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Publication Date

2026-09-11

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA

Los Angeles

Structure, Phase Stability, and Transport in Hydrogen-Bearing Magma Oceans

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

by

Sarah Marcum

2026

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2026

ABSTRACT OF THE DISSERTATION

Structure, Phase Stability, and Transport in Hydrogen-Bearing Magma Oceans

by

Sarah Marcum

Doctor of Philosophy in Geochemistry

University of California, Los Angeles, 2026

Professor Edward Donald Young, Chair

Sub-Neptune exoplanets are often modeled as rocky interiors surrounded by hydrogen-rich envelopes, but at the pressures and temperatures expected inside these planets, the boundary between rock and atmosphere may not remain sharp. Hydrogen can dissolve into silicate liquids and form supercritical silicate–hydrogen mixtures whose equations of state, conductivities, and phase behavior differ from those of pure end-member materials. This thesis uses first-principles molecular dynamics simulations to quantify the properties of hydrogen-bearing silicate liquids under conditions relevant to sub-Neptune interiors. I first develop a thermodynamically consistent equation of state for supercritical $\text{MgSiO}_3\text{--H}_2$ mixtures and use it to evaluate how these fluids affect planetary density structure and thermal profiles. I then calculate the electrical and thermal conductivities of these mixtures to assess whether hydrogen-bearing silicate liquids could influence magnetic field generation. Finally, I perform targeted simulations of ternary $\text{MgSiO}_3\text{--H}_2\text{--Fe}$ mixtures to test whether silicate-rich and iron-rich liquids remain separated or dissolve into a single mixed phase. This thesis therefore links the atomic-scale behavior of hydrogen-bearing silicate liquids to the planetary-scale properties of sub-Neptunes.

The dissertation of Sarah Marcum is approved.

Peng Ni

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Edward Donald Young, Committee Chair

University of California, Los Angeles

2026

To Mom, Dad, Katie, and Max

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ACKNOWLEDGMENTS

I have been so lucky to have worked, studied, and played with so many wonderful people over the course of my time at UCLA. The support that I received while writing this thesis has been so heartening and I am so grateful.

First, I want to thank my advisor, Ed Young. You taught me to value parsimonious explanations, ambitious questions, and the occasional bit of epistemic trespassing. Your encouragement to zig while my peers in the field zag has profoundly shaped how I value my own work and given me the confidence to step outside my scientific comfort zone. Here's to our super-sub-Neptune! I would also like extend my appreciation to the other members of my committee, Edwin Schauble, Peng Ni, and especially to Lars Stixrude. In my third year at UCLA, my research focus pivoted entirely, and I felt so welcomed into your group. None of this work would have been possible without your guidance.

My group mates, past and present, have encouraged me daily and kept my spirits high in the office and in the lab. Thanks to Lauren Tafla, Isabella Trierweiler, Jairui Liu, Laetitia Guibourdenche, Aaron Werlen, Kaitlyn McCain and Quinn Shollenberger.

To my step-group mates on the first floor, thank you for helping me compile VASP and letting me hang out on your couch before group meeting: Travis Gilmore, David James, Francis Dragulet, Bing Chua Hong, Junjie Dong, and my fellow interloper Akash Gupta. I should also mention my group mates-in-law on the fourth floor. Thanks for letting me crash your field work: Jaahnavee Venkatraman, Tyler Horvath, Elisha Jhoti, and Tyler Powell. I would also like to thank the mini-liquidus crew. Spending time in the lab in 2020 would have been so lonely were it not for you all: Nozomi Matsuda, Lvcian Vltava, Beth Ann Bell, Hugo Abe, Bidong Zhang, and Heather Kirkpatrick.

I've made so many amazing friends in EPSS and I don't think there is room to mention everyone. So thank you to everyone in our building for the wonderful conversations about science and beyond. My graduate experience was so much richer for having been surrounded

by such lovely people. In particular, thank you to my massive cohort and to those who have not fallen into any category yet: Randy Flores, Mark Hubert, Will Misener, Valeria Jaramillo, Ethan Tsai, Jewel Abbate, Ariel Garykowski, and Colin Wilkins.

A very special thank you to Leslie Insixiengmay and Ken Mei: to the joys and pains of sitting at the coffee table and getting angry about cardboard.

And to Ashley Schoenfeld and Hannah Tandy with whom I shared 152 wonderful Saturdays and countless pounds of bagels.

Thanks to my distant friends who were always happy to distract me from my work. To the Monday crew for starting my weeks out with so much fun: Jill, Sam, and Benno. To my dear William and Gwyn for talking on the phone for hours. To Madison who has cheered me on forever.

A special shout out to the American Cinematheque for being the coolest thing about LA, to Mammoth Mountain for being the coolest thing near LA, and to Colapasta for being the best food in the entire world (and to Stefano who fed me whenever I was stressed, celebrating, or anything in between).

To my parents who thought I would be a lawyer... and then a doctor (but a different kind). Thank you for supporting and loving me unconditionally while I figured it all out. To Aunt Jo, Aunt Sherri, Grandma, Nana, and RieRie for making me laugh and telling me that my work is cool. And to Katie for being the best sister I could ask for. You have no idea how much you inspire me.

And finally, to Max Parks. As I write this, it is almost exactly six years since we arrived in Los Angeles together. On September 8, 2020, we stayed in Death Valley and watched Mars rise from a geothermal pool. I remember feeling the same mix of excitement and uncertainty that I do now—the feeling of setting off into the unknown. Whatever comes tomorrow, I know I want to meet it the same way: with you, watching the sun rise over Zabriskie Point, and heading on towards Santa Monica.

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PUBLICATIONS

E.D. Young, A. Werlen, **S.P. Marcum**, L. Stixrude, and C.P. Dullemond, 2025, Differentiation, the exception, not the rule: Evidence for full miscibility in sub-Neptune interiors, *The Planetary Science Journal*, 6:251, 15 pp. DOI: 10.3847/PSJ/ae1012

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S.P. Marcum, L. Stixrude, and E.D. Young, Exoplanet Dynamos: Conductivity of Hydrogen-Bearing Silicate Liquids, (Manuscript in preparation).

CHAPTER 1

Introduction

The most common planets found around other stars have no Solar System analog. These planets are super-Earths and sub-Neptunes, exoplanets with masses and radii between those of Earth and Neptune (e.g., Fressin et al., 2013; Fulton et al., 2017). They dominate the current census of close-in exoplanets, yet their interiors remain poorly understood.

The language used to describe planetary interiors is inherited largely from the terrestrial planets: a metal core, a silicate mantle, and, in some cases, a comparatively thin atmosphere. This picture is appropriate for Earth today, where metal and silicate are separated into distinct reservoirs and where the atmosphere contains negligible mass relative to the solid planet. It is less clear that the same conceptual model applies to larger rocky planets that accreted hydrogen-rich primary atmospheres. In such planets, the atmosphere can be a significant thermal and chemical reservoir. The pressures and temperatures at the base of the envelope may be high enough to maintain long-lived magma oceans and to promote chemical exchange between hydrogen, silicate melt, and iron-rich metal. Under these conditions, the boundaries between atmosphere, magma ocean, and interior may become less sharply defined than in the terrestrial planets.

Rather than treating these planets as distinct layers of iron, silicate, and hydrogen, this thesis explores how miscibility among these components may alter the thermodynamics, transport properties, and phase equilibria of their interiors. Using first-principles molecular dynamics simulations, I quantify these effects by developing equations of state, calculating electrical and thermal conductivities, and testing phase stability in supercritical silicate–

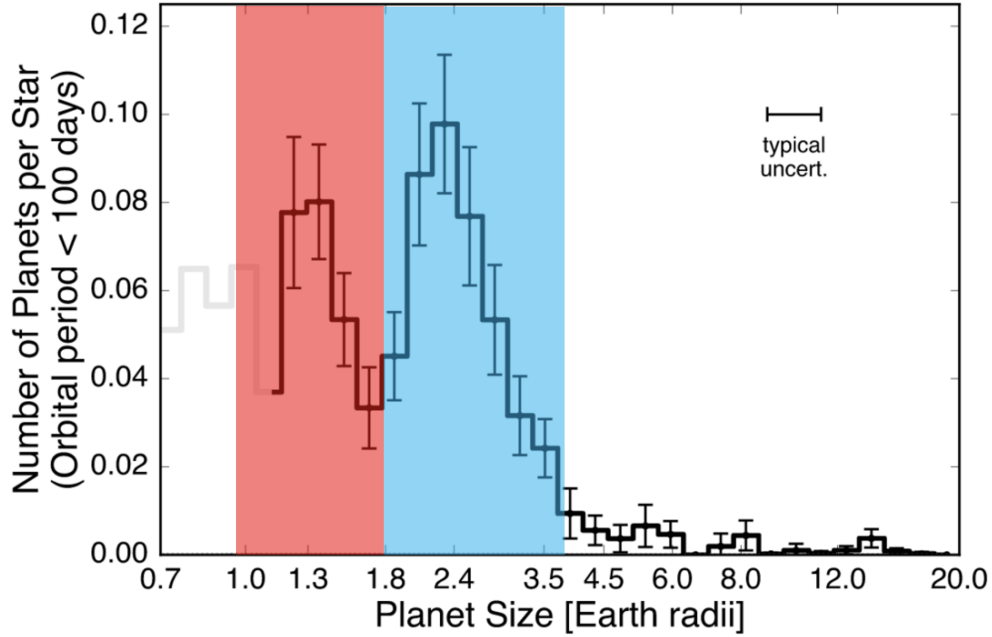


Figure 1.1: Radius distribution of close-in exoplanets, showing the radius valley near $\sim 1.8 R_{\oplus}$ that separates smaller super-Earths from larger sub-Neptunes. Modified from Fulton et al. (2017).

hydrogen mixtures.

1.1 Super-Earths and Sub-Neptunes

Super-Earths and sub-Neptunes are commonly distinguished by their radii and bulk densities. Super-Earths are typically smaller planets with radii below the observed radius valley and densities broadly consistent with rocky compositions. Sub-Neptunes are larger, lower-density planets that require some low-density material, such as hydrogen, helium, water-rich volatiles, or a combination of these components, in addition to rock and metal. The observed radius valley near $\sim 1.8 R_{\oplus}$ separates these two populations and is one of the clearest demographic signatures in the small-exoplanet population (Fulton et al., 2017; Van Eylen et al., 2018; Petigura et al., 2022).

A leading interpretation of the radius valley is that many super-Earths and sub-Neptunes formed as a single underlying population of rocky planets with hydrogen-rich envelopes. In this view, lower-mass and more highly irradiated planets lost their primordial atmospheres through photoevaporation, core-powered mass loss, or related escape processes, leaving behind rocky super-Earths. More massive planets, or planets at larger orbital distances, retained a fraction of their hydrogen-rich envelopes and remain sub-Neptunes (Lopez and Fortney, 2013; Owen and Wu, 2013; Ginzburg et al., 2018; Gupta and Schlichting, 2019; Rogers and Owen, 2021). In this picture, the radius valley records the coupled evolution of rocky interiors and volatile envelopes.

This shared evolutionary history makes it useful to consider super-Earths and sub-Neptunes together. In both cases, early interaction between a hot condensed interior and a primary atmosphere may have shaped the planet’s chemical inventory, thermal state, and later evolution. Magma oceans are expected during rocky planet formation because accretion, impacts, short-lived radionuclides, and core formation can all drive widespread melting. Although such magma oceans are often treated as transient in terrestrial planets, they may persist much longer in sub-Neptunes. An H_2 -rich envelope comprising only a few percent of the planet’s mass can substantially increase planetary radius, insulate the underlying rocky material, and help maintain molten interiors over long timescales. (Ginzburg et al., 2016; Misener and Schlichting, 2022; Rogers et al., 2024b).

1.2 Compositional Degeneracies and Equations of State

The primary observational constraints on most small exoplanets are mass and radius. These quantities provide a bulk density, but they do not uniquely determine composition. Sub-Neptunes have bulk densities of order $1\text{--}3\text{ g cm}^{-3}$, lower than expected for planets composed only of compressed rock and metal. These low densities are commonly interpreted in two broad ways: as evidence for volatile-rich, water-bearing interiors, or as evidence for rocky

planets overlain by H_2 -rich primary atmospheres (e.g., Fortney et al., 2007; Zeng et al., 2019; Chachan and Stevenson, 2018; Bean et al., 2021). Distinguishing between these possibilities is difficult because the same mass and radius can be produced by different combinations of rock, metal, water-rich material, and hydrogen. Similarly, variations in core mass fraction, mantle composition, thermal state, atmospheric mass, and volatile partitioning can produce comparable bulk densities. The inference of interior structure from mass and radius alone is therefore highly degenerate (Rogers, 2015; Rogers et al., 2023).

The interpretation of K2-18b illustrates how this degeneracy can persist even when atmospheric information is available. K2-18b has been discussed as a possible “Hycean” planet, a proposed class of water-rich sub-Neptunes in which a hydrogen-rich atmosphere overlies a volatile-rich interior or surface ocean (Madhusudhan et al., 2021). However, this interpretation remains highly debated: similar observations are also consistent with a gas-rich sub-Neptune hosting a magma ocean rather than a stable liquid-water ocean (Shorttle et al., 2024; Werlen et al., 2025b).

The importance of interior model assumptions has already been demonstrated for volatile-bearing magma ocean planets. Models that include rock melting and volatile redistribution between atmosphere and magma ocean can predict different radii for the same bulk composition and mass than models that neglect these effects (Dorn and Lichtenberg, 2021). Such differences can be comparable to observational uncertainties and can lead to substantially different inferred volatile inventories. This provides a useful precedent for the problem addressed in this thesis: when a volatile component is stored in, reacts with, or becomes miscible with a magma ocean, the material properties of the mixed interior must be treated explicitly.

Equations of state play a central role in this problem. An equation of state relates thermodynamic variables such as pressure, temperature, volume, density, and internal energy. In planetary structure calculations, an equation of state determines how density varies with depth and how temperature changes along an adiabat. It therefore controls the relationship

between a planet’s composition and its observable radius. For terrestrial planets, equations of state for iron and silicate phases provide the foundation for mass-radius models. For sub-Neptunes and volatile-rich super-Earths, however, the relevant materials may not be pure iron, pure silicate, pure water, or pure hydrogen.

A common simplifying approach is to approximate the density of a mixture by combining the volumes of its end-members. This type of volume-mixing model may be adequate when interactions between components are weak or when only bulk density is required. However, it cannot capture changes in bonding, coordination, compressibility, thermal expansivity, entropy, or heat capacity that arise from chemical interaction. These derivative properties are essential because they determine the thermal structure and evolution of a planet. A model that reproduces density but fails to reproduce the correct thermodynamic derivatives may still predict incorrect adiabats, convective behavior, or cooling histories.

Hydrogen-bearing silicate liquids provide a concrete example of this problem. The first project of this thesis develops a thermodynamically consistent equation of state for supercritical $\text{MgSiO}_3\text{--H}_2$ mixtures and uses it to evaluate how these liquids affect the interior structure of sub-Neptunes.

1.3 Planetary Dynamos and Conductive Fluids

In addition to affecting the structure of sub-Neptunes, hydrogen-bearing silicate liquids also may provide a large reservoir of electrically conductive fluid. This raises a further question: can such fluids influence, or even participate in, planetary magnetic field generation? Magnetic fields are among the few possible observational consequences of deep interior dynamics, and they connect material properties to thermal evolution, atmospheric escape, and planetary habitability. Although no magnetic field has yet been unambiguously detected for an exoplanet, magnetic fields are common in the Solar System and are expected to occur in at least some exoplanets (Brain et al., 2024).

Planetary magnetic fields are generated by dynamos, the requirements for which are simple in principle. A planet must contain a sufficiently large reservoir of conductive fluid, that fluid must be in motion, and magnetic diffusion must not erase the field faster than it is regenerated. In practice, these conditions depend on factors such as a planet’s composition, thermal state, cooling history, rotation, and internal structure. A conductive fluid that is stably stratified or transports heat primarily by conduction may fail to sustain a dynamo, even if its electrical conductivity is high.

Many different materials are capable of generating planetary dynamos. Earth’s magnetic field is generated in its liquid iron outer core, where thermal and compositional buoyancy drive convection in a highly conductive metallic fluid. Jupiter and Saturn generate magnetic fields in deep hydrogen-rich interiors where hydrogen becomes electrically conducting at high pressure. Uranus and Neptune also possess magnetic fields, though their strongly non-dipolar geometries suggest more complex dynamo regions. Any sufficiently large, convecting, electrically conductive fluid layer can in principle generate a magnetic field.

