Earths, where a thermal dynamo is forbidden, this compositional phase may be the only viable mechanism for field generation by the core, but the long solidification timescales mean that, once underway, it would persist for many billions of years.

Several sources of uncertainty could affect these conclusions. On the core side, our calculations assume pure iron; dissolved light elements (S, O, Si) would reduce the thermal conductivity. At Earth’s core conditions, ab initio calculations indicate that physically plausible light element concentrations reduce k_{el} by roughly 30% relative to pure iron [8, 25]. However, the effect of light elements at the higher pressures of super-Earth core conditions is unconstrained. Electron-electron scattering, neglected here, would further reduce k_{el} [26]; this effect is modest in iron at Earth’s core conditions (<20%) because of strong thermal disorder, and we expect it to remain modest at super-Earth conditions where thermal disorder is even greater. Radiogenic heating in the core, also not included, would affect the thermal evolution of the core, with a recent study suggesting that potassium, thorium, and uranium become siderophile at super-Earth core conditions [27]. All three of these core-side corrections would push toward more favorable thermal dynamo conditions than our models predict.

The mantle side is more uncertain. Mantle viscosity and conductivity are held constant in

our thermal boundary layer model but in reality vary with planet mass, mineralogy, and thermal state [28, 29]. More consequentially, we treat the mantle as fully solid. Basal magma oceans, increasingly thought to be common in young or massive rocky planets [30, 31], would insulate the core and slow its cooling, suppressing Q_{CMB} and disfavoring thermal dynamos. A BMO could, however, host a self-sustaining silicate dynamo of its own [15, 16, 32, 33], offering an alternative pathway to magnetic field generation in cases where the core dynamo is not possible. Whether the net effect of these uncertainties favors or opposes magnetic field generation in any specific super-Earth therefore depends on the details of its mantle state and bulk composition.

7.4 Methods

7.4.1 Molecular Dynamics Simulations

Our molecular dynamics simulations are based on density functional theory in the PBEsol approximation [34], utilizing the projector augmented plane wave method, as implemented in VASP [35, 36]. We perform Born–Oppenheimer molecular dynamics simulations in the NVT ensemble with periodic boundary conditions, a Nosé–Hoover thermostat, and a duration of 5-15 ps with 0.5-1 fs time step, with the smaller timestep being used at the most extreme pressures and temperatures. We assume thermal equilibrium between the ions and electrons via the Mermin functional [37]. Sampling the Brillouin zone at the Gamma point and a basis-set energy cutoff of 500 eV converges the energy and pressure to within 3 meV/atom and 0.2 GPa, respectively. The number of atoms used in our simulations are 108 for fcc, 128 for bcc, and 144 for hcp and liquid phases.

7.4.2 Electrical and Thermal Conductivity

The electronic contributions to the electrical and thermal conductivity are computed by the Chester–Thellung formulation of the Kubo–Greenwood method:

$$\sigma_{\text{el}}(\omega) = L_{11}(\omega) \quad (7.3)$$

$$k_{\text{el}}(\omega) = \frac{1}{e^2 T} \left(L_{22}(\omega) - \frac{L_{12}(\omega)L_{21}(\omega)}{L_{11}(\omega)} \right) \quad (7.4)$$

$$S = \frac{L_{12}}{e T L_{11}} \quad (7.5)$$

The kinetic coefficients $L_{\alpha\beta}(\omega)$ at the electric field frequency ω are defined as

$$L_{\alpha\beta}(\omega) = \frac{2\pi e^2 \hbar^2}{3m_e^2 \omega \Omega} \sum_{i,j} (f_i - f_j) \delta(\epsilon_i - \epsilon_j - \hbar\omega) |\langle \psi_i | \nabla | \psi_j \rangle|^2 \times (-1)^{\alpha+\beta} (\epsilon_i - \mu)^{\alpha-1} (\epsilon_j - \mu)^{\beta-1} \quad (7.6)$$

where the summation is over pairs of states i, j , f is the Fermi occupation, ψ is the wavefunction, ϵ is the corresponding single-electron eigenvalue, Ω is the simulation volume, m_e is the electron mass, and μ is the chemical potential. The values of α and β denote whether the electrons are transporting charge or heat. In practice, the δ function is replaced by a Gaussian with a width given by the average spacing between eigenvalues weighted by the corresponding change in the Fermi function. To obtain the DC conductivity, the frequency dependent conductivity is extrapolated to zero frequency using a linear fit at small ω .

We compute σ_{el} , k_{el} , S and the electronic density of states by averaging over 10 uncorrelated molecular dynamics simulation snapshots. We obtained converged results with 4000 electronic bands. We also found σ_{el} , k_{el} , and S to be well converged with a $2 \times 2 \times 2$ k-point mesh for the liquid simulations, and a $3 \times 3 \times 3$ k-point mesh for the crystal simulations.