Molten silicates are also of interest in dynamo studies. Early Earth may have hosted a basal magma ocean, and if such a layer was both electrically conductive and vigorously convecting, it could have contributed to magnetic field generation before or alongside the core dynamo (Ziegler and Stegman, 2013; Blanc et al., 2020; Stixrude et al., 2020). Similar questions arise for super-Earths, where high internal pressures and temperatures may increase the electrical conductivity of silicate liquids (Soubiran and Militzer, 2018).

Previous work on silicate liquids has shown that electrical and thermal conductivity can depend strongly on composition, with Fe enrichment modifying the conductivity of basal magma ocean liquids (Dragulet and Stixrude, 2025). If hydrogen also modifies the local structure and electronic properties of silicate liquids, it may change their electrical and thermal conductivity as well. This is especially important for sub-Neptunes, where the relevant fluid regions may be large and long-lived. Even conductivities far below those of liquid iron could become dynamically important if the convecting region is sufficiently thick.

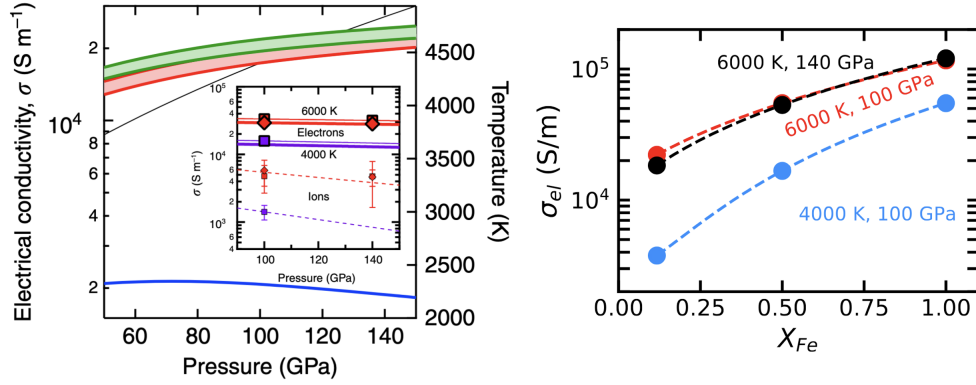


Figure 1.2: Electrical conductivity of liquid silicates at basal magma ocean conditions. Conductivity depends on temperature and pressure (left; Stixrude et al., 2020) and can be strongly enhanced by increasing Fe content (right; Dragulet and Stixrude, 2025).

In this sense, hydrogen-bearing silicate liquids may occupy an intermediate regime between terrestrial silicate magma oceans and the conducting hydrogen-rich interiors of giant planets.

The conductivity of these fluids also matters for thermal evolution. Electrical conductivity controls magnetic diffusion and ohmic dissipation, while electronic thermal conductivity contributes to heat transport. A highly conductive fluid may be favorable for magnetic induction, but if thermal conduction becomes too efficient, it may also reduce the buoyancy available to drive convection.

The second project in this thesis investigates the electrical and thermal conductivity of supercritical $\text{MgSiO}_3\text{--H}_2$ liquids using first-principles molecular dynamics simulations. The goal is to determine whether hydrogen-bearing silicate liquids approach metallic or semi-metallic behavior at super-Earth and sub-Neptune interior conditions, and whether their conductivities are large enough to affect magnetic field generation.

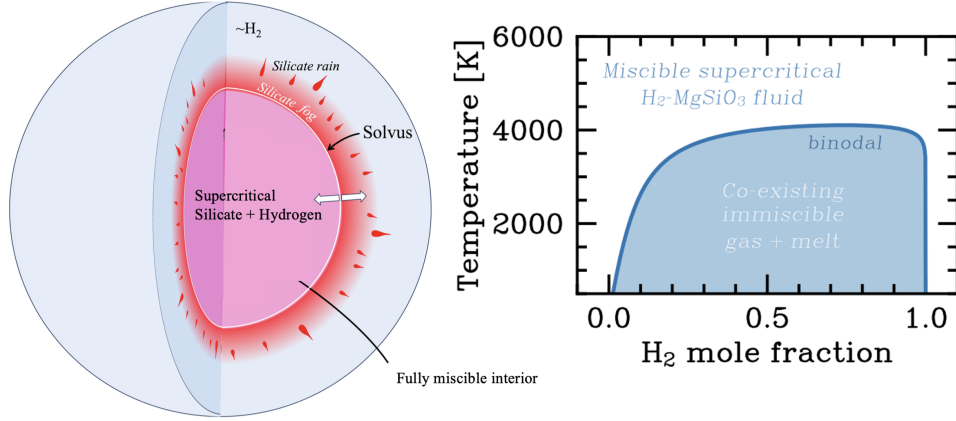


Figure 1.3: Left: Schematic illustration of silicate–hydrogen miscibility in a sub-Neptune interior, modified from Young et al. (2024a). Right: Silicate–hydrogen solvus/binodal separating a fully miscible supercritical $\text{MgSiO}_3\text{--H}_2$ fluid from coexisting silicate-rich and H_2 -rich phases, from Rogers et al. (2025).

1.4 Phase Equilibria and Core Formation

Planetary structure models often treat the atmosphere–interior boundary as a surface separating a silicate-rich condensed region from an H_2 -rich envelope. Chemical exchange across this boundary can be described using solubility: hydrogen dissolves into the magma ocean, while silicate-derived species evaporate into the atmosphere. This approach is useful when one component is dilute in the other and when the two reservoirs remain distinct. However, it may be incomplete if the relevant pressure–temperature conditions approach those of complete miscibility.

Recent work has suggested that the silicate–hydrogen system may reach supercritical or fully miscible conditions at pressures and temperatures relevant to atmosphere–magma ocean interfaces in sub-Neptunes (Markham et al., 2022; Young et al., 2024a; Gilmore and Stixrude, 2026; Rogers et al., 2025). In this regime, the traditional distinction between a silicate magma ocean and an overlying hydrogen atmosphere becomes blurred. The boundary

between interior and envelope may correspond to a phase boundary separating a homogeneous supercritical silicate–hydrogen fluid from coexisting silicate-rich and hydrogen-rich phases.

In a binary mixture, this phase boundary is the binodal. The binodal defines the compositions of coexisting phases at thermodynamic equilibrium and separates the one-phase region from the two-phase region. For the silicate–hydrogen system, the binodal describes the pressure–temperature–composition conditions under which a single supercritical silicate–hydrogen fluid separates into silicate-rich and hydrogen-rich phases. In this picture, the surface of a sub-Neptune magma ocean is a thermodynamic boundary set by the phase behavior of the mixture.

The phase-equilibrium problem becomes even richer when iron is included. Iron is a major constituent of rocky planets and, in the terrestrial planets, separates efficiently from silicate to form a metallic core. It is not obvious that this same outcome must occur in sub-Neptunes. At high pressure and temperature, hydrogen can dissolve into iron-rich metal, silicate components can become more soluble in metal, and metal droplets may approach neutral buoyancy in a deep magma ocean. Recent thermodynamic models suggest that while silicate-rich and iron-rich liquids may remain distinct at shallow conditions, they may become increasingly miscible at depth in the presence of hydrogen (Young et al., 2024a; Young and Werlen, 2026).

For planets that formed with substantial hydrogen-rich envelopes, the usual picture of a rocky planet with a distinct metallic core and silicate mantle may not always apply. If hydrogen promotes mixing among iron-rich, silicate-rich, and volatile-rich liquids, then some sub-Neptunes may be partially or effectively coreless, with iron retained in a deep mixed interior rather than segregated into a separate central core. Core formation and magma-ocean evolution may therefore be controlled by the phase behavior of hydrogen-bearing liquids. The third project of this thesis examines whether silicate-rich and iron-rich liquids remain separated or become mixed at sub-Neptune interior conditions.

The ultimate goal of this dissertation is to determine how hydrogen-bearing rocky materials behave at sub-Neptune interior conditions, and how those properties shape planetary structure and evolution.

CHAPTER 2

Computational Methods

The work presented in this thesis uses first-principles molecular dynamics simulations to study the thermodynamic, structural, and transport properties of hydrogen-bearing silicate liquids and related multicomponent systems at high pressure and temperature. These simulations combine a quantum-mechanical description of the electronic structure with a classical description of ionic motion. At each molecular dynamics time step, the electronic structure is solved using density functional theory, and the resulting forces are used to propagate the atomic positions. The trajectories generated in this way provide access to pressure, internal energy, density, local structure, diffusion, and transport properties under conditions relevant to planetary interiors.

This chapter describes the computational methods that are common to the projects in this thesis. I begin with a brief overview of density functional theory and its implementation in first-principles molecular dynamics. I then describe the practical electronic-structure choices used in the calculations, including plane-wave basis sets, projector augmented-wave potentials, Brillouin-zone sampling, electronic convergence, and finite-temperature occupations. I next describe the molecular dynamics ensembles used to generate trajectories, followed by the methods used to obtain time averages and uncertainties from correlated simulation data.

2.1 Density Functional Theory

Density functional theory (DFT) is used to solve the electronic structure problem for each ionic configuration sampled during a molecular dynamics trajectory. The central difficulty in electronic structure theory is that the exact many-electron wave function depends on the coordinates of all electrons in the system and is therefore not tractable for systems containing many atoms. DFT reformulates this problem in terms of the electron density, $n(\mathbf{r})$, rather than the full many-electron wave function. This makes it possible to compute the energy and interatomic forces for systems containing hundreds of atoms, as required for simulations of liquids at planetary interior conditions.

2.1.1 Kohn–Sham Density Functional Theory

The foundation of modern DFT is given by the Hohenberg–Kohn theorems, which show that the ground-state energy of an interacting electron system is a unique functional of the electron density and that the correct ground-state density minimizes this energy functional (Hohenberg and Kohn, 1964). Kohn and Sham introduced a practical way to compute this density by mapping the interacting electron system onto a fictitious non-interacting system with the same ground-state density (Kohn and Sham, 1965). In this approach, the electron density is written in terms of one-electron Kohn–Sham orbitals,

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2, \quad (2.1)$$

where ψ_i is a Kohn–Sham orbital and f_i is its occupation. For a fixed ionic configuration, the total energy can be written schematically as

$$E[n; \mathbf{R}] = T_s[n] + \int v_{\text{ext}}(\mathbf{r}; \mathbf{R}) n(\mathbf{r}) d\mathbf{r} + E_H[n] + E_{xc}[n] + E_{\text{II}}(\mathbf{R}), \quad (2.2)$$

where $T_s[n]$ is the kinetic energy of the non-interacting Kohn–Sham system, $v_{\text{ext}}(\mathbf{r}; \mathbf{R})$ is

the external potential due to the ions at positions $\mathbf{R}$, $E_H[n]$ is the classical Hartree energy describing electron–electron repulsion, $E_{xc}[n]$ is the exchange–correlation energy, and $E_{\text{II}}(\mathbf{R})$ is the ion–ion interaction energy. The Hartree energy is

$$E_H[n] = \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (2.3)$$

The Kohn–Sham orbitals are obtained by solving an effective one-electron equation,

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.4)$$

where m_e is the electron mass, ϵ_i is a Kohn–Sham eigenvalue, and the effective potential is

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}). \quad (2.5)$$

The exchange–correlation potential is the functional derivative of the exchange–correlation energy,

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (2.6)$$

The Kohn–Sham equations are solved self-consistently. An initial electron density is used to construct v_{eff} , the Kohn–Sham equations are solved to obtain orbitals and a new density, and the process is repeated until the density and total energy satisfy the chosen convergence criteria. In molecular dynamics, this self-consistent electronic-structure calculation is performed repeatedly as the ions move through the trajectory.

2.1.2 Exchange–Correlation Approximation

The exchange–correlation functional contains the many-body effects that are not included explicitly in the non-interacting kinetic energy and classical Hartree terms. Its exact form is unknown and must be approximated. The simplest approximation is the local density

approximation (LDA), in which the exchange-correlation energy density at each point is assumed to be that of a homogeneous electron gas with the same local density. More flexible approximations include generalized gradient approximation (GGA) functionals, in which the exchange-correlation energy depends on both the electron density and its gradient,

$$E_{xc}^{\text{GGA}}[n] = \int n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})] d\mathbf{r}. \quad (2.7)$$

GGA functionals are widely used for condensed matter and planetary materials because they provide a useful balance between accuracy and computational efficiency. The calculations in this thesis use the PBEsol GGA functional (Perdew et al., 2008), except where otherwise noted. PBEsol was designed for solids and condensed matter by restoring the gradient expansion for exchange over density variations characteristic of densely packed systems.

The choice of exchange-correlation functional is an important approximation in DFT calculations. It can affect equilibrium volumes, pressures, bonding, band gaps, and transport properties. This is especially important for the high-pressure liquids studied here because pressure, temperature, and composition are inferred from small differences in the total energy, stress tensor, and electronic structure. For this reason, any convergence or functional sensitivity tests relevant to a particular set of calculations are discussed in the project-specific chapters.

2.1.3 Projector Augmented-Wave Method and Plane-Wave Basis Sets

All calculations in this thesis were performed using periodic boundary conditions. Periodic boundary conditions are natural for crystalline materials and are also useful for liquids because they allow a finite simulation cell to represent a bulk material without surfaces. In a periodic system, the electronic wave functions can be written using Bloch’s theorem as a product of a plane wave and a lattice-periodic function. Equivalently, a Kohn–Sham orbital can be expanded as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (2.8)$$

where $\mathbf{k}$ is a wave vector in the Brillouin zone, $\mathbf{G}$ is a reciprocal lattice vector, and $c_{\mathbf{k}+\mathbf{G}}$ are expansion coefficients. In principle, this expansion contains infinitely many plane waves. In practice, the basis set is truncated by including only plane waves with kinetic energies below a chosen cutoff energy,

$$\frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 < E_{\text{cut}}. \quad (2.9)$$

Increasing E_{cut} improves the completeness of the basis set but increases the computational cost. The cutoff energy must therefore be chosen to converge the quantities of interest, including total energies, pressures, stresses, and forces.

The rapid oscillations of all-electron wave functions near nuclei would require an impractically large plane-wave basis. This problem is addressed using the projector augmented-wave (PAW) method (Blöchl, 1994; Kresse and Joubert, 1999), which transforms a smooth pseudo-wave function into the corresponding all-electron wave function. The transformation can be written as

$$|\psi\rangle = \mathcal{T}|\tilde{\psi}\rangle, \quad (2.10)$$

where $|\psi\rangle$ is the all-electron wave function, $|\tilde{\psi}\rangle$ is the pseudo-wave function, and $\mathcal{T}$ is a linear transformation. In the PAW formalism, the pseudo and all-electron wave functions differ only within augmentation regions around the nuclei,

$$\mathcal{T} = 1 + \sum_R \hat{\mathcal{T}}_R, \quad (2.11)$$

where $\hat{\mathcal{T}}_R$ is nonzero only inside the augmentation sphere around atom R . This approach retains much of the accuracy of all-electron methods while remaining efficient enough for

molecular dynamics simulations of large cells. The calculations in this thesis use PAW potentials for Mg, Si, O, H, and Fe; the specific PAW datasets and valence configurations are summarized below in Section 2.3.3.

2.1.4 Finite-Temperature Electronic Occupations

The simulations in this thesis are performed at temperatures of several thousand kelvin. Under these conditions, finite-temperature electronic occupations are appropriate, especially for liquids that approach metallic or semi-metallic behavior. At nonzero electronic temperature, the occupation of electronic state i is given by the Fermi–Dirac distribution,

$$f_i = \frac{1}{1 + \exp[(\epsilon_i - \mu)/(k_B T_e)]}, \quad (2.12)$$

where ϵ_i is the Kohn–Sham eigenvalue, μ is the electronic chemical potential, k_B is Boltzmann’s constant, and T_e is the electronic temperature. In the finite-temperature extension of DFT developed by Mermin (1965a), the minimized quantity is the electronic free energy rather than the zero-temperature internal energy. The electronic free energy can be written as

$$F_{\text{el}} = E_{\text{el}} - T_e S_{\text{el}}, \quad (2.13)$$

where E_{el} is the electronic internal energy and S_{el} is the electronic entropy. For independent fermions, the electronic entropy is

$$S_{\text{el}} = -k_B \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)]. \quad (2.14)$$

In the molecular dynamics simulations, the electronic temperature was set equal to the ionic temperature unless otherwise noted. In VASP, this is controlled through the electronic smearing width. For Fermi–Dirac smearing,

$$\sigma_{\text{smear}} = k_B T, \quad (2.15)$$

where σ_{smear} is expressed in electron volts when used as an input parameter. Equivalently,

$$\sigma_{\text{smear}} [\text{eV}] = 8.6173 \times 10^{-5} T [\text{K}]. \quad (2.16)$$

This finite-temperature treatment is especially important in the conductivity calculations discussed in Chapter 5, where the electronic occupations determine the states available for low-energy electronic transitions.

2.2 First-Principles Molecular Dynamics

First-principles molecular dynamics (FPMD) combines electronic-structure calculations with classical molecular dynamics. The electrons are treated quantum mechanically using DFT, while the ions are propagated classically according to the forces obtained from the electronic structure. This separation is appropriate for the high-temperature liquids studied here because the nuclear thermal de Broglie wavelengths are small compared with typical interatomic distances, while the electronic structure must be treated quantum mechanically. FPMD is well suited to high-pressure, high-temperature fluids because it does not require an empirical interatomic potential and can capture changes in bonding, coordination, and chemical speciation as they emerge from the electronic structure.

2.2.1 Born–Oppenheimer Approximation

The Born–Oppenheimer approximation separates electronic and nuclear motion by taking advantage of the large mass difference between nuclei and electrons (Born and Oppenheimer, 1927). Because electrons are much lighter than nuclei, they respond rapidly to changes in nuclear positions. The total wave function can therefore be approximated as a product of

electronic and nuclear parts,

$$\Psi_{\text{total}}(\mathbf{r}, \mathbf{R}) = \psi_{\text{el}}(\mathbf{r}; \mathbf{R})\chi(\mathbf{R}), \quad (2.17)$$

where $\mathbf{r}$ represents electronic coordinates and $\mathbf{R}$ represents nuclear coordinates. In Born–Oppenheimer molecular dynamics, the electronic structure is solved for each instantaneous ionic configuration, and the resulting electronic energy defines a potential-energy surface on which the nuclei move.

The electronic Hamiltonian depends parametrically on the nuclear positions,

$$\hat{H}_{\text{el}}(\mathbf{r}; \mathbf{R})\psi_{\text{el}}(\mathbf{r}; \mathbf{R}) = E_{\text{el}}(\mathbf{R})\psi_{\text{el}}(\mathbf{r}; \mathbf{R}). \quad (2.18)$$

The ionic dynamics are then propagated on the potential-energy surface $E_{\text{el}}(\mathbf{R})$.

2.2.2 Hellmann–Feynman Forces

The connection between the electronic-structure calculation and the classical motion of the ions is made through the forces. The Hellmann–Feynman theorem relates the derivative of the total energy with respect to a parameter λ to the expectation value of the derivative of the Hamiltonian,

$$\frac{dE_\lambda}{d\lambda} = \left\langle \psi_\lambda \left| \frac{d\hat{H}_\lambda}{d\lambda} \right| \psi_\lambda \right\rangle. \quad (2.19)$$

For molecular dynamics, the relevant parameter is the position of ion i . The force on that ion is

$$\mathbf{F}_i = -\frac{\partial E}{\partial \mathbf{R}_i} = -\left\langle \psi \left| \frac{\partial \hat{H}}{\partial \mathbf{R}_i} \right| \psi \right\rangle. \quad (2.20)$$

These forces are used to propagate the ionic positions through Newton’s equations of motion,

$$\mathbf{F}_i = m_i \mathbf{a}_i, \quad (2.21)$$

where m_i is the mass of ion i and $\mathbf{a}_i$ is its acceleration.

2.2.3 Molecular Dynamics Timesteps and Trajectory Generation

The molecular dynamics trajectories are generated by integrating Newton's equations of motion using a finite timestep Δt . A Taylor expansion of the position gives

$$\mathbf{R}_i(t + \Delta t) = \mathbf{R}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{1}{2}\mathbf{a}_i(t)\Delta t^2 + O(\Delta t^3), \quad (2.22)$$

where $\mathbf{v}_i$ is the velocity. In practice, molecular dynamics simulations use stable finite-difference integration schemes such as the velocity Verlet algorithm (Verlet, 1967). In this approach, positions and velocities are updated according to

$$\mathbf{R}_i(t + \Delta t) = \mathbf{R}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{\mathbf{F}_i(t)}{2m_i}\Delta t^2, \quad (2.23)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)}{2m_i}\Delta t. \quad (2.24)$$

The timestep must be small enough to resolve the fastest motions in the system. Hydrogen-bearing systems require particular care because hydrogen has a small mass and can move rapidly at high temperature. Most hydrogen-bearing simulations in this thesis used a timestep of 0.5 fs.

Initial velocities were assigned according to a Maxwell-Boltzmann distribution at the target temperature,

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{mv^2}{2k_B T} \right), \quad (2.25)$$

where m is the particle mass, v is speed, and T is temperature. Simulations were then equilibrated before production averages were calculated, as described below.

2.3 Electronic Structure Calculation Details

All first-principles molecular dynamics simulations in this thesis were performed using the Vienna *ab initio* Simulation Package (VASP) (Kresse and Furthmüller, 1996). VASP implements Kohn–Sham DFT with periodic boundary conditions, plane-wave basis sets, and PAW potentials. The following sections summarize the electronic-structure choices common to the calculations in this thesis. Additional project-specific settings, convergence tests, and post-processing choices are given in the relevant chapters.

2.3.1 Energy Cutoff and Electronic Convergence

The plane-wave energy cutoff controls the size of the basis set through Equation 2.9. A larger cutoff includes more plane waves and generally improves convergence of total energies, pressures, stresses, and forces. However, the computational cost of plane-wave DFT increases rapidly with basis-set size. The cutoff must therefore be chosen to ensure that the quantities of interest are converged.

Unless otherwise stated, production molecular dynamics simulations used a plane-wave energy cutoff of 500 eV. The electronic self-consistency loop was converged to an energy tolerance of 10^{-5} eV. These values were chosen to provide stable forces and pressures for high-pressure, high-temperature liquid simulations. Calculations requiring more detailed electronic information, including the conductivity and density-of-states calculations discussed in Chapter 5, were subjected to additional convergence tests with respect to cutoff energy, number of bands, and Brillouin-zone sampling.

2.3.2 Brillouin-Zone Sampling

The Brillouin zone was sampled using $\mathbf{k}$ -points. For a periodic simulation cell, the Brillouin-zone volume decreases as the real-space simulation cell increases. Molecular dynamics simulations in this thesis use large supercells containing many atoms, so the Brillouin zone is small and Γ -point sampling is generally sufficient for the thermodynamic and structural properties of interest. The Γ -point corresponds to

$$\mathbf{k} = (0, 0, 0). \tag{2.26}$$

For large, disordered liquid cells, Γ -point sampling provides a practical balance between accuracy and computational efficiency. Selected calculations, especially those involving electronic density of states or Kubo–Greenwood conductivity, may require additional sampling or separate convergence tests. Those post-processing choices are discussed in the relevant project chapters.

2.3.3 Pseudopotentials and Valence Configurations

The PAW potentials define which electrons are treated explicitly as valence electrons and which are included in the frozen core. The choice of PAW potential can affect high-pressure behavior because compression increases the importance of interactions between nominal core and valence regions. For this reason, PAW potentials must be chosen with care for high-pressure calculations.

The $\text{MgSiO}_3\text{--H}$ simulations used PAW datasets for Mg, Si, O, and H, and Fe-bearing simulations additionally used an Fe PAW dataset. The outermost core radii, in Bohr, and the numbers of electrons treated as valence were H (1.10, 1), Mg (2.00, 8), Si (1.90, 4), O (1.52, 6), and Fe (2.20, 14), respectively. Examination of representative trajectories shows that nominal PAW sphere overlap occurs for some short-range H–H, O–H, and Si–O contacts, with the frequency of overlapping contacts increasing with compression. The Mg and Fe potentials

include semicore states, an important consideration at high pressure where compression can increase interactions between nominal core and valence regions.

2.4 Molecular Dynamics Ensembles

Molecular dynamics simulations sample microscopic configurations from a statistical mechanical ensemble. The choice of ensemble determines which macroscopic variables are held fixed and which are allowed to fluctuate. The principal ensembles used in this thesis are the canonical ensemble, NVT , and the isothermal-isobaric ensemble, NPT . In the NVT ensemble, the number of atoms N , volume V , and temperature T are held fixed. In the NPT ensemble, the number of atoms N , pressure P , and temperature T are held fixed, while the simulation cell volume is allowed to fluctuate.

2.4.1 NVT Simulations and Thermostat Choice

Most production simulations in this thesis were performed in the NVT ensemble. This ensemble is useful for equation-of-state calculations because simulations at fixed volume and temperature yield time-averaged pressures and internal energies. By performing simulations over a range of volumes and temperatures, one can construct pressure–volume–temperature relations and fit thermodynamic models.

Temperature control in NVT simulations was achieved using a thermostat. A thermostat exchanges energy with the system to maintain the desired average temperature while allowing the instantaneous kinetic energy to fluctuate. The temperature is related to the kinetic energy by

$$\langle E_{\text{kin}} \rangle = \frac{N_{\text{dof}}}{2} k_B T, \quad (2.27)$$

where N_{dof} is the number of ionic degrees of freedom. For an unconstrained system with

N atoms, $N_{\text{dof}} \approx 3N$, with small corrections if center-of-mass motion or other degrees of freedom are removed.

The production simulations used a Nosé–Hoover thermostat to maintain the target temperature (Nosé, 1984; Hoover, 1985a). In this approach, the ionic system is coupled to an additional thermostat variable that allows the kinetic energy to fluctuate around the value corresponding to the desired temperature. In VASP, this coupling is controlled through molecular dynamics thermostat settings such as **SMASS**. The specific thermostat settings used for each project are given in the relevant chapters or input-file summaries.

2.4.2 NPT Simulations and Variable-Cell Calculations

Selected simulations were performed in the *NPT* ensemble to equilibrate volumes, explore pressure conditions, or generate initial structures for later fixed-volume production runs. In *NPT* simulations, the simulation cell responds to the difference between the internal stress and the target external pressure. The Parrinello–Rahman formalism describes the simulation cell using a matrix $\mathbf{h}$ whose columns are the lattice vectors,

$$\mathbf{h} = (\mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (2.28)$$

with cell volume

$$\Omega = \det(\mathbf{h}) = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}). \quad (2.29)$$

Atomic positions can be written in terms of fractional coordinates $\mathbf{s}_i$,

$$\mathbf{R}_i = \mathbf{h}\mathbf{s}_i. \quad (2.30)$$

Allowing $\mathbf{h}$ to evolve permits the cell volume, and in the most general case its shape, to fluctuate in response to the applied pressure (Parrinello and Rahman, 1980, 1981). A ther-

mostat is coupled to the barostat to maintain the target temperature, producing an NPT ensemble.

For liquid simulations, fully flexible cell shapes can sometimes introduce shear or distortions that are not useful for the intended calculation. In some cases, especially for two-phase or interface simulations, it is desirable to allow the volume to fluctuate while preserving a cubic or orthorhombic cell shape. Where such constraints were required, they were imposed using the VASP `ICONST` file, which allows selected geometric degrees of freedom of the simulation cell to be constrained during variable-cell dynamics. These cell-shape constraints allow pressure equilibration without introducing artificial changes in the geometry of the interface.

Pressure matching was used when separately equilibrated liquid regions were combined into a single simulation cell. In these calculations, the initial silicate-rich and metal-rich or hydrogen-rich regions were prepared at comparable pressure and temperature before being joined. This reduces artificial pressure imbalances, so the subsequent evolution more directly reflects phase stability, mixing, or miscibility rather than relaxation from a poorly matched initial condition.

2.5 Equilibration, Time Averaging, and Uncertainty Analysis

Molecular dynamics simulations produce time series of fluctuating quantities such as pressure, temperature, internal energy, volume, and stress. These quantities fluctuate around equilibrium values, but adjacent time steps are correlated because each configuration evolves from the previous one. As a result, uncertainties cannot be estimated by treating every molecular dynamics step as an independent measurement. This section describes how equilibration intervals, time averages, block averaging, and error propagation were used to obtain meaningful averages and uncertainties.

2.5.1 Equilibration and Production Intervals

The initial portion of each molecular dynamics simulation was discarded as equilibration. During this interval, the system relaxes from its initial configuration toward the target thermodynamic state. After equilibration, the remaining trajectory is treated as the production interval used for calculating averages. The equilibration interval was chosen by inspecting the time evolution of thermodynamic quantities such as pressure, temperature, and internal energy, and by excluding the portion of the trajectory affected by relaxation from the initial configuration.

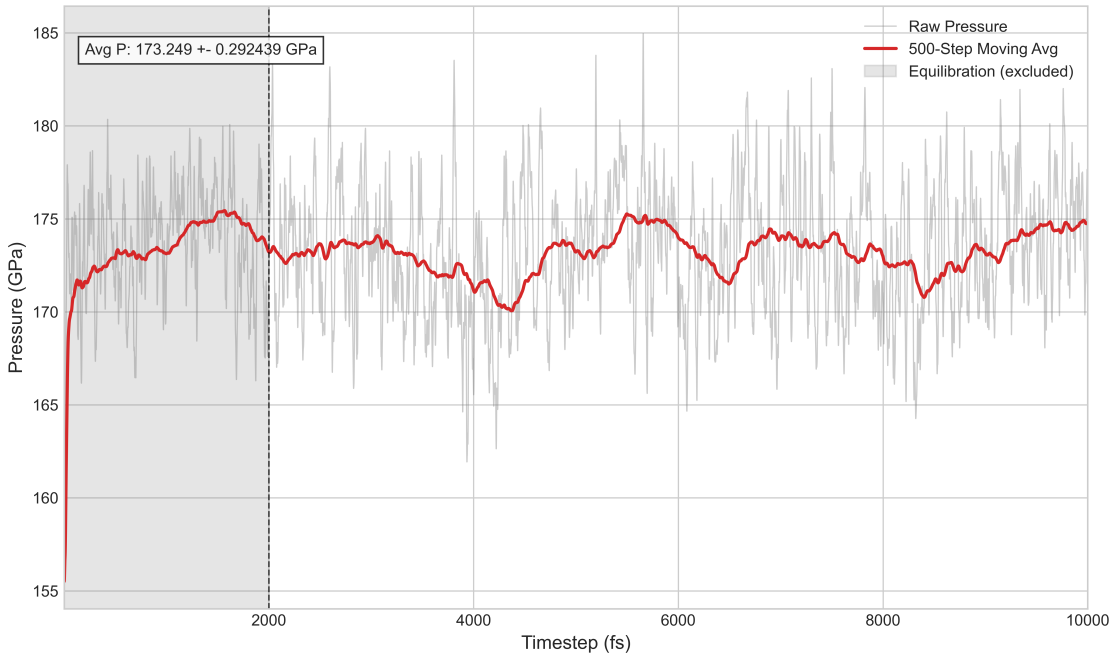


Figure 2.1: Representative pressure time series from an NVT first-principles molecular dynamics simulation. The shaded region indicates the equilibration interval excluded from the production average. The gray curve shows the instantaneous pressure, and the red curve shows a 500-step moving average. After equilibration, the pressure fluctuates about a stable mean value, illustrating the procedure used to define production intervals for time averaging.

For a time-dependent quantity $x(t)$ sampled at discrete time steps, the production average

is

$$\bar{x} = \frac{1}{N_{\text{samp}}} \sum_{i=1}^{N_{\text{samp}}} x_i, \quad (2.31)$$

where N_{samp} is the number of samples in the production interval. This expression was used to compute average pressure, temperature, internal energy, volume, stress, and other quantities extracted from the molecular dynamics trajectories. Derived quantities, such as enthalpy, were computed from these averages, and their uncertainties were estimated using the error-propagation procedures described below.

2.5.2 Block Averaging for Correlated Molecular Dynamics Data

Because molecular dynamics trajectories are correlated in time, the uncertainty in the mean is larger than the naive standard error that would be obtained by assuming independent samples. Block averaging provides a practical way to estimate the uncertainty of a time average when data are correlated (Flyvbjerg and Petersen, 1989a). The basic idea is to divide the production trajectory into blocks that are long enough that the average values of different blocks are approximately independent.

For a time series $x_1, x_2, \dots, x_{N_{\text{samp}}}$, the full-sample mean is

$$\bar{x} = \frac{1}{N_{\text{samp}}} \sum_{i=1}^{N_{\text{samp}}} x_i. \quad (2.32)$$

For a block length b , the trajectory is divided into M blocks, where $M = N_{\text{samp}}/b$ if N_{samp} is evenly divisible by b . The average of block j is

$$\bar{x}_j^{(b)} = \frac{1}{b} \sum_{i=(j-1)b+1}^{jb} x_i, \quad j = 1, \dots, M. \quad (2.33)$$

The variance of the mean estimated from the block averages is

$$\sigma_{\bar{x}}^2(b) = \frac{1}{M(M-1)} \sum_{j=1}^M \left(\bar{x}_j^{(b)} - \bar{x} \right)^2. \quad (2.34)$$

The corresponding standard error is

$$\sigma_{\bar{x}}(b) = \left[\frac{1}{M(M-1)} \sum_{j=1}^M \left(\bar{x}_j^{(b)} - \bar{x} \right)^2 \right]^{1/2}. \quad (2.35)$$

For small block sizes, adjacent block averages remain correlated and the uncertainty is underestimated. As the block size increases beyond the correlation time of the data, the block averages become approximately independent and $\sigma_{\bar{x}}(b)$ approaches a plateau. The uncertainty reported for a time-averaged quantity is taken from this plateau region. If no clear plateau is reached, the largest stable estimate is used as a conservative uncertainty estimate.