7.4.3 Interior Structure Model

We model the interior structure of rocky planets by assuming two layers (mantle and core) and solving hydrostatic equilibrium coupled with the Adams–Williamson equation and the adiabatic temperature gradient:

$$\frac{dP}{dr} = -\rho g, \quad \frac{d\rho}{dr} = -\frac{\rho^2 g}{K_S}, \quad \frac{dT}{dr} = -\frac{\rho g \gamma T}{K_S}, \quad g = \frac{GM}{r^2} \quad (7.7)$$

where K_S is the adiabatic bulk modulus, γ is the Grüneisen parameter, and g is the gravitational acceleration. The mantle structure is determined by the thermodynamic code HeFesTo, assuming a pyrolite composition [38, 39]. On the core side, as in a recent study [40], we use a third-order Vinet equation of state, with parameters for liquid iron from Wicks *et al.* [41] and for solid iron from Smith *et al.* [42]. Unlike reference [40], we do not enforce the bulk modulus to be continuous across the core-mantle boundary.

7.4.4 Heat and entropy

The entropy available for ohmic dissipation in a fully liquid core with no inner core is $E_\Phi = E_S - E_k$, where the secular cooling entropy is

$$E_S = Q_{\text{CMB}} \left(\frac{1}{T_{\text{CMB}}} - \frac{1}{\langle T \rangle_\rho} \right) \quad (7.8)$$

with $\langle T \rangle_\rho$ being the average temperature in the core:

$$\langle T \rangle_\rho \equiv \frac{\int_0^{R_c} 4\pi r^2 \rho(r) T(r) dr}{\int_0^{R_c} 4\pi r^2 \rho(r) dr}. \quad (7.9)$$

The entropy consumed by thermal conduction along the adiabat is

$$E_k = \int_V k \left(\frac{\nabla T}{T} \right)^2 dV \quad (7.10)$$

where the integral is over the volume of the core, V . The thermal conductivity $k(r)$ is evaluated from Eq. 7.2 at the local pressure and temperature. A dynamo is thermodynamically permitted when $E_\Phi > 0$.

As in reference [17], we estimate Q_{CMB} from a local thermal boundary layer (TBL) model at the base of the mantle. The well-mixed mantle interior follows a 1600 K adiabat, and a thermal boundary layer of thickness d accommodates the temperature jump $\Delta T = T_{\text{CMB}} - T_m$ between the adiabatic mantle and the core. We assume the boundary layer self-regulates to a state of marginal convective instability, in which the local Rayleigh number based on the TBL thickness,

$$\text{Ra}_d = \frac{\rho_m^2 C_{p,m} \alpha_m g \Delta T d^3}{\eta k_m} \quad (7.11)$$

is held at a critical value $\text{Ra}_c \sim \mathcal{O}(10^3)$. This is equivalent to the high-Rayleigh-number scaling $\text{Nu} \propto \text{Ra}^{1/3}$, in which the heat flux through the boundary layer becomes independent of the layer

depth and depends only on local properties. Solving $Ra_d = Ra_c$ for d gives

$$d = \left(\frac{Ra_c \eta k_m}{\rho_m^2 \alpha_m g C_{p,m} \Delta T} \right)^{1/3}, \quad (7.12)$$

where η and k_m are the mantle viscosity and thermal conductivity, and the remaining mantle properties ($\rho_m, \alpha_m, C_{p,m}, g$) are determined by the thermodynamic code HeFesTo [38, 39]. The heat flowing across the CMB is then

$$Q_{\text{CMB}} = \frac{4\pi r_c^2 k_m \Delta T}{d}. \quad (7.13)$$

We treat η and k_m as constants across all planets, calibrated against Earth's present-day CMB heat flow of ~ 15 TW ($\eta = 4.4 \times 10^{21}$ Pa·s, $k_m = 8$ W/m/K). T_{CMB} is determined by what core adiabatic temperature profile gives a fully molten core just prior to nucleation ($T(R=0) = T_{\text{melt}}$) or a fully solidified core ($T_{\text{CMB}} = T_{\text{melt}}$), where the melting temperature in the core is given by

$$T_{\text{melt}} = T_{\text{melt}}^{\text{Fe}} (1 - \ln x_0)^{-1} \quad (7.14)$$

where $T_{\text{melt}}^{\text{Fe}}$ is the melting curve of pure iron [24] and $x_0 = 0.9$, the mole fraction of the pure substance, is chosen to give a value of T_{melt} that agrees with estimates of the inner-core boundary temperature on Earth.

7.5 Supplementary Information

Includes Figs. 7.5 and 7.6.