Block averaging provides a practical estimate of the increased uncertainty caused by temporal correlations without requiring an explicit calculation of the autocorrelation function or correlation time. For uncorrelated data, the block-averaged uncertainty reduces to the usual standard error of the mean. For correlated molecular dynamics data, the block-averaged uncertainty is larger because adjacent samples do not provide independent information.

2.5.3 Error Propagation

Many quantities used in this thesis are derived from multiple averaged simulation outputs. Their uncertainties were estimated by propagating the uncertainties of the underlying quantities. For a quantity y that depends on variables $x_1, x_2, \dots, x_n$,

$$y = y(x_1, x_2, \dots, x_n), \quad (2.36)$$

the uncertainty in y can be approximated by

$$\sigma_y^2 \approx \sum_i \left(\frac{\partial y}{\partial x_i} \right)^2 \sigma_{x_i}^2 + 2 \sum_{i < j} \left(\frac{\partial y}{\partial x_i} \right) \left(\frac{\partial y}{\partial x_j} \right) \text{cov}(x_i, x_j). \quad (2.37)$$

If covariances are negligible or unavailable, this reduces to

$$\sigma_y^2 \approx \sum_i \left(\frac{\partial y}{\partial x_i} \right)^2 \sigma_{x_i}^2. \quad (2.38)$$

This propagation framework was applied to thermodynamic quantities derived from simulation averages, including quantities such as enthalpy, density, composition, and fitted equation-of-state parameters where appropriate.

Chapter-specific applications, including fit uncertainties and derived thermodynamic quantities, are described in the relevant project chapters.

CHAPTER 3

Equation of State for Supercritical Silicate–Hydrogen Mixtures

3.1 Introduction

Sub-Neptunes are among the most abundant classes of exoplanets identified in the current census of the Galaxy (e.g., Fressin et al., 2013; Fulton et al., 2017). These planets have radii intermediate between Earth and Neptune and bulk densities of $1\text{--}3\text{ g cm}^{-3}$, lower than expected for compressed rock and metal alone. Interpreting their interiors therefore depends fundamentally on the equations of state assigned to candidate planetary materials. Equations of state for silicates, iron metal, water, and H_2 have been used to infer the compositions and layer mass fractions of sub-Neptunes from measured masses and radii (e.g., Seager et al., 2007; Valencia et al., 2006; Sotin et al., 2007; Rogers and Seager, 2010; Lopez and Fortney, 2014; Zeng et al., 2016; Nixon and Madhusudhan, 2021; Agüichine et al., 2021; Vazan et al., 2022). Because similar masses and radii can be produced by different combinations of silicate, metal, water, and H_2 , the inferred interior structure depends strongly on the adopted equations of state.

The low densities of sub-Neptunes have commonly been interpreted either as evidence for volatile-rich, water-bearing interiors (e.g., Fortney et al., 2007; Zeng et al., 2019), or as rocky planets with molten or partially molten interiors overlain by H_2 -rich primary atmospheres (Chachan and Stevenson, 2018; Bean et al., 2021). In the latter picture, even percent-level H_2 envelopes can strongly influence the observed radii and bulk densities of sub-Neptunes.

Such envelopes also affect the thermal evolution of the planet: dense H_2 -rich atmospheres can slow cooling and allow initially molten silicate interiors to persist over Gyr timescales (Ginzburg et al., 2016; Misener and Schlichting, 2022; Rogers et al., 2024b). As a result, many observed sub-Neptunes may contain long-lived magma oceans beneath their envelopes.

If magma oceans persist beneath H_2 -rich atmospheres, chemical exchange between the atmosphere and condensed interior is expected. Hydrogen can dissolve into molten silicate, while silicate-derived species may be transferred into the overlying envelope (e.g., Kite et al., 2019; Schlichting and Young, 2022; Misener et al., 2023; Charnoz et al., 2023; Young et al., 2024a; Rogers et al., 2025; Nixon et al., 2025; Werlen et al., 2025a).

The traditional picture of a sharp boundary between a silicate magma ocean and an H_2 -rich atmosphere may be incomplete at sub-Neptune interior conditions. Recent work by Gilmore and Stixrude (2026) shows that MgSiO_3 and H_2 can become fully miscible at the relevant pressures and temperatures. In this case, the atmosphere–interior boundary corresponds to a phase change from a supercritical magma ocean composed of silicate and hydrogen and a separate hydrogen-rich phase (Markham et al., 2022; Young et al., 2024a). Interior to this boundary, the condensed region is a hydrogen-bearing supercritical fluid whose thermodynamic properties must be determined directly. Recent population models further emphasize that hydrogen–silicate–metal miscibility may influence the structures and demographics of sub-Neptunes by controlling whether planets retain fully miscible interiors (Young and Werlen, 2026).

This miscible regime introduces a material property problem for planetary structure models. Existing treatments commonly rely on ideal volume mixing and endmember equations of state for dry silicate, H_2 , and other components. Such approaches are unlikely to accurately capture the density of silicate-hydrogen fluids. Moreover, thermodynamic derivatives such as heat capacity, thermal expansivity, bulk modulus, and the Grüneisen parameter control the interior adiabat and therefore influence the density and thermal structure inferred from mass–radius models. A self-consistent equation of state for supercritical MgSiO_3 – H mix-

tures is therefore needed to connect the phase-equilibrium picture of sub-Neptune interiors to planetary structure calculations.

In this work, we use first-principles molecular dynamics simulations to construct an equation of state for supercritical MgSiO_3H_4 (corresponding to 3.86 wt% hydrogen expressed as equivalent H_2). We fit the simulation results with a Helmholtz free-energy formulation that yields pressure, internal energy, entropy, heat capacity, thermal expansivity, bulk modulus, and Grüneisen parameter from a single thermodynamic surface. To apply the equation of state to planets with different hydrogen abundances, we combine the MgSiO_3H_4 free-energy surface with a dry MgSiO_3 liquid equation of state to construct a MgSiO_3 –H lookup table spanning the compositional interval from dry MgSiO_3 to MgSiO_3H_4 . We then compare the resulting material properties with dry MgSiO_3 liquid, analyze the local structure of the hydrogen-bearing fluid, and implement our equation of state into a sub-Neptune structure model.

3.2 Supercritical Silicate–Hydrogen Equation of State

3.2.1 First-Principles Simulations

We performed ab initio molecular dynamics simulations of supercritical MgSiO_3H_4 using density functional theory (DFT) in the Born–Oppenheimer approximation. The simulations were carried out with the projector augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP) (Kresse and Furthmüller, 1996), using the PBEsol exchange–correlation functional (Perdew et al., 2008). Each simulation cell contains 243 atoms: 27 Mg, 27 Si, 81 O, and 108 H atoms.

Initial liquid structures were generated by melting crystalline MgSiO_3 in a cubic cell for 10 ps at 8000 K and approximately 4 GPa. Hydrogen was then added to the liquid configuration by randomly inserting 108 H atoms into available voids of the simulation cell, with a minimum separation of 1.5 Å from all other atoms to avoid nonphysical overlaps

(Figure 3.1).

The hydrogen-bearing structures were equilibrated for an additional 10 ps at the target isotherm temperature, 4000, 6000, or 8000 K, starting from volumes corresponding to pressures of a few GPa. We used a timestep of 0.5 fs, consistent with recent first-principles simulations of hydrogen-bearing systems (Gupta et al., 2024; Gilmore and Stixrude, 2026). Isothermal compression paths were then constructed by reducing the cell volume stepwise and running simulations for 10–15 ps at each volume.

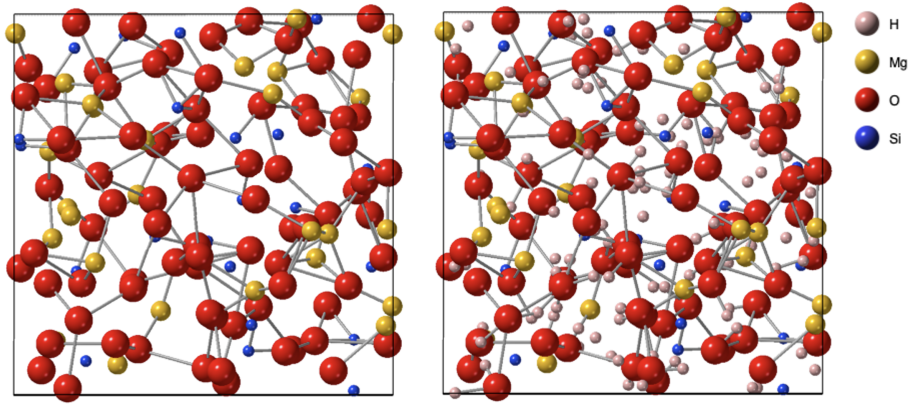


Figure 3.1: Initial simulation configuration before and after hydrogen insertion. Hydrogen was added to a pre-equilibrated MgSiO_3 liquid structure, producing the MgSiO_3H_4 composition simulated in this work. This composition corresponds to 3.86 wt% hydrogen by mass.

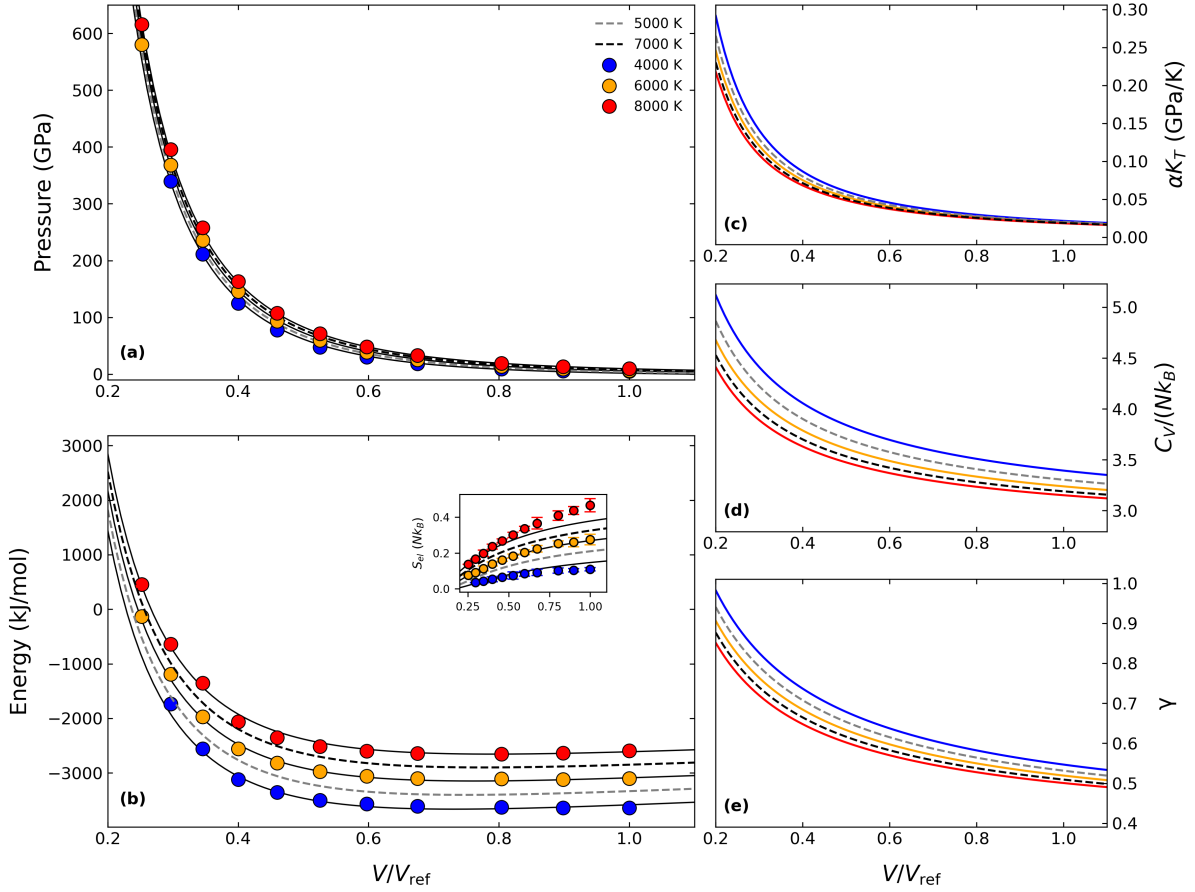


Figure 3.2: Our simulations results and our global EOS fit for supercritical MgSiO_3H_4 . Panels (a) and (b) show pressure and internal energy along the 4000, 6000, and 8000 K isotherms; solid lines are the EOS fit and filled circles are DFT-MD simulation results. The inset in panel (b) shows the electronic entropy, S_{el} . Panels (c)–(e) show derived thermodynamic properties calculated from the same fitted free-energy surface: the thermal pressure coefficient, αK_T , isochoric heat capacity, C_V , and Grüneisen parameter, γ . Dashed gray lines show interpolation to 5000 and 7000 K.

All simulations were performed in the canonical (NVT) ensemble using a Nosé–Hoover thermostat (Nosé, 1984; Hoover, 1985b). The Brillouin zone was sampled at the Γ point and a plane-wave cutoff energy of 500 eV was used. These settings yield total energy and pressure convergence within 10 meV atom $^{-1}$ and 0.5 GPa, respectively. Electronic thermal

effects were included using the Mermin functional (Mermin, 1965b), with the electronic temperature set equal to the ionic temperature. Thermodynamic averages were calculated after discarding the first 20% of each trajectory, and uncertainties were estimated using the blocking method (Flyvbjerg and Petersen, 1989b).

3.2.2 Supercritical Equation of State

To describe the thermodynamic properties of the simulated supercritical MgSiO_3H_4 fluid, we adopt the liquid equation-of-state formalism of de Koker and Stixrude (2009). In this approach, pressure, internal energy, entropy, heat capacity, and other thermodynamic properties are derived from a single fitted Helmholtz free-energy surface,

$$F(V, T) = F_{\text{ig}}(V, T) + F_{\text{xs}}(V, T) + F_{\text{el}}(V, T). \quad (3.1)$$

where F_{ig} is the ideal atomic contribution, F_{el} is the thermal electronic contribution, and F_{xs} is the excess interatomic contribution.

Figure 3.2 shows the fitted EOS compared with the DFT-MD simulation data along the 4000, 6000, and 8000 K isotherms. The model reproduces the simulated pressures and internal energies over the sampled pressure range, extending to approximately 600 GPa.

The panels to the right of Figure 3.2 show thermodynamic derivatives calculated directly from the fitted Helmholtz free-energy surface. The thermal pressure coefficient, αK_T , isochoric heat capacity, C_V , and Grüneisen parameter, γ , vary smoothly across the sampled pressure–temperature range. This regular behavior is important for planetary structure calculations, where the EOS is used to construct isentropic temperature profiles and evaluate density and thermodynamic properties along the condensed-interior adiabat.

Additional details of the Helmholtz free-energy formulation and the derivation of thermodynamic quantities are provided in Section 3.6.

3.3 Material Properties

3.3.1 Comparison with Dry MgSiO_3 Liquid

We first compare the simulated MgSiO_3H_4 densities with an ideal specific-volume mixture of dry MgSiO_3 liquid and pure H_2 at the same pressure and temperature. This comparison provides a useful reference because it represents the density that would be predicted without explicitly simulating a miscible $\text{MgSiO}_3\text{--H}$ fluid. The dry MgSiO_3 and H_2 reference densities are taken from de Koker and Stixrude (2009) and Chabrier et al. (2019), respectively.

The ideal mixture density is calculated by additive specific-volume mixing at fixed pressure and temperature; that is, the volume per unit mass of the mixture is taken to be the mass-weighted sum of the dry MgSiO_3 and H_2 specific volumes:

$$\frac{1}{\rho_{\text{ideal}}} = \frac{1 - w_{\text{H}}}{\rho_{\text{MgSiO}_3}} + \frac{w_{\text{H}}}{\rho_{\text{H}_2}}, \quad (3.2)$$

where w_{H} is the hydrogen mass fraction of MgSiO_3H_4 , expressed as an equivalent H_2 component.

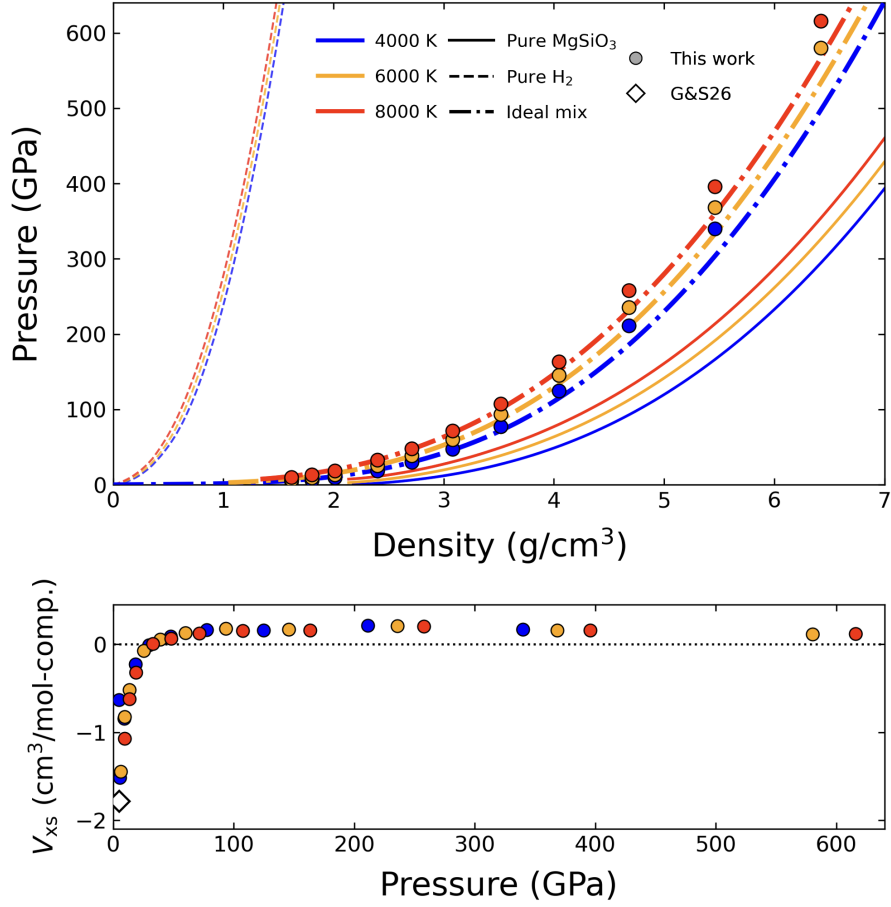


Figure 3.3: Equation of state and excess-volume comparison for MgSiO_3H_4 . (top) Density of MgSiO_3H_4 from our simulations (circles) compared with ideal mixing between dry MgSiO_3 and H_2 (dashed lines). Also shown are the equations of state of dry MgSiO_3 (de Koker and Stixrude, 2009) and H_2 (Chabrier et al., 2019). Colors indicate temperature: 4000 K (blue), 6000 K (orange), and 8000 K (red). (bottom) Excess volume of MgSiO_3H_4 computed from our simulations (circles; same color scheme as the top panel), compared with the excess volume at MgSiO_3H_4 composition from Gilmore and Stixrude (2026) (white diamond).

The simulated MgSiO_3H_4 densities deviate systematically from the ideal-mixture prediction. The discrepancy reaches several percent at high pressure and increases with compression, indicating that the density of the hydrogen-bearing fluid cannot be described as a

simple physical mixture of dry silicate liquid and hydrogen.

The excess volume provides a direct measure of this non-ideality. It is defined as the difference between the simulated MgSiO_3H_4 volume and the volume predicted by ideal specific-volume mixing. As shown in the lower panel of Figure 3.3, the excess volume changes across the simulated pressure range, demonstrating that the interaction between hydrogen and the silicate network evolves with compression. This behavior is consistent with the results of Gilmore and Stixrude (2026), who also find non-ideal volumes of solution in miscible silicate–hydrogen fluids. The pressure dependence of the excess volume provides a thermodynamic measure of the same structural changes discussed below, including the breakdown of H–H bonding and the increasing interaction between hydrogen and the silicate framework.

3.3.2 Radial Distribution Function

We use radial distribution functions (RDFs) to characterize the local structure of the simulated supercritical MgSiO_3H_4 fluid. Following standard definitions (McQuarrie, 1976), for each atomic pair, A – B , we compute

$$g_{AB}(r) = \frac{V}{4\pi r^2 N_A N_B} \left\langle \sum_{i \in A} \sum_{\substack{j \in B \\ j \neq i}} \delta(r - r_{ij}) \right\rangle, \quad (3.3)$$

where V is the simulation-cell volume, N_A and N_B are the numbers of atoms of species A and B , r_{ij} is the distance between atoms i and j , and the angle brackets indicate time averaging. RDFs are averaged over the equilibrated portion of each trajectory.

Figure 3.4 shows representative RDFs along the 6000 K isotherm at 6.4 GPa and 580 GPa. The Si–O and Mg–O correlations retain distinct first-neighbor peaks over the pressure range considered, indicating persistent short-range silicate structure in the supercritical fluid. Hydrogen also participates in the short-range structure, as shown by O–H and H–H correlations. The most pronounced pressure-induced change is in the H–H RDF: the sharp low-pressure H–H first-neighbor peak associated with molecular hydrogen is strongly reduced

at high pressure. This indicates breakdown of molecular H–H bonding and a transition from a more molecular hydrogen environment toward one with more atomic hydrogen within the silicate fluid.

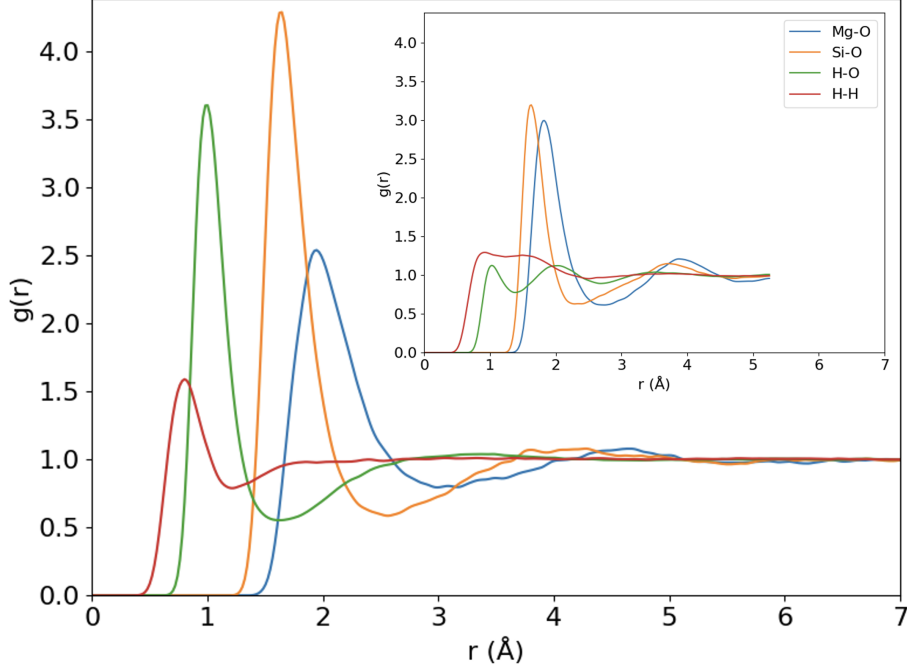


Figure 3.4: Radial distribution functions for Si–O, Mg–O, O–H, and H–H pairs at 6000 K. The main panel shows the low-pressure simulation at 6.40 GPa, and the inset shows the high-pressure simulation at 580.32 GPa.

3.3.3 Coordination and Hydrogen Persistence

From the RDFs, we determine coordination numbers by integrating the first peak:

$$\text{CN}_{A-B} = 4\pi\rho_B \int_0^{r_{\text{cut}}} g_{AB}(r)r^2 dr, \quad (3.4)$$

where ρ_B is the number density of species B , and r_{cut} is the location of the first minimum after the primary peak in $g_{AB}(r)$.

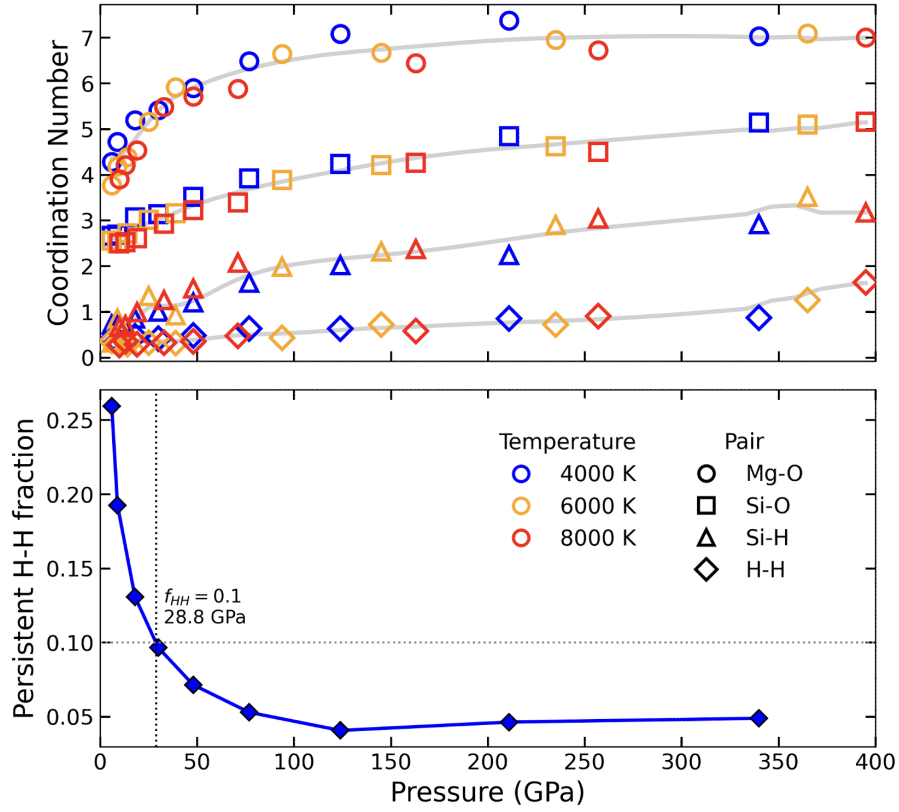


Figure 3.5: Coordination numbers and H–H persistence in supercritical MgSiO_3H_4 . Top: Mg–O, Si–O, Si–H, and H–H coordination numbers as a function of pressure. Symbols show individual simulations colored by temperature; gray curves show temperature-averaged trends. Bottom: time-averaged fraction of H atoms in persistent H–H contacts at 4000 K. Persistent contacts are defined as H–H pairs that remain shorter than the first minimum in the H–H RDF for at least 100 fs.

Figure 3.5 shows the Mg–O, Si–O, Si–H, and H–H coordination numbers as a function of pressure, together with the fraction of hydrogen atoms participating in persistent H–H contacts at 4000 K. For the RDF-derived coordination numbers, coordination generally increases with compression, as expected from the increasing density of the fluid. However, Si–O coordination remains below 5 over the pressure range explored here. This behavior differs

from dry MgSiO_3 and related silicate liquids, in which Si–O coordination increases more rapidly with pressure and is known to exceed 6 under comparable high-pressure conditions (Stixrude and Karki, 2005a; Sun et al., 2011; Sanloup et al., 2013; Luo and Deng, 2025).

The limited pressure-induced growth in Si–O coordination in the H-bearing fluid, compared with pure MgSiO_3 liquid, indicates that hydrogen changes how the silicate framework responds to compression. The origin of this effect is increasing Si–H bonding. Si–H bonds are present at all pressures, and the Si–H coordination number increases with pressure. Our results are consistent with those of Gilmore and Stixrude (2026), who also find that miscible silicate–hydrogen fluids contain a substantial population of Si–H bonds.

We perform a pair-persistence analysis to distinguish long-lived H–H contacts from transient near-neighbor encounters. For each simulation, an H–H pair is first identified using the same RDF-based criterion used for the coordination analysis: the H–H distance must lie within the first minimum in the H–H RDF. Along the 4000 K isotherm, this cutoff decreases from $r_{\text{HH,cut}} = 1.29 \text{ \AA}$ at 6 GPa to $r_{\text{HH,cut}} = 1.07 \text{ \AA}$ at 340 GPa. An H–H contact is then considered persistent only if the same pair remains continuously within this cutoff for at least 100 fs. We report the time-averaged fraction of H atoms participating in at least one such persistent H–H contact.

The H–H coordination number increases with pressure, but the persistence analysis shows that this trend does not correspond to increasing molecular H_2 abundance. At 4000 K, the persistent H–H fraction decreases rapidly with pressure and falls below 0.1 near the same pressure range as the $V^{\text{xs}} = 0$ crossover in Figure 3.3. Thus, high-pressure H–H coordination primarily reflects compression-driven near-neighbor proximity rather than long-lived molecular H_2 .

3.4 Supercritical Interior Models

3.4.1 MgSiO₃–H Lookup Table

To incorporate hydrogen-bearing silicate fluids into planetary structure calculations, we constructed a composition-dependent MgSiO₃–H lookup EOS using HeFESTo (Stixrude and Lithgow-Bertelloni, 2011). The lookup table is based on two liquid Helmholtz free-energy surfaces: the dry MgSiO₃ liquid EOS of de Koker and Stixrude (2009) and the supercritical MgSiO₃H₄ EOS fit in this work. These two compositions are treated as endmembers for representing intermediate MgSiO₃–H compositions.

Each endmember is described by a Helmholtz free energy, $F(V, T)$. At a specified pressure and temperature, HeFESTo evaluates the corresponding Gibbs free energy by finding the volume that satisfies the target pressure and applying the Legendre transform

$$G(P, T) = F(V, T) + PV. \quad (3.5)$$

The composition-dependent fluid EOS is then constructed in Gibbs free-energy space, which is the natural thermodynamic potential for fixed-pressure, fixed-temperature calculations.

Intermediate compositions are represented as

$$\text{MgSiO}_3\text{H}_n, \quad 0 \leq n \leq 4, \quad (3.6)$$

where n is the number of hydrogen atoms per MgSiO₃ formula unit. Thus $n = 0$ corresponds to dry MgSiO₃, while $n = 4$ corresponds to the MgSiO₃H₄ endmember simulated in this work. Equivalently, we define the MgSiO₃H₄ endmember fraction as

$$X = \frac{n}{4}, \quad 0 \leq X \leq 1. \quad (3.7)$$

The hydrogen mass fraction corresponding to a given stoichiometric composition is

$$w_{\text{H}} = \frac{nM_{\text{H}}}{M_{\text{MgSiO}_3} + nM_{\text{H}}}, \quad (3.8)$$

where M_{H} is the molar mass of atomic hydrogen (1.008 g mol^{-1}) and M_{MgSiO_3} is the molar mass of one MgSiO_3 formula unit ($100.39 \text{ g mol}^{-1}$). Written in terms of the MgSiO_3H_4 endmember fraction, this is equivalently

$$w_{\text{H}} = \frac{X(4M_{\text{H}})}{(1-X)M_{\text{MgSiO}_3} + X(M_{\text{MgSiO}_3} + 4M_{\text{H}})}. \quad (3.9)$$

The MgSiO_3H_4 endmember therefore corresponds to approximately 3.86 wt% H.

For the lookup table, the MgSiO_3 –H fluid is treated as an ideal solution between dry MgSiO_3 and MgSiO_3H_4 . In terms of the endmember fraction X , the mixed liquid Gibbs free energy is

$$\begin{aligned} G_{\text{liq}} = & (1-X)G_{\text{dry}} + XG_{\text{hyd}} \\ & + RT[(1-X)\ln(1-X) + X\ln X], \end{aligned} \quad (3.10)$$

where G_{dry} and G_{hyd} are the Gibbs free energies of the dry MgSiO_3 and MgSiO_3H_4 endmembers, respectively. Density and the other thermodynamic properties are then derived from the mixed Gibbs free-energy surface.

The final EOS table is indexed by hydrogen concentration, pressure, and temperature. For each point in (w_{H}, P, T) space, the table reports density, entropy, enthalpy, heat capacity, thermal expansivity, adiabatic bulk modulus, reference density, compression ratio, and Grüneisen parameter. The table spans the binary interval from dry MgSiO_3 to MgSiO_3H_4 , corresponding to approximately 0–3.86 wt% H.

The MgSiO_3 –H equation of state table is available at <https://github.com/s-marcum/MgSiO3-H-EOS>.

3.4.2 Planet Model Setup

We use the PlanetLab model as a vehicle for applying the MgSiO_3 –H lookup EOS to sub-Neptune interior structure calculations (Young et al., 2025). The details of the model have been described previously, but we summarize the aspects most relevant to the condensed

interior here. The planet is modeled as a spherically symmetric body consisting of a well-mixed condensed interior overlain by an H_2 -rich atmosphere. The condensed interior is assumed to be single phase over the pressure–temperature range considered. Its hydrogen abundance is set by mass balance between the total hydrogen inventory and the hydrogen contained in the overlying atmosphere.