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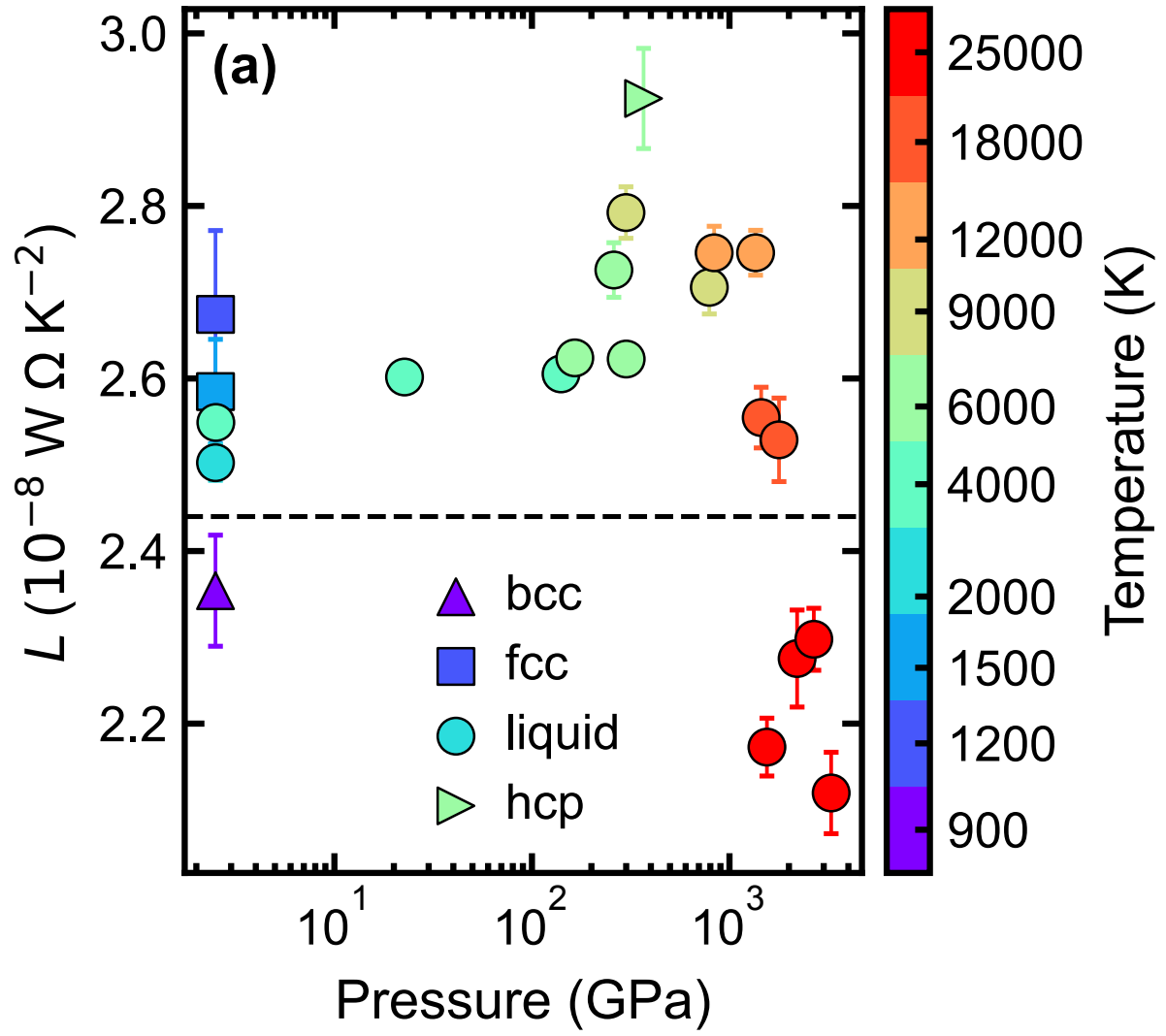


Figure 7.5: Lorenz number as a function of pressure, computed from the electrical and thermal conductivity in Fig. 7.2. The horizontal dashed line is the theoretical value for the Lorenz number derived from the Sommerfeld model (see Section 3.4).