For a specified total H_2 inventory and atmosphere–interior boundary pressure, the atmospheric mass fraction is determined self-consistently rather than prescribed independently. The atmosphere is integrated outward from the MgSiO_3 – H_2 binodal, which sets the pressure, temperature, and gas composition at the base of the envelope. In hydrostatic form, the boundary pressure corresponds to the weight of the overlying atmosphere,

$$P_{\text{surf}} = \int_{R_{\text{surf}}}^{\infty} \rho_{\text{atm}}(r, T, x_i) g(r) dr, \quad (3.11)$$

where R_{surf} is the radius of the condensed interior, R_{out} is the outer atmosphere, and x_i denotes the gas composition. The envelope is H_2 -rich rather than strictly pure H_2 : near the atmosphere–interior boundary, its composition is set by equilibrium with the condensed phase, while the outer atmosphere is H_2 dominated. The resulting atmospheric hydrogen mass is subtracted from the total hydrogen inventory, and the remaining hydrogen sets the fixed composition of the condensed MgSiO_3 –H interior.

The condensed structure is calculated by solving the standard equations of mass conservation and hydrostatic equilibrium (e.g., Seager et al., 2007),

$$\frac{dm}{dr} = 4\pi r^2 \rho, \quad (3.12)$$

$$\frac{dP}{dr} = -\frac{Gm\rho}{r^2}, \quad (3.13)$$

where m is the mass enclosed within radius r , ρ is density, P is pressure, and G is the gravitational constant. For the condensed interior, the density is obtained using the MgSiO_3 –H equation of state,

$$\rho = \rho_{\text{EOS}}(w_{\text{H}}, P, T), \quad (3.14)$$

where w_{H} is the hydrogen mass fraction in the condensed $\text{MgSiO}_3\text{--H}$ phase. This hydrogen abundance is held fixed throughout the condensed interior for a given model, consistent with efficient convection and complete miscibility in the supercritical regime.

Because the condensed interior is fluid and expected to convect efficiently, its thermal profile is assumed to be isentropic. In the constant-entropy implementation, the adiabat is anchored at the atmosphere–interior boundary condition, $(P_{\text{surf}}, T_{\text{surf}})$. The entropy at this boundary defines the entropy of the condensed interior,

$$S_{\text{surf}} = S_{\text{EOS}}(w_{\text{H}}, P_{\text{surf}}, T_{\text{surf}}). \quad (3.15)$$

At each deeper pressure, the adiabatic temperature is then found by solving

$$S_{\text{EOS}}(w_{\text{H}}, P, T_{\text{ad}}) = S_{\text{surf}}. \quad (3.16)$$

The resulting function $T_{\text{ad}}(P)$ is used during the interior structure calculation. For each trial central pressure, the structure equations are integrated through the condensed mass while density is evaluated from the EOS along the precomputed constant-entropy path. The central pressure is adjusted until the integrated outer boundary pressure matches the atmosphere-imposed surface pressure. This procedure yields self-consistent radial profiles of pressure, temperature, density, and thermodynamic properties for the condensed interior.

3.4.3 Planet Models

In Figure 6, we compare two representative sub-Neptune models with the same planet mass, $M_p = 6.0 M_{\oplus}$, the same equilibrium temperature, $T_{\text{eq}} = 1000$ K, and the same total H_2 inventory of 4.0 wt%. The models differ only in the pressure of the atmosphere–interior boundary, which is set by the $\text{MgSiO}_3\text{--H}_2$ binodal (Gilmore and Stixrude, 2026). This boundary pressure controls how the fixed hydrogen inventory is partitioned between the H_2 -rich atmosphere and the supercritical $\text{MgSiO}_3\text{--H}$ condensed interior.

In model A, the atmosphere–interior boundary occurs at $P_{\text{surf}} = 1$ GPa and $T_{\text{surf}} = 3746$ K. The atmosphere contains 0.60% of the planet mass, while the condensed interior

contains 3.44 wt% H_2 equivalent. In model B, the boundary occurs at $P_{\text{surf}} = 5.0$ GPa and $T_{\text{surf}} = 3204$ K. The atmosphere is more massive, comprising 2.50% of the planet mass, and the condensed interior contains 1.52 wt% H_2 equivalent.

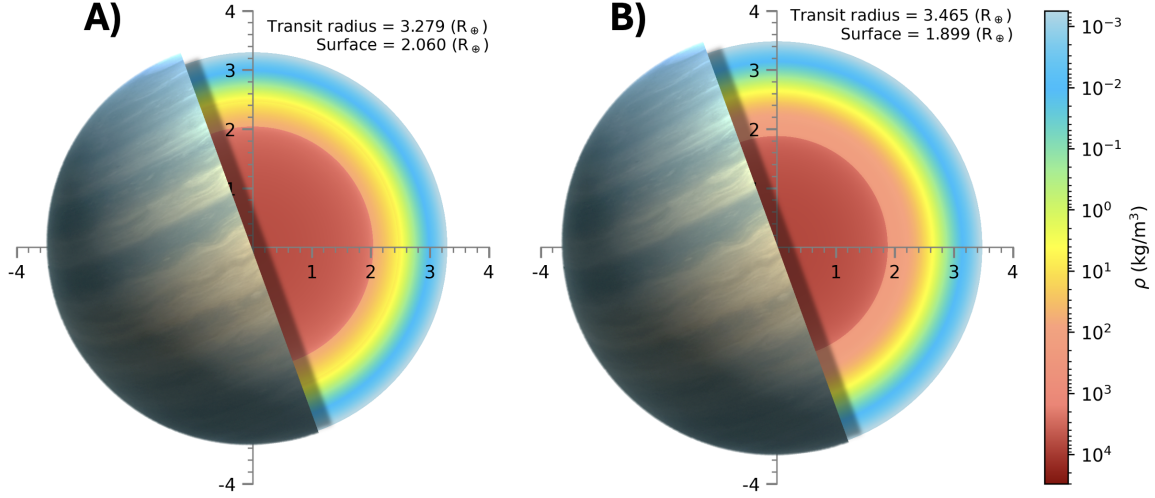


Figure 3.6: Comparison of two $6.0 M_{\oplus}$ sub-Neptune models with the same equilibrium temperature and total H_2 mass fractions of 4%, but different MgSiO_3 – H_2 binodal pressures. The lower-pressure model ($P_{\text{surf}} = 1$ GPa; model A) retains more hydrogen in the supercritical MgSiO_3 – H condensed interior, while the higher-pressure model ($P_{\text{surf}} = 5.0$ GPa; model B) partitions more hydrogen into the atmosphere.

In planet A, the larger hydrogen abundance in the condensed phase lowers the interior density and increases the condensed-interior radius to $2.060 R_{\oplus}$. In planet B, more hydrogen resides in the atmosphere, leaving a comparatively drier and denser condensed interior with a smaller radius of $1.899 R_{\oplus}$. The bulk density of the condensed interior increases from 3.76 g cm^{-3} to 4.71 g cm^{-3} .

The atmospheric structure changes in the opposite direction. Planet A has a smaller H_2 atmosphere and a transit radius of $3.279 R_{\oplus}$, while planet B has a more massive atmosphere and a transit radius of $3.465 R_{\oplus}$. The two transit radii differ by $0.186 R_{\oplus}$, or about 5.7%. This

fractional difference is larger than the few-percent radius uncertainties achieved for many well-characterized sub-Neptune-size planets (Fulton and Petigura, 2018; Van Eylen et al., 2018). The comparison illustrates that hydrogen affects sub-Neptune structure through both reservoirs: it can inflate the observable atmosphere and, when dissolved into the supercritical interior, change the density and radius of the condensed planet itself.

To assess the melting state of the modeled sub-Neptune interiors, we compare the planetary temperature profiles with the MgSiO_3 melting curve from Fei et al. (2021). The effect of dissolved hydrogen is incorporated through the activity of MgSiO_3 ,

$$a_{\text{MgSiO}_3} = \gamma_{\text{MgSiO}_3} X_{\text{MgSiO}_3}, \quad (3.17)$$

where X_{MgSiO_3} is the mole fraction of MgSiO_3 and γ_{MgSiO_3} is its activity coefficient. The liquidus temperature is calculated as

$$T_{\text{m,H}} = \frac{T_{\text{m,0}}}{1 - R \ln(a_{\text{MgSiO}_3}) / \Delta S_m}, \quad (3.18)$$

where $T_{\text{m,0}}$ is the dry MgSiO_3 melting temperature and ΔS_m is the entropy of melting. Following previous first principles simulation studies Stixrude and Karki (2005b); Deng et al. (2023), we adopt $\Delta S_m / R = 7.5$.

The activity coefficient is obtained from a binary fit to the asymmetric subregular-solution model for $\text{MgSiO}_3\text{--H}_2$ mixing by Gilmore and Stixrude (2026) at conditions near the low-pressure silicate–hydrogen binodal.

Both modeled planets remain super-liquidus and therefore fully molten throughout their interiors (Figure 3.7). Hydrogen depresses the MgSiO_3 liquidus in both cases, although the effect differs substantially between the two models. Planet A retains more hydrogen in its interior and remains well above the hydrogen-adjusted melting curve, whereas the more hydrogen-poor planet B lies much closer to the liquidus over a broad pressure range. This contrast highlights the sensitivity of the melting state to interior hydrogen abundance: as less hydrogen is retained at depth, the melting-point depression weakens and the interior approaches conditions favorable for crystallization. Uncertainties in the high-pressure MgSiO_3

liquidus and in the magnitude of the hydrogen-induced melting-point depression limit the significance of the exact temperature offsets, but both models remain fully molten for the representative treatment considered here.

Planet B’s proximity to the liquidus may become important during subsequent planetary evolution. In the miscible sub-Neptune models of Rogers et al. (2025), the binodal surface contracts inward as the planet cools, moving to higher pressures and reducing the extent of the miscible interior. At the same time, hydrogen is progressively transferred from the interior into the overlying envelope. As the interior becomes more hydrogen-poor, the melting-point depression weakens. Thus, the evolution toward a deeper, higher-pressure binodal and a lower interior hydrogen abundance may bring some sub-Neptunes closer to the liquidus, potentially allowing partial crystallization at later evolutionary stages.

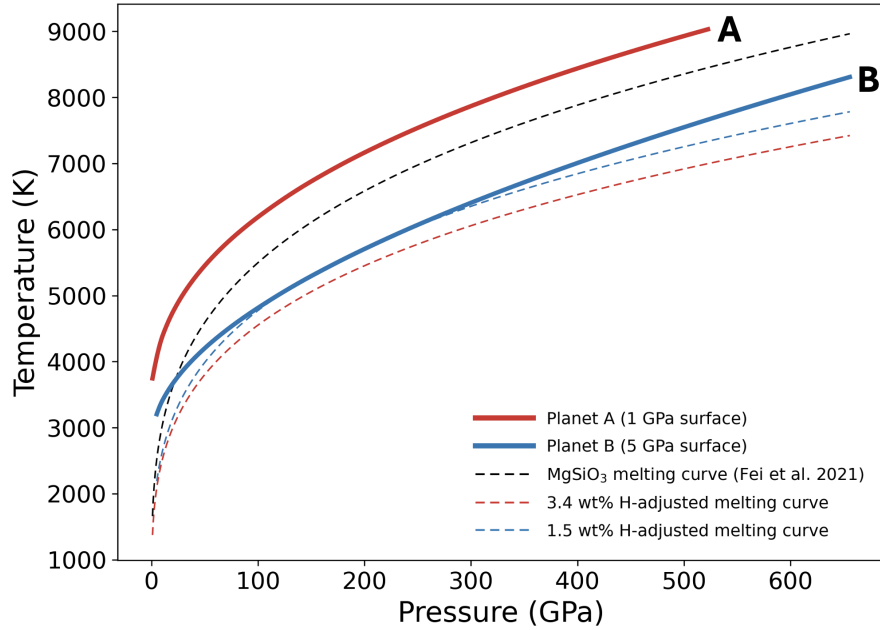


Figure 3.7: Pressure–temperature profiles of the interior portions for the two modeled sub-Neptunes compared with the dry MgSiO_3 melting curve of Fei et al. (2021) and the corresponding hydrogen-adjusted melting curves for representative non-ideal $\text{MgSiO}_3\text{--H}_2$ mixing. Planet A has a more hydrogen-rich interior than Planet B.

3.5 Conclusions

In this study, we used first-principles molecular dynamics simulations to construct a self-consistent equation of state for supercritical MgSiO_3H_4 , a hydrogen-bearing silicate fluid relevant to fully miscible sub-Neptune interiors. Previous work has shown that the MgSiO_3 – H_2 binodal can define the boundary between an H_2 -rich envelope and a supercritical silicate–hydrogen interior, but the thermodynamic properties of the miscible condensed phase have remained poorly constrained. By fitting the DFT-MD results with a Helmholtz free-energy formulation, we derive density and thermodynamic derivatives from a single free-energy surface and construct a MgSiO_3 –H lookup table spanning the interval from dry MgSiO_3 to MgSiO_3H_4 .

Relative to dry MgSiO_3 liquid, the hydrogen-bearing fluid is lower in density at all pressure and temperature conditions, by an amount that deviates significantly from ideal mixing between MgSiO_3 and pure H_2 fluids. The fitted MgSiO_3H_4 EOS also differs from dry MgSiO_3 liquid in its compressional and thermal derivatives. These differences are reflected in the self-consistent planetary adiabats shown in Figure 3.7: for the representative sub-Neptune models considered here, both MgSiO_3 –H temperature profiles remain super-liquidus throughout the condensed interior, but the more hydrogen-poor model lies closer to its hydrogen-adjusted liquidus over much of the modeled pressure range.

The local structure of the fluid provides a microscopic basis for these thermodynamic differences. With increasing pressure, hydrogen interacts more strongly with the silicate framework, as shown by increasing Si–H coordination. At the same time, persistent H–H contacts decrease with compression, indicating loss of long-lived molecular H_2 -like bonding. Thus, the high-pressure fluid is not simply dry MgSiO_3 liquid diluted by molecular hydrogen. Rather, compression reduces persistent H–H bonding and increases Si–H coordination, indicating that hydrogen becomes increasingly incorporated into the local silicate bonding environment. These results support treating fully miscible MgSiO_3 –H fluid as a distinct

planetary material.

The PlanetLab calculations illustrate how this material behavior affects sub-Neptune structure. For the same planet mass and total hydrogen inventory, changing the atmosphere–interior boundary pressure changes the partitioning of hydrogen between the atmosphere and condensed interior. The lower-pressure model retains more hydrogen in the condensed phase, producing a lower-density and larger condensed interior. The higher-pressure model places more hydrogen in the atmosphere, producing a denser and smaller condensed interior but a larger atmospheric contribution to the radius. Hydrogen therefore influences sub-Neptune radii through both reservoirs: by inflating the H_2 -rich atmosphere and by modifying the density and thermal structure of the supercritical condensed interior.

Further progress will require extending this thermodynamic description to additional chemical components and testing it experimentally. Iron is particularly important because Fe–silicate–hydrogen interactions may alter the density, redox state, phase relations, and transport properties of the supercritical interior. Recent experiments are beginning to test predictions for H_2 –silicate–metal interactions at high pressure and temperature, including hydrogen dissolution in silicate melts and reactions involving FeO reduction and water production (Miozzi et al., 2025; Horn et al., 2025). These measurements provide important constraints on the chemistry of hydrogen-bearing magma oceans, but direct experimental determinations of density, compressibility, and thermal properties for supercritical silicate–hydrogen fluids remain scarce. Coordinated experimental and first-principles studies will be needed to build predictive equations of state across the full composition, pressure, and temperature range relevant to sub-Neptunes.

3.6 Thermodynamic EOS Formalism

The MgSiO_3H_4 EOS was fit using the Helmholtz free-energy framework of de Koker and Stixrude (2009) which we briefly review here.. The total Helmholtz free energy is written as

$$F(V, T) = F_{\text{ig}}(V, T) + F_{\text{el}}(V, T) + F_{\text{xs}}(V, T), \quad (3.19)$$

where F_{ig} is the ideal atomic contribution, F_{el} is the thermal electronic contribution, and F_{xs} is the excess interatomic contribution.

The excess free energy is represented as a low-order expansion in Eulerian finite strain and temperature,

$$F_{\text{xs}} = \sum_i \sum_j \frac{a_{ij}}{i! j!} f^i \theta^j + \sum_i a_{iL} f^i t, \quad (3.20)$$

where f is the Eulerian finite strain, θ is the nonlinear thermal variable, and t is the linear-temperature variable. For the present fit, $m = 0.60$ is used in the definition of θ .