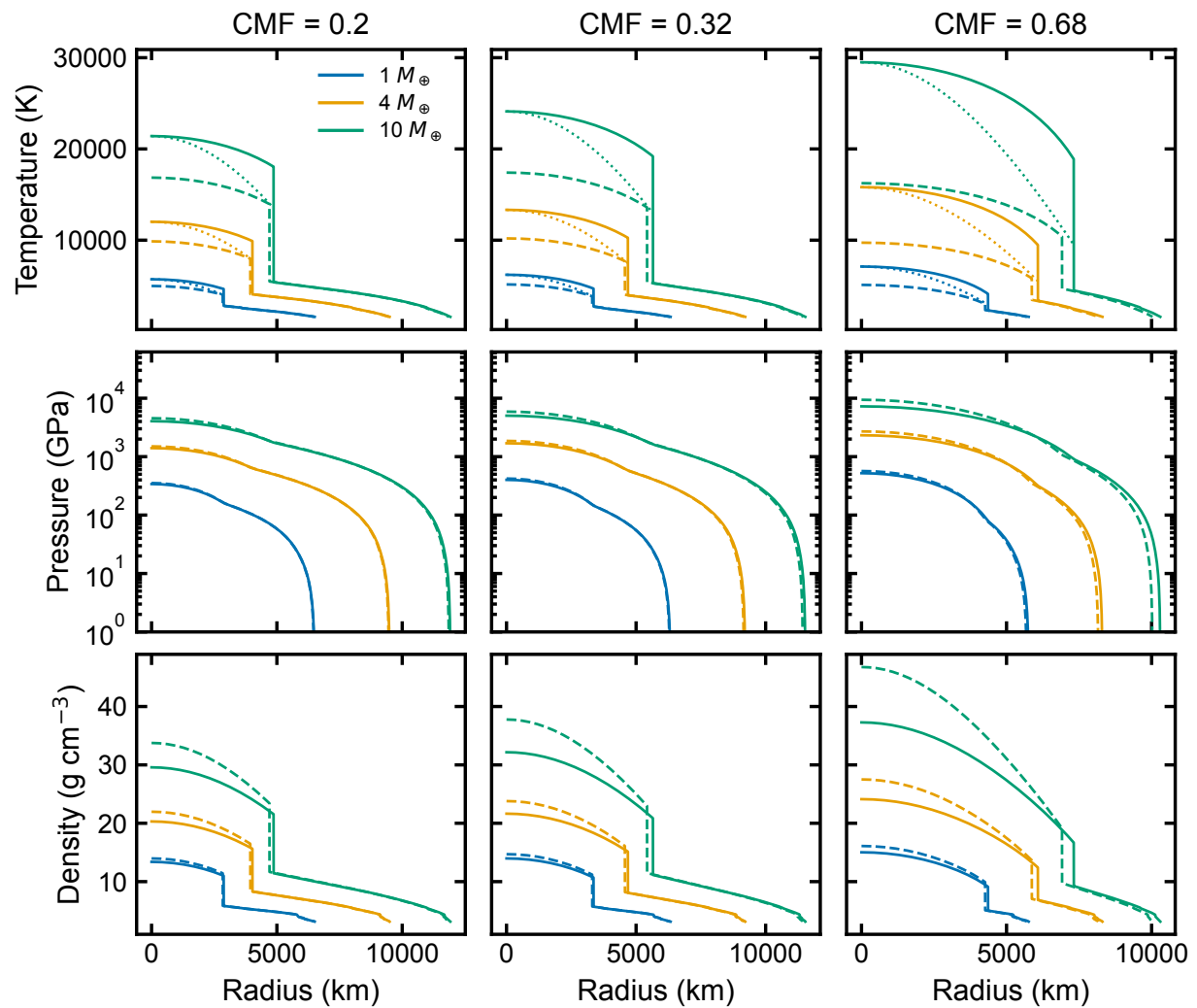


Figure 7.6: Interior structure of Earth-like planets, as determined by Eqs. 7.7. Solid lines refer to profiles with entirely molten core, while dashed lines represent profiles with a frozen core, with both determined by the iron melting curve (dotted line).

CHAPTER 8

Results: Fe partitioning between (Mg,Fe)SiO₃ liquid and post-perovskite

8.1 Introduction

Mass-radius relations of discovered exoplanets reveal that many are consistent with bulk compositions broadly similar to Earth's - a metallic iron core surrounded by a silicate mantle - but at much higher central pressures (see Chapter 7). At the pressures of Earth's mantle, MgSiO₃ adopts the bridgmanite (perovskite) structure. Above ~ 120 GPa, however, MgSiO₃ transforms to the post-perovskite (ppv) structure [1], which is expected to remain stable up to ~ 700 GPa [2]. Post-perovskite is therefore expected to be the dominant silicate phase throughout most of a super-Earth mantle.

The interiors of super-Earths are expected to be significantly hotter than Earth's due to greater accretional energies and shorter orbital radii [3], so deep-mantle melting in these planets is likely more widespread and longer-lived than in Earth. For Earth, it appears likely that crystallization of a global magma ocean produced a basal magma ocean that survived for billions of years [4]. This longevity arises because iron is incompatible in lower-mantle minerals [5–7], so that bridgmanite and ferropericlase crystals solidifying out of the magma ocean are buoyant in the residual iron-enriched liquid (see Chapter 5). Whether an analogous reservoir exists, or has existed, in super-Earth mantles is a key question for the long-term thermal and chemical evolution of these planets, and depends on whether post-perovskite is similarly buoyant at the higher pressures and temperatures of super-Earth interiors.

The relevant quantity is the Fe–Mg distribution coefficient between post-perovskite and iron-bearing silicate liquid, K_D . Existing experimental constraints come from diamond-anvil-cell melting experiments at the upper end of Earth's lower-mantle pressure range and into the post-perovskite stability field [7, 8], which find K_D values of ~ 0.04 – 0.10 , indicating that iron is strongly incompatible in post-perovskite. The trend of K_D with pressure beyond Earth's core-mantle boundary (CMB), and the consequent gravitational stability of a basal magma ocean at super-Earth condi-

tions, remain unconstrained.