The thermal electronic contributions are controlled by the electronic heat-capacity amplitude, ζ , and the volume-dependent electronic onset temperature,

$$\tau(V) = \tau_{\infty} + (\tau_0 - \tau_{\infty}) \left(\frac{V}{V_0} \right)^{-\eta}. \quad (3.21)$$

All thermodynamic properties are computed from derivatives of the fitted Helmholtz free-energy surface. For example, pressure is obtained from

$$P = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (3.22)$$

Entropy is obtained from

$$S = - \left(\frac{\partial F}{\partial T} \right)_V. \quad (3.23)$$

The product of thermal expansivity and isothermal bulk modulus is obtained from the mixed derivative,

$$\alpha K_T = \left(\frac{\partial P}{\partial T} \right)_V = - \left(\frac{\partial^2 F}{\partial V \partial T} \right). \quad (3.24)$$

The same Helmholtz free-energy surface is used to derive the remaining EOS quantities through the appropriate derivatives and standard thermodynamic identities. This ensures internal thermodynamic consistency throughout the $\text{MgSiO}_3\text{--H}$ lookup table. The fitted parameters are listed in Table 3.1.

3.7 Simulation Data

The temperature, pressure, and density points from our simulations can be found in Table 3.2.

Table 3.1: Parameters for the supercritical MgSiO_3H_4 equation of state.

Parameter	Symbol	Value	Unit
Reference volume	V_0	71.21599	$\text{cm}^3 \text{ mol}^{-1}$
Reference temperature	T_0	4000.0	K
Thermal exponent	m	0.60	–
Atoms per formula unit	N	9.0	–
<i>Excess coefficients</i>			
Energy coefficient	a_{00}	-1426.73962	kJ mol^{-1}
Pressure coefficient	a_{10}	-929.67740	kJ mol^{-1}
Bulk modulus coefficient	a_{20}	10163.14329	kJ mol^{-1}
Higher-order strain coefficient	a_{30}	6139.31016	kJ mol^{-1}
Thermal energy coefficient	a_{01}	1978.38149	kJ mol^{-1}
Thermal pressure coefficient	a_{11}	1893.08545	kJ mol^{-1}
Thermal strain coefficient	a_{21}	814.32873	kJ mol^{-1}
<i>Linear-temperature coefficients</i>			
Linear energy term	a_{0L}	1404.50416	kJ mol^{-1}
Linear strain term	a_{1L}	-507.86613	kJ mol^{-1}
<i>Electronic parameters</i>			
Electronic heat-capacity amplitude	ζ	0.01667178	$\text{kJ mol}^{-1} \text{ K}^{-1}$
Onset temperature at V_0	τ_0	1229.01101	K
Large-volume onset temperature	τ_∞	848.19186	K
Volume-dependence exponent	η	1.04986	–

Table 3.2: Time-averaged pressure and density for DFT-MD simulations of MgSiO_3H_4 at 4000, 6000, and 8000 K. Pressure uncertainties are given after the $\pm$ symbol.

$T = 4000 \text{ K}$		$T = 6000 \text{ K}$		$T = 8000 \text{ K}$	
$P \text{ (GPa)}$	$\rho \text{ (g cm}^{-3}\text{)}$	$P \text{ (GPa)}$	$\rho \text{ (g cm}^{-3}\text{)}$	$P \text{ (GPa)}$	$\rho \text{ (g cm}^{-3}\text{)}$
339.98 ± 0.84	5.461	580.32 ± 0.45	6.422	615.83 ± 0.47	6.422
211.29 ± 0.32	4.682	368.43 ± 1.0	5.461	395.74 ± 0.36	5.461
124.77 ± 0.40	4.044	235.78 ± 0.35	4.682	257.90 ± 0.56	4.682
77.50 ± 0.43	3.518	145.62 ± 0.35	4.044	163.31 ± 0.20	4.044
47.64 ± 0.25	3.078	93.59 ± 0.26	3.518	107.52 ± 0.37	3.518
29.83 ± 0.22	2.709	59.88 ± 0.17	3.078	71.50 ± 0.39	3.078
18.48 ± 0.16	2.397	38.99 ± 0.16	2.709	48.16 ± 0.35	2.709
9.02 ± 0.13	2.013	25.48 ± 0.15	2.397	32.89 ± 0.14	2.397
5.64 ± 0.13	1.801	13.60 ± 0.11	2.013	18.77 ± 0.13	2.013
4.90 ± 0.13	1.618	9.38 ± 0.10	1.801	13.32 ± 0.094	1.801
		6.40 ± 0.12	1.618	9.69 ± 0.13	1.618

CHAPTER 4

Exoplanet Dynamos: Conductivity of Hydrogen-Bearing Silicate Liquids

4.1 Introduction

Planetary magnetic fields provide a window into the composition and dynamics of otherwise inaccessible planetary interiors, although no unambiguous magnetic-field measurements have yet been made for exoplanets (Brain et al., 2024). Dynamo action requires the motion of an electrically conducting fluid to regenerate the magnetic field against Ohmic diffusion, but the material hosting this process need not be metallic iron. Within the Solar System, dynamos operate in chemically diverse conducting fluids, including iron-rich liquids in terrestrial planets, metallic hydrogen in Jupiter and Saturn, and ionically conducting fluids in Uranus and Neptune.

Molten silicates have also been considered as possible dynamo materials, particularly in the context of long-lived basal magma oceans. After a global magma ocean begins to crystallize, the steep pressure dependence of the silicate liquidus may allow melt to persist near the core–mantle boundary, forming a basal magma ocean that can remain isolated beneath the solid mantle for long timescales (Labrosse et al., 2007; Boukaré et al., 2025). The dynamo implications of such a long-lived basal magma ocean have been explored in many studies, such as Ziegler and Stegman (2013), who considered whether an electrically conducting silicate layer could contribute to Earth’s ancient magnetic field.

First-principles calculations have since provided more direct constraints on the conduc-

tivity of silicate liquids at planetary interior conditions. Soubiran and Militzer (2018) showed that melting at super-Earth conditions can drive mantle silicates toward semimetallic behavior and predicted electrical conductivities of order 10^4 S m^{-1} , large enough to be relevant for dynamo action for plausible convective velocities. Stixrude et al. (2020) calculated comparable conductivities for silicate liquid at Earth’s basal-magma-ocean conditions and evaluated whether such a layer could satisfy basal-magma-ocean dynamo criteria, following the framework of Ziegler and Stegman (2013). More recent work has demonstrated that composition can be as important as pressure and temperature in determining the transport properties of silicate liquids. In particular, iron enrichment substantially enhances the electronic conductivity of silicate liquids and may prolong the lifetime of a silicate dynamo as a basal magma ocean crystallizes (Dragulet and Stixrude, 2025). Thermal evolution calculations further suggest that basal magma oceans in super-Earths may provide long-lived dynamo regions over a broad range of planetary masses and core fractions (Lherm et al., 2024, 2026).

High electrical conductivity does not necessarily guarantee dynamo action. The competition between magnetic induction and magnetic diffusion can be characterized by the magnetic Reynolds number,

$$Rm = \mu_0 \sigma U L, \quad (4.1)$$

where σ is the electrical conductivity, U is a characteristic fluid velocity, and L is a characteristic length scale of the convecting region. Dynamo viability therefore depends jointly on material properties, convective energetics, rotation, and the geometry of the conducting layer. Recent simulations of thin basal-magma-ocean dynamos emphasize that rotational constraints can reduce convective velocities and increase the energetic requirements for strong-field dynamo action (Schaeffer et al., 2025). In addition, when conductivity varies strongly with depth, a single representative conductivity may not adequately describe the dynamo region. Studies of Jupiter-like dynamos have shown that radial conductivity gradients can modify magnetic diffusion and separate a deeper self-sustaining dynamo region

from an outer diffusion-dominated region (Wicht et al., 2019). These results motivate treating conductivity as a depth-dependent input to the magnetic Reynolds number calculation, rather than assuming a single representative value for the entire molten interior.

The relevance of silicate dynamos may extend beyond terrestrial planets and super-Earth basal magma oceans. In sub-Neptune interiors, hydrogen-rich envelopes can insulate underlying molten rocky material and may chemically interact with silicate magma oceans. Recent work suggests that, at sufficient pressure and temperature, silicate and hydrogen may become miscible and form a single supercritical fluid rather than remaining separated into a rocky interior and overlying atmosphere (Markham et al., 2022; Young et al., 2024b, 2025; Gilmore and Stixrude, 2026; Rogers et al., 2025). In this picture, large amounts of hydrogen can be incorporated into the planet’s molten interior.

This emerging view creates an important gap in our understanding of planetary transport properties. Existing studies have shown that silicate-liquid conductivity depends on pressure, temperature, and composition, but the transport properties of hydrogen-bearing silicate liquids at sub-Neptune interior conditions remain poorly constrained. In particular, it is not yet clear how dissolved hydrogen modifies the electronic structure of MgSiO_3 liquid and, in turn, its electronic conductivity. Determining the conductivity as a function of pressure, temperature, and hydrogen content is therefore necessary for assessing whether miscible hydrogen-bearing silicate interiors can participate in planetary dynamo action.

Here, we use density-functional-theory molecular dynamics to determine the electronic transport properties of hydrogen-bearing MgSiO_3 liquids over a range of pressures, temperatures, and hydrogen concentrations relevant to miscible sub-Neptune interiors. We quantify the electronic contributions to electrical and thermal conductivity as functions of thermodynamic conditions and composition, and examine the associated evolution of the electronic density of states. We then construct continuous pressure–temperature–composition models, $\sigma_{\text{el}}(P, T, n_{\text{H}})$ and $k_{\text{el}}(P, T, n_{\text{H}})$, and map the electrical-conductivity model onto radial pressure–temperature profiles for a representative sub-Neptune interior. Combining the re-

sulting depth-dependent conductivity with estimates of convective velocity and characteristic length scale, we evaluate where magnetic induction can overcome diffusion and estimate the magnetic-field strengths that such supercritical interiors could sustain.

4.2 Conductivity Calculations

4.2.1 Molecular-Dynamics Snapshots and Electronic Transport Calculations

To determine the transport properties of hydrogen-bearing MgSiO_3 liquids, we generated a new suite of first-principles molecular-dynamics simulations spanning the conditions of interest. The hydrogen concentration was varied by changing the number of H atoms in the simulation cell, producing systems with 189–307 atoms. For each target pressure, temperature, and composition, we first used short NPT simulations to relax the simulation cell and identify the appropriate equilibrium volume. We then ran fixed-volume NVT production simulations, like those detailed in Chapter 3, at that volume and selected 10 uncorrelated snapshots from each trajectory for the conductivity calculations. These production simulations used a 0.5 fs timestep and were 10–20 ps long.

Static electronic-structure calculations were then performed on the selected snapshots. In these calculations, the ionic positions are fixed and the electronic structure is solved for each instantaneous liquid configuration. The resulting eigenvalues, Fermi occupations, wavefunctions, and optical transition matrix elements are used to compute the electronic contributions to electrical and thermal conductivity. Following previous first-principles studies of electronic transport in silicate and oxide liquids (Desjarlais et al., 2002; Scipioni et al., 2017; Holmström et al., 2018; Stixrude et al., 2020; Dragulet and Stixrude, 2025), we compute electronic transport properties from static Kubo–Greenwood calculations.

For the electrical and thermal conductivities, we use the Chester–Thellung transport-moment formulation of the Kubo–Greenwood method, following Dragulet and Stixrude (2025). In this formulation, the frequency-dependent electronic electrical conductivity is

given by the first kinetic coefficient,

$$\sigma_{\text{el}}(\omega) = L_{11}(\omega), \quad (4.2)$$

and the electronic thermal conductivity is computed from the coupled charge–heat transport moments,

$$k_{\text{el}}(\omega) = \frac{1}{e^2 T} \left[L_{22}(\omega) - \frac{L_{12}(\omega)L_{21}(\omega)}{L_{11}(\omega)} \right]. \quad (4.3)$$

The kinetic coefficients are given by

$$L_{\alpha\beta}(\omega) = \frac{2\pi e^2 \hbar^2}{3m_e^2 \omega \Omega} \sum_{i,j} (f_i - f_j) \delta(\epsilon_i - \epsilon_j - \hbar\omega) |\langle \psi_i | \nabla | \psi_j \rangle|^2 (-1)^{\alpha+\beta} (\epsilon_i - \mu)^{\alpha-1} (\epsilon_j - \mu)^{\beta-1}. \quad (4.4)$$

Here, the sums are over pairs of electronic states, e is the electron charge, Ω is the simulation-cell volume, f_i and f_j are the Fermi–Dirac occupations of states i and j , ϵ_i and ψ_i are the corresponding Kohn–Sham eigenvalue and wavefunction, μ is the chemical potential, m_e is the electron mass, and ω is the electric-field frequency. The delta function enforces energy conservation for transitions with energy $\hbar\omega$, and the matrix element gives the transition strength. The indices α and β distinguish charge transport, heat transport, and their coupling. Thus, L_{11} describes charge transport, while L_{12} , L_{21} , and L_{22} account for the coupling between charge and heat transport.

For the static electronic-structure calculations in this chapter, we used a 500 eV plane-wave energy cutoff, 2600 electronic bands, and Γ -point Brillouin-zone sampling. Because the number of electrons varies with hydrogen concentration, convergence with respect to the number of unoccupied electronic states was tested directly at representative compositions. Additional tests using different plane-wave cutoffs and k -point sampling showed that the extrapolated DC conductivities were stable within the snapshot-to-snapshot uncertainty.

4.2.2 DC Extrapolation and Snapshot Averaging

The transport spectra obtained from the Kubo–Greenwood calculations are frequency dependent, whereas the conductivity model requires the zero-frequency limit. In a finite simulation cell, the electronic eigenvalue spectrum is discrete, so the delta function in Equation 4.4 is replaced by a Gaussian broadening function. The Gaussian width is determined from the average spacing between eigenvalues, weighted by the corresponding change in the Fermi occupation function (Stixrude et al., 2020; Dragulet and Stixrude, 2025). This procedure converts the discrete electronic transitions of each snapshot into a continuous spectrum.

For each snapshot, the electrical conductivity is calculated along the three Cartesian directions. We average these components to obtain an isotropic spectrum,

$$\bar{\sigma}_{\text{el},s}(\omega) = \frac{\sigma_{x,s}(\omega) + \sigma_{y,s}(\omega) + \sigma_{z,s}(\omega)}{3}, \quad (4.5)$$

where s indexes the snapshot. The DC value for each snapshot is then obtained by extrapolating the frequency-dependent conductivity to $\omega = 0$ using a linear fit at small ω ,

$$\bar{\sigma}_{\text{el},s}(\omega) = m_s \omega + b_s. \quad (4.6)$$

The intercept of this fit gives the snapshot-level estimate of the DC electrical conductivity,

$$\sigma_{\text{DC},s} = b_s. \quad (4.7)$$

The reported electronic conductivity for each pressure–temperature– composition condition is the average over the selected snapshots,

$$\sigma_{\text{el}} = \frac{1}{N} \sum_{s=1}^N \sigma_{\text{DC},s}, \quad (4.8)$$

with $N = 10$ for the production calculations. The uncertainty is estimated from the standard error of the snapshot-level DC values,

$$\text{SEM}_\sigma = \frac{\text{std}(\sigma_{\text{DC},s})}{\sqrt{N}}. \quad (4.9)$$

This uncertainty captures variation among the liquid configurations selected from a trajectory. It does not include systematic effects associated with the fitting interval, Gaussian broadening, finite simulation size, or the number of unoccupied electronic bands.

The same extrapolation and averaging procedure is applied to the electronic thermal-conductivity spectra. For each snapshot, $k_{\text{el},s}(\omega)$ is extrapolated to $\omega = 0$ using a linear fit at small ω , and the reported k_{el} is the mean of the snapshot-level intercepts.