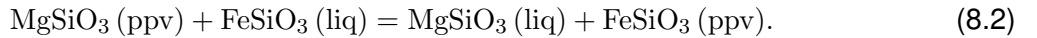
Here we use first-principles molecular dynamics simulations and thermodynamic integration to compute K_D between post-perovskite and (Mg,Fe)SiO₃ liquid at conditions spanning the mantles of terrestrial planets up to $\sim 5 M_\oplus$. The methodology generalizes that used previously for bridgmanite (Chapter 5) [6] and (Mg,Fe)O [5]. We then combine the computed distribution coefficient with equations of state for both phases to evaluate crystal buoyancy and the gravitational stability of a basal magma ocean in super-Earth interiors.

8.2 Methods

The methodology follows that developed in Chapter 5 for bridgmanite [6]. In brief, the Fe-Mg distribution coefficient between post-perovskite and (Mg,Fe)SiO₃ liquid is

$$K_D = \frac{X_{\text{Fe}}^{\text{ppv}} X_{\text{Mg}}^{\text{liq}}}{X_{\text{Fe}}^{\text{liq}} X_{\text{Mg}}^{\text{ppv}}} = \exp\left(-\frac{\Delta\tilde{\mu}_R}{k_B T}\right), \quad (8.1)$$

where $\Delta\tilde{\mu}_R$ is the chemical-potential change of the cation-exchange reaction



We compute $\Delta\tilde{\mu}_R$ via thermodynamic integration, transmuting one Mg atom into one Fe atom along a coupling parameter λ that interpolates between iron-free ($\lambda = 0$) and iron-bearing ($\lambda = 1$) Hamiltonians, and applying the trapezoidal-rule approximation justified in Chapter 5.

Two aspects of our simulations differ from the bridgmanite calculations of Chapter 5. First, the simulation cell contains 24 MgSiO₃ formula units (120 atoms), with one Mg atom substituted by an Fe²⁺ atom for the iron-bearing trajectory ($X_{\text{Fe}} = 1/24 \approx 4.2\%$). The larger cell is dictated by the symmetry of the post-perovskite structure, whose primitive cell contains four formula units.

Second, whereas our bridgmanite simulations fixed the magnetic moment of iron at $m = 4$ for high-spin and $m = 0$ for low-spin and then computed the equilibrium high-spin fraction from the free-energy difference, here we allow the magnetic moment to evolve freely during the molecular dynamics trajectory. The reason is that, at the extreme pressures relevant to super-Earth mantles, the magnetic state of iron in silicates is unlikely to be dominated by either pure high-spin or pure

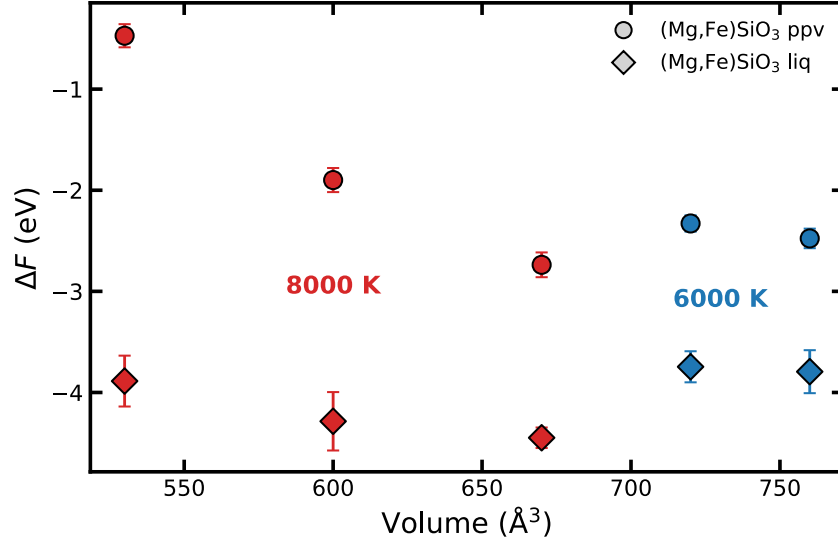


Figure 8.1: Free energy change of iron substitution, vs simulation cell volume for post-perovskite (circles) and silicate liquid (diamonds), at temperatures of 6000 K (blue) and 8000 K (red).

low-spin configurations. We therefore initialize each spin-polarized simulation without a fixed-moment constraint and report the time-averaged magnetic moment $\langle \mu_B \rangle$ on the iron atom over the trajectory in each phase.

Equations of state for both phases are obtained by simulating iron-free systems on isotherms spanning the volume range of interest and fitting a third-order Birch–Murnaghan equation to the resulting P – V data. As in Chapter 5, the substitution of Mg by Fe expands the unit-cell volume of both phases approximately linearly with X_{Fe} .

8.3 Results

The results presented here mirror those of Chapter 5, but for the post-perovskite–silicate liquid system. Fig. 8.1 shows the free energy change of iron substitution for the two phases. As in the bridgmanite system, iron prefers the liquid phase: ΔF is consistently lower for the liquid than for post-perovskite. As volume decreases, ΔF increases for both phases, but more steeply for post-perovskite, indicating that iron becomes increasingly incompatible in post-perovskite upon compression.

Unlike iron in bridgmanite and silicate liquid at Earth’s mantle conditions, iron in these phases at super-Earth conditions does not predominantly adopt a high-spin state. Fig. 8.2 shows that the

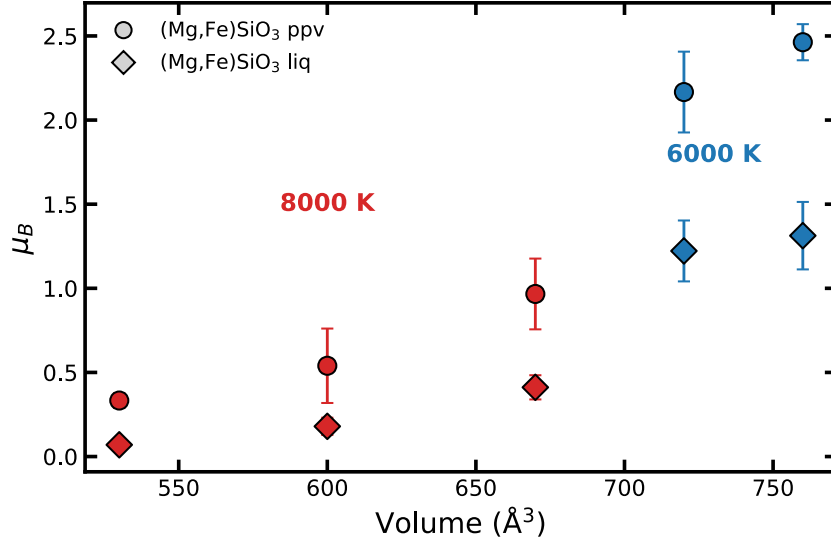


Figure 8.2: Time-averaged magnetic moment of iron atom, vs simulation cell volume for post-perovskite (circles) and silicate liquid (diamonds), at temperatures of 6000 K (blue) and 8000 K (red).

time-averaged magnetic moment of iron decreases with decreasing volume in both phases, as expected from crystal-field arguments: greater compression increases the energy splitting between t_{2g} and e_g orbitals, progressively favoring lower-spin configurations. Across the volume range explored, $\langle \mu_B \rangle$ in post-perovskite spans roughly intermediate-spin values, while in the liquid it decreases more rapidly and approaches the low-spin limit at the smallest volumes. The persistently larger moment in post-perovskite likely reflects the more rigid octahedral coordination environment around Fe^{2+} in the crystal, whereas the liquid offers a continuum of local geometries that can more readily accommodate the contracted electronic configuration of low-spin iron. The fact that neither phase is well described by a pure spin state across this pressure range justifies our decision to allow the magnetic moment to evolve freely during the trajectory rather than imposing a fixed-moment constraint as in Chapter 5.

The distribution coefficient K_D is significantly less than unity, as expected, and decreases with increasing pressure (Fig. 8.3). At the lower end of the pressure range explored (130–180 GPa), our results are in good agreement with diamond-anvil-cell measurements [7, 8]. K_D appears to increase slightly with increasing temperature, although additional data would be needed to confirm

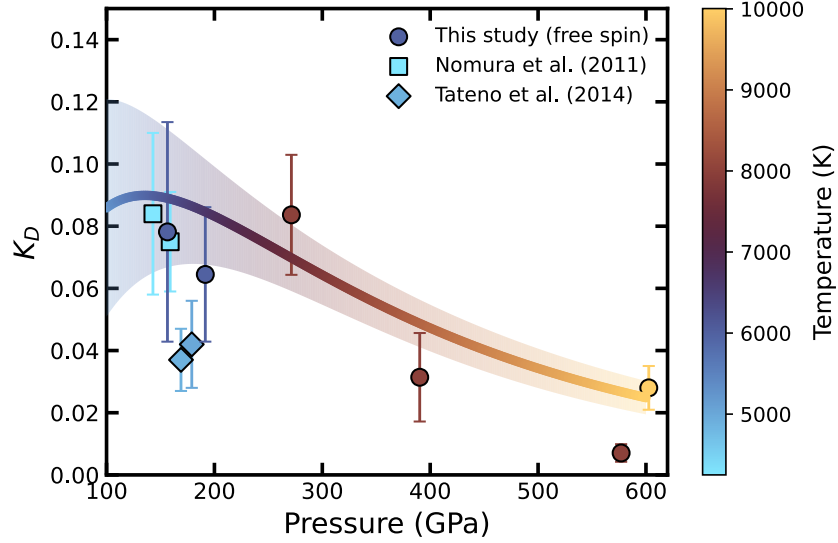


Figure 8.3: Fe-Mg distribution coefficient between post-perovskite and silicate liquid, K_D , vs pressure. The circles are our results, while other symbols denote experimental results [7, 8]; all points colored by temperature. We fit our results to Eq. 8.3, obtaining $\Delta H = 91.34 \pm 74.40$ kJ/mol, $\Delta S = 8.853 \pm 12.71$ J/mol/K, and $\Delta V = 0.5345 \pm 0.0985$ cm³/mol. The solid line shows this fit evaluated along the post-perovskite melting curve [9].

this trend. We fit our results to

$$K_D = \exp [- (\Delta H - T\Delta S + P\Delta V) / k_B T]. \quad (8.3)$$

Evaluated along the post-perovskite melting curve [9], this multivariate fit shows that K_D decreases gradually with pressure, indicating that iron remains strongly incompatible in post-perovskite throughout the relevant range of super-Earth mantle conditions.

We use our results for the distribution coefficient, together with our *ab initio* equations of state along the 8000 K isotherm, to evaluate whether post-perovskite floats in super-Earth magma oceans. As in Chapter 5, we consider both fractional and batch crystallization models. We assume that, prior to any solidification, the magma ocean has a composition of (Mg_{0.9},Fe_{0.1})SiO₃, and that the volume of each phase varies linearly with iron content. Although equations of state for the FeSiO₃ end-member are not available at these conditions, we assume that the volume of FeSiO₃ exceeds that of MgSiO₃ by 30 Å³ in post-perovskite and 20 Å³ in the liquid, consistent with our previous results at slightly lower pressures and temperatures [6].

We find that the pressure of neutral buoyancy begins at approximately 340 GPa and decreases

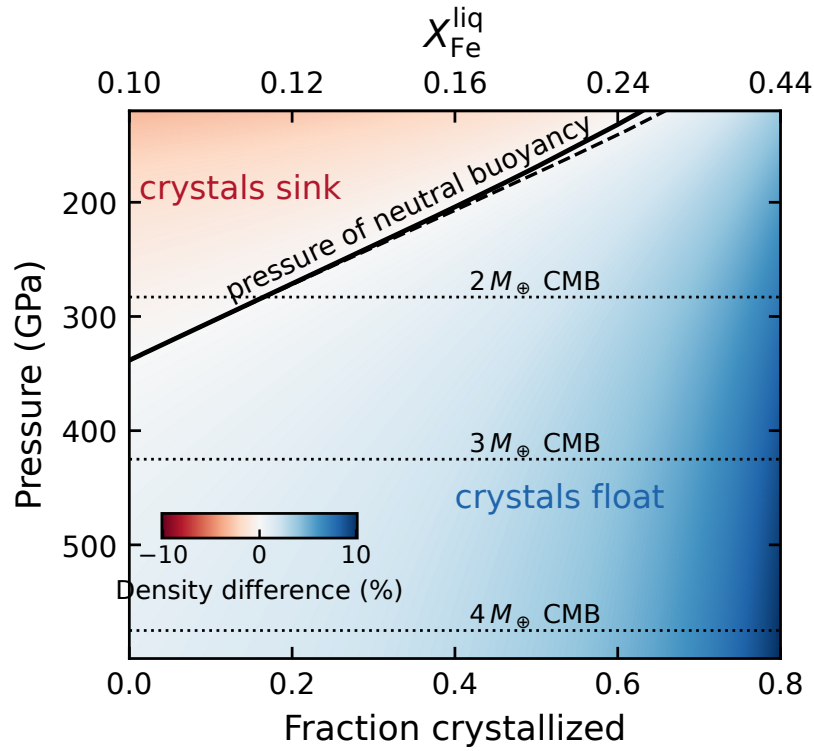


Figure 8.4: Pressure versus the crystallized fraction of a $(\text{Mg,Fe})\text{SiO}_3$ magma ocean with initial iron concentration $X_{\text{Fe}} = 0.1$. Color indicates the density difference between the two phases under fractional crystallization, with blue corresponding to the liquid being denser than the solid. Black lines denote the pressure of neutral buoyancy for fractional (solid) and batch (dashed) crystallization. Horizontal dotted lines mark estimates of the core-mantle boundary pressure for Earth-like planets of various masses.

as the magma ocean crystallizes (Fig. 8.4). Consequently, all Earth-like planets in this pressure range will host a gravitationally stable basal magma ocean at some point during crystallization. Planets of 3 and 4 $M_{\oplus}$, whose CMB pressures are greater than the initial neutral-buoyancy pressure, will host a basal magma ocean as soon as crystallization initiates. The 2 $M_{\oplus}$ case, however, is more nuanced: its CMB pressure lies below the initial neutral-buoyancy pressure, so the first post-perovskite crystals to form are denser than the coexisting liquid and sink to the base of the mantle. As crystallization proceeds, iron is progressively rejected into the residual liquid, lowering the neutral-buoyancy pressure until it falls below the CMB pressure. Beyond this point, newly formed post-perovskite is buoyant, and any sunken crystals would also become unstable and rise. The implication is that a basal magma ocean in such intermediate-mass planets emerges only after a finite degree of solidification has driven the residual liquid to sufficiently iron-rich compo-

sitions. As in the bridgmanite system, our results suggest that once established, a basal magma ocean may initially grow in size as crystallization proceeds.

8.4 Discussion

We find low values of K_D , indicating that iron is strongly incompatible in post-perovskite, and increasingly so with increasing pressure—paralleling the behavior of the bridgmanite system. As a result, a basal magma ocean is gravitationally stable in super-Earth interiors. The presence of such a reservoir would substantially affect the long-term evolution of these planets. A basal magma ocean would insulate the core, reducing its cooling rate and influencing the planet’s thermal history. Iron enrichment in the basal magma ocean would lower its melting temperature relative to the overlying mantle, further prolonging its lifetime. Moreover, these layers are expected to have high electrical conductivity, and may therefore be capable of generating a global magnetic field [10–12].

The intermediate-mass case ($\sim 2 M_\oplus$) is particularly interesting because it illustrates that the existence of a basal magma ocean depends not only on planetary mass but also on the evolutionary stage of the mantle. The implied structure—an early-formed solid layer at the CMB, overlain by a later-emerging basal magma ocean, in turn overlain by the crystallizing mantle—is qualitatively distinct from the structure expected in more massive planets. Whether the deepest solid layer remains isolated or is remobilized as the residual liquid evolves depends on chemical exchange timescales and rheological properties beyond the scope of this work; resolving this would require coupling our partitioning results to a dynamical model of the crystallizing mantle.

The magnetic-moment results carry implications beyond their methodological role. The slight increase of K_D with temperature seen in our results may reflect the temperature dependence of the spin state itself: between 6000 and 8000 K, $\langle \mu_B \rangle$ drops more in post-perovskite than in the liquid, narrowing the spin-state contrast between the two phases and reducing the energetic cost of partitioning iron into the crystal. Spin state is also important for electronic transport, with low-spin iron in silicate liquid linked to enhanced electrical conductivity [10, 11], reinforcing the dynamo case made above.

Combining the present results with those for bridgmanite (Chapter 5) reveals a range of pres-

tures and crystallized fractions over which post-perovskite crystals sink while bridgmanite crystals float. This raises the possibility that, at least during the early stages of solidification, a molten layer could be gravitationally stable between two solid layers in the mantles of these planets. Future work will aggregate the partitioning relations and densities of the major lower-mantle minerals to provide a more complete picture of magma ocean crystallization in super-Earth interiors.

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CHAPTER 9

Conclusions

This dissertation set out to determine whether rocky planets can generate magnetic fields through mechanisms other than the conventional core dynamo, and to establish the mineral physics basis for those mechanisms across a range of planetary scales. The central question was whether a basal magma ocean, a layer of iron-enriched silicate liquid at the base of the mantle, could have powered Earth's early magnetic field prior to inner-core nucleation, and whether the same pathway extends to super-Earths. Answering it required computing, from first principles, a set of material properties that are either poorly constrained by experiment or lie entirely beyond laboratory reach.

The results support a coherent and unified picture. Iron is strongly incompatible in bridgmanite, the dominant lower-mantle phase in Earth, and even more so in post-perovskite, its high-pressure counterpart in super-Earth mantles. In both cases, the resulting density crossover between iron-enriched liquid and buoyant crystals supports a gravitationally stable basal magma ocean. Long-lived BMOs are therefore not a peculiarity of Earth's thermal history but a generic consequence of magma-ocean crystallization in rocky planets across a wide range of masses.

For Earth's BMO, the electrical conductivity of iron-enriched silicate liquid at lowermost-mantle conditions increases significantly with iron content, and exceeds the threshold for self-sustaining dynamo action. Meanwhile, the electronic thermal conductivity remains low enough that convection is not suppressed by conductive heat transport. A silicate dynamo operating in the BMO is therefore energetically and dynamically viable, providing a natural mechanism for the geomagnetic field in the billions of years before the inner core existed.

For super-Earth cores, the thermal conductivity of iron rises steeply with pressure and temperature, and the resulting growth of the adiabatic heat flux is the central obstacle to thermally driven dynamos in larger planets. The outcome depends sensitively on core mass fraction: for Mars-like and Earth-like compositions, Q_{CMB} and Q_{ad} remain within a factor of two of each other, and a purely thermal dynamo becomes viable above $\sim 2 M_{\oplus}$; for Mercury-like, iron-rich compositions, Q_{ad} exceeds Q_{CMB} at all masses, thermodynamically forbidding thermal dynamos regardless of planet size. Compositional convection following inner-core nucleation provides a more robust path-

way in both cases, and the lengthening of the solidification timescale with planet mass implies that larger super-Earths host longer-lived compositional dynamos. The Seebeck coefficient of liquid iron, computed here for the first time at deep planetary conditions, provides the core-side input required to evaluate thermoelectric currents at core–mantle boundaries; the mantle-side Seebeck coefficients of candidate phases remain to be determined.

Taken together, these findings place the magnetic histories of rocky planets on a common material-physics foundation. The set of material properties examined in this dissertation - iron partitioning, electronic transport, and thermoelectric response - governs BMO stability, silicate dynamo viability, and core dynamo longevity from Earth to the most massive super-Earths. The behavior of iron under extreme conditions proves to be a central thread connecting the interior structure, thermal evolution, magnetic field generation, and long-term habitability of rocky planets.