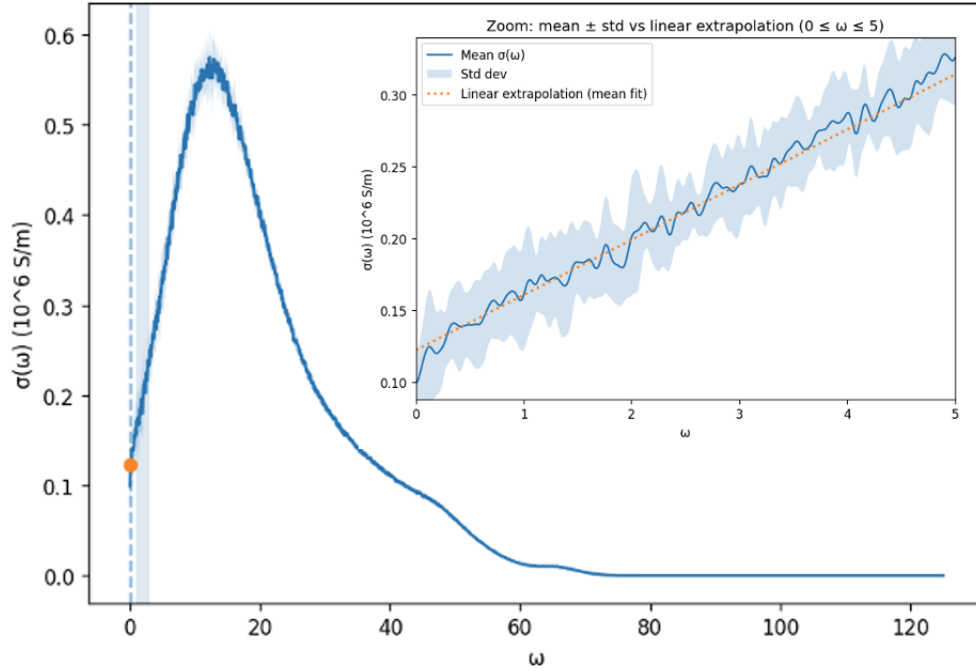


Figure 4.1: Example frequency-dependent electronic conductivity spectrum for a hydrogen-bearing MgSiO_3 liquid. Static electronic-structure calculations are performed on uncorrelated molecular-dynamics snapshots, producing $\sigma_{\text{el}}(\omega)$ at finite frequency. The DC conductivity is estimated by extrapolating the spectrum to $\omega = 0$ using a linear fit at small ω .

4.3 Electrical and Thermal Conductivity Results

The conductivity calculations described above produce electronic electrical and thermal conductivities for a discrete set of pressure, temperature, and hydrogen-composition conditions. These calculations allow us to evaluate how transport in hydrogen-bearing MgSiO_3 liquids changes with thermodynamic state and composition. We consider two types of trends. First, we examine the pressure–temperature dependence using Arrhenius-style fits at approximately fixed hydrogen content. Second, we examine the hydrogen-composition dependence using local polynomial fits at fixed pressure and temperature. These local fits are used to visualize the trends in the calculated data; the continuous pressure–temperature–composition models used in the planetary calculations are developed separately below.

The main results are that temperature and hydrogen content strongly increase both σ_{el} and k_{el} . Pressure has a weaker effect over the range sampled here. For the electronic electrical conductivity, the isothermal pressure dependence is generally negative, consistent with previous first-principles calculations of silicate liquids (Stixrude et al., 2020). The electronic thermal conductivity follows broadly similar temperature and composition trends, but its pressure dependence is not identical to that of σ_{el} because charge and heat transport are computed from related but distinct transport moments.

4.3.1 Pressure–Temperature Dependence

At approximately fixed hydrogen content, we describe the pressure–temperature dependence of the electronic electrical conductivity using an empirical Arrhenius-like form,

$$\sigma_{\text{el}}(P, T) = \sigma_0 T^{-1} \exp \left[-\frac{E_\sigma + PV_\sigma}{RT} \right], \quad (4.10)$$

where σ_0 , E_σ , and V_σ are fit parameters, R is the gas constant, P is pressure, and T is temperature. The corresponding empirical fit for the electronic thermal conductivity is

$$k_{\text{el}}(P, T) = k_0 T \exp \left[-\frac{E_k + PV_k}{RT} \right], \quad (4.11)$$

where k_0 , E_k , and V_k are the analogous fit parameters for thermal transport. Arrhenius-type expressions are commonly used as first-order descriptions of silicate-melt transport properties, although they are not generally expected to provide a unique mechanistic description over broad pressure–temperature ranges (Ni et al., 2015). We therefore use Equations 4.10 and 4.11 as empirical descriptions of the local pressure–temperature trends in the calculated data. The parameters E_σ , V_σ , E_k , and V_k should be interpreted as empirical coefficients over the sampled range, rather than as a unique microscopic model for the electronic transport mechanism.

Figure 4.2 summarizes the pressure–temperature dependence of both transport properties. At fixed hydrogen content, temperature is the dominant control on σ_{el} . The 6000 and 8000 K simulations are systematically more conductive than the 4000 K simulations over the same pressure interval. For mixtures containing approximately 4 wt% H, the conductivity increases from values of order 10^4 S m^{-1} at 4000 K to values of order 10^5 S m^{-1} at 8000 K.

The pressure dependence of σ_{el} is weaker than the temperature dependence and is negative over the range sampled here. Along a given isotherm and at fixed hydrogen content, increasing pressure produces only modest decreases in σ_{el} . This behavior is consistent with previous first-principles calculations for silicate liquid, which found that electrical conductivity increases with temperature but decreases with increasing pressure (Stixrude et al., 2020).

The electronic thermal conductivity also increases strongly with temperature. Its pressure dependence is weaker than its temperature dependence, but it does not exactly mirror the electrical conductivity. In particular, the 6000 K thermal-conductivity data suggest a slight increase in k_{el} between 170 and 245 GPa at comparable hydrogen content.

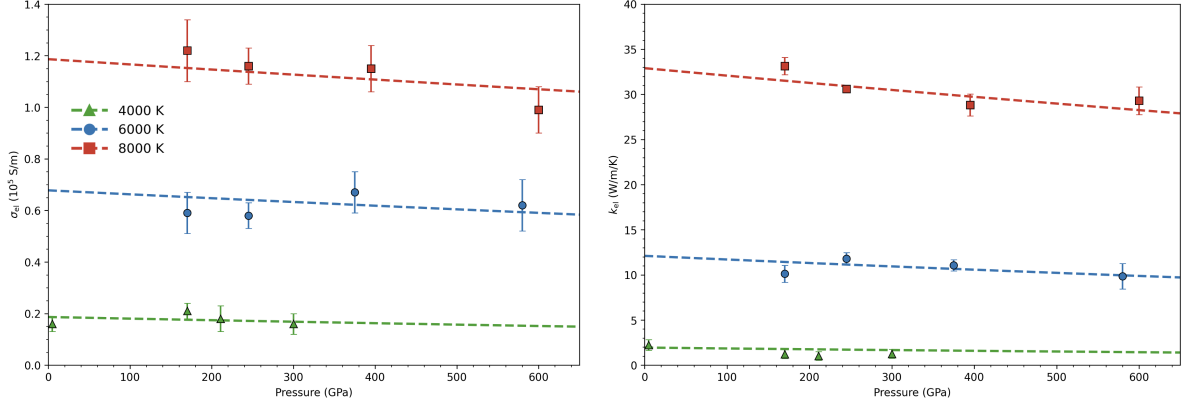


Figure 4.2: Pressure–temperature dependence of electronic transport in hydrogen-bearing MgSiO_3 liquids. Left: electronic electrical conductivity, σ_{el} . Right: electronic thermal conductivity, k_{el} . Symbols show the extrapolated zero-frequency values from the Kubo–Greenwood calculations.

For sub-Neptune interiors, where both pressure and temperature increase inward, these competing effects mean that the radial conductivity profile depends on the balance between thermal structure, compression, and hydrogen content. Because the temperature and composition effects dominate in our calculations, the electrical conductivity generally increases toward hotter, deeper regions despite the weakly negative isothermal pressure dependence.

4.3.2 Hydrogen-Composition Dependence

We express composition using

$$n_{\text{H}} = \frac{N_{\text{H}}}{N_{\text{Si}}}, \quad (4.12)$$

where N_{H} is the number of hydrogen atoms and N_{Si} is the number of silicon atoms. Equivalently, n_{H} gives the number of hydrogen atoms per MgSiO_3 formula unit. This variable is convenient for the simulations because it is tied directly to the atomic composition of each cell. It also provides a natural bridge to the thermodynamic lookup tables and PlanetLab

profiles used later in this chapter.

At fixed pressure and temperature, the composition dependence of the electronic electrical conductivity is fit locally with a quadratic function of n_{H} ,

$$\sigma_{\text{el}}(n_{\text{H}})|_{P,T} = A_{\sigma}n_{\text{H}}^2 + B_{\sigma}n_{\text{H}} + C_{\sigma}, \quad (4.13)$$

where A_{σ} , B_{σ} , and C_{σ} are determined separately for each fixed-pressure and fixed-temperature composition series. The electronic thermal conductivity is fit in the same way,

$$k_{\text{el}}(n_{\text{H}})|_{P,T} = A_k n_{\text{H}}^2 + B_k n_{\text{H}} + C_k, \quad (4.14)$$

with independent coefficients A_k , B_k , and C_k for each composition series. These polynomial fits are used only to visualize the local hydrogen-composition dependence in the calculated data.

Figure 4.3 shows the composition dependence of both σ_{el} and k_{el} . Adding hydrogen systematically increases the electronic electrical conductivity. This trend is clearest in the 6000 and 8000 K composition series, where σ_{el} rises by approximately an order of magnitude across the range of hydrogen contents sampled. For example, at 6000 K and approximately 245 GPa, the conductivity increases from $\sim 1.5 \times 10^4 \text{ S m}^{-1}$ at low hydrogen content to greater than 10^5 S m^{-1} at the highest hydrogen contents considered. At 8000 K, the same composition trend is shifted to still higher conductivities.

The electronic thermal conductivity also increases with hydrogen content. At 6000 K, the 245 GPa series lies slightly above the 170 GPa series at comparable n_{H} , suggesting a weak positive pressure effect in k_{el} over this interval. This pressure effect is small compared with the increase caused by hydrogen content and temperature, but it illustrates that k_{el} and σ_{el} need not have identical pressure dependences.

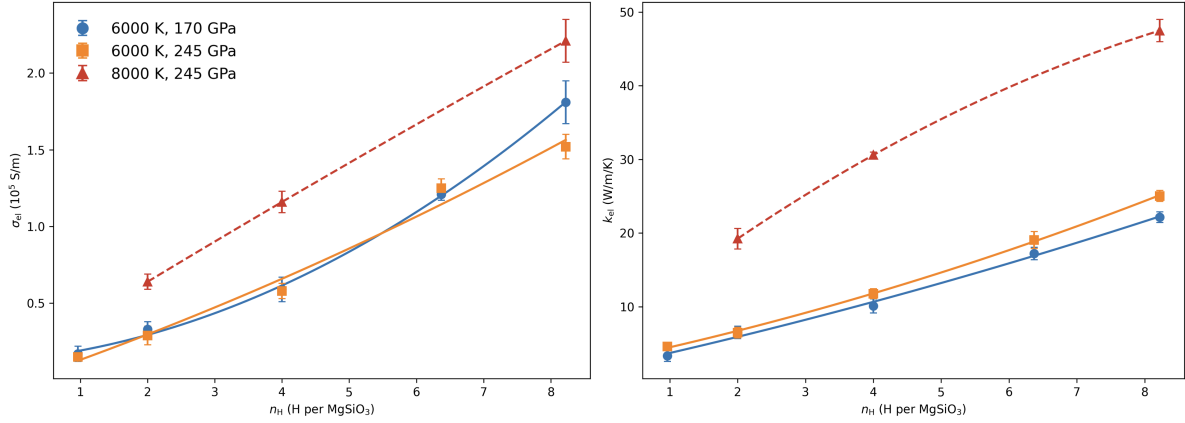


Figure 4.3: Hydrogen-composition dependence of electronic transport in hydrogen-bearing MgSiO_3 liquids. Left: electronic electrical conductivity, σ_{el} . Right: electronic thermal conductivity, k_{el} . Symbols show the extrapolated zero-frequency values from the Kubo–Greenwood calculations.

The strong increase in transport with n_{H} indicates that adding hydrogen changes the electronic structure of the silicate liquid in a way that enhances electronic transport at small ω . This composition dependence is therefore central to evaluating whether hydrogen-bearing silicate interiors can act as dynamo-capable conducting regions. The simultaneous increase in σ_{el} and k_{el} is consistent with a liquid that is becoming more electronically conducting, though still distinct from a fully metallic fluid.

4.3.3 Electronic Structure Interpretation

To interpret the conductivity trends, we calculate the electronic density of states for the same static snapshots used in the Kubo–Greenwood analysis. The energy axis is shifted so that the Fermi level lies at $E - E_{\text{F}} = 0$. We then compare the density of states near the Fermi level, $g(E_{\text{F}})$, across the hydrogen-composition series.

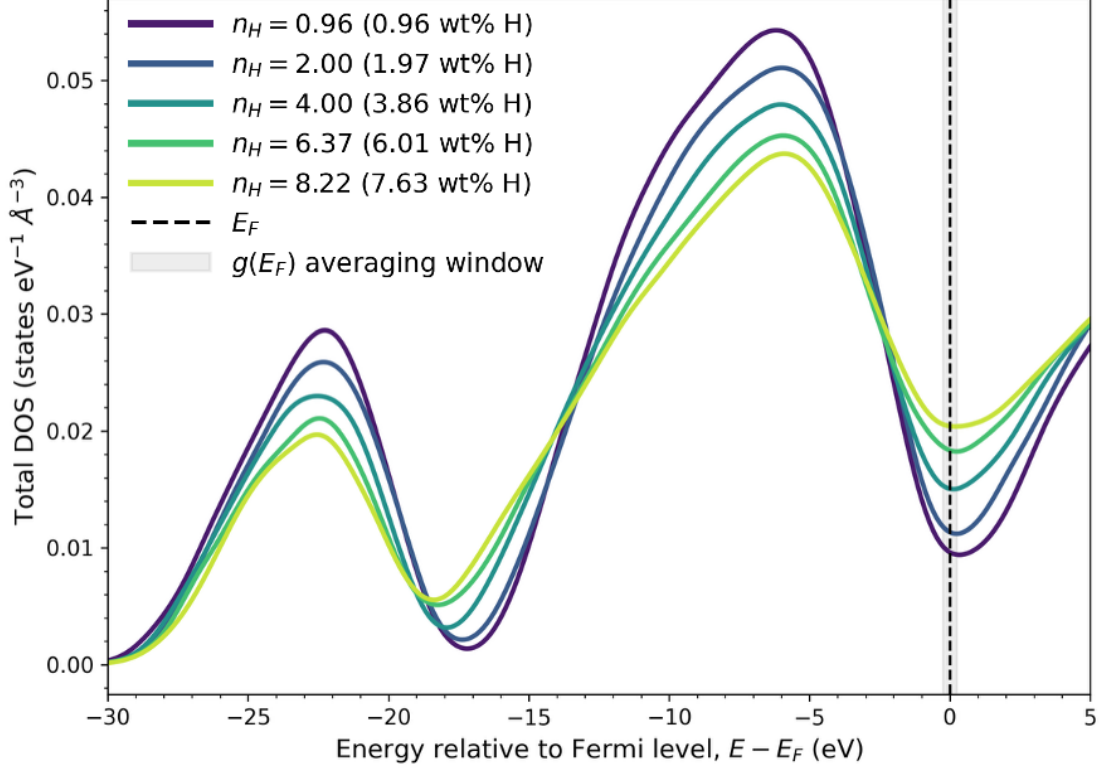


Figure 4.4: Electronic density of states for hydrogen-bearing MgSiO_3 liquids. Energies are referenced to the Fermi level, $E - E_F = 0$. Adding hydrogen redistributes electronic states toward the Fermi level and increases $g(E_F)$, consistent with the observed increase in electronic electrical conductivity.

Figure 4.4 shows that adding hydrogen redistributes electronic states toward the Fermi level. The increase in $g(E_F)$ with hydrogen content accompanies the strong increase in σ_{el} and is consistent with an increasingly metal-like electronic structure. A larger density of states near E_F provides more electronic states that can participate in low-energy transitions.

To further characterize how the electronic transport changes with hydrogen content, we calculate the Lorenz number directly from the Kubo–Greenwood transport spectra,

$$L(\omega) = \frac{k_{\text{el}}(\omega)}{\sigma_{\text{el}}(\omega)T}, \quad (4.15)$$

where $k_{\text{el}}(\omega)$ and $\sigma_{\text{el}}(\omega)$ are the frequency-dependent electronic thermal and electrical conductivities, respectively. For each molecular-dynamics snapshot, $L(\omega)$ is extrapolated to the zero-frequency limit using the same general approach applied to the conductivity spectra. The reported Lorenz number for each pressure–temperature–composition condition is the mean of the snapshot-level zero-frequency intercepts, and the uncertainty is the standard error of those values.

We compare the calculated Lorenz numbers with the Sommerfeld value,

$$L_0 = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}, \quad (4.16)$$

which is the value predicted by the Wiedemann–Franz relation for a simple degenerate metal and therefore provides a useful reference for metal-like electronic transport.

Figure 4.5 shows that the Lorenz number decreases systematically with increasing hydrogen content. At 6000 K, the low-hydrogen liquids have Lorenz numbers of approximately $5\text{--}6 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, more than twice L_0 , whereas the most hydrogen-rich liquids approach the Sommerfeld value. The 170 and 245 GPa composition series show very similar behavior over most of the sampled composition range, indicating that the dependence on hydrogen content is considerably stronger than the pressure dependence over this interval. The 8000 K calculations show the same general decrease in L with increasing hydrogen content.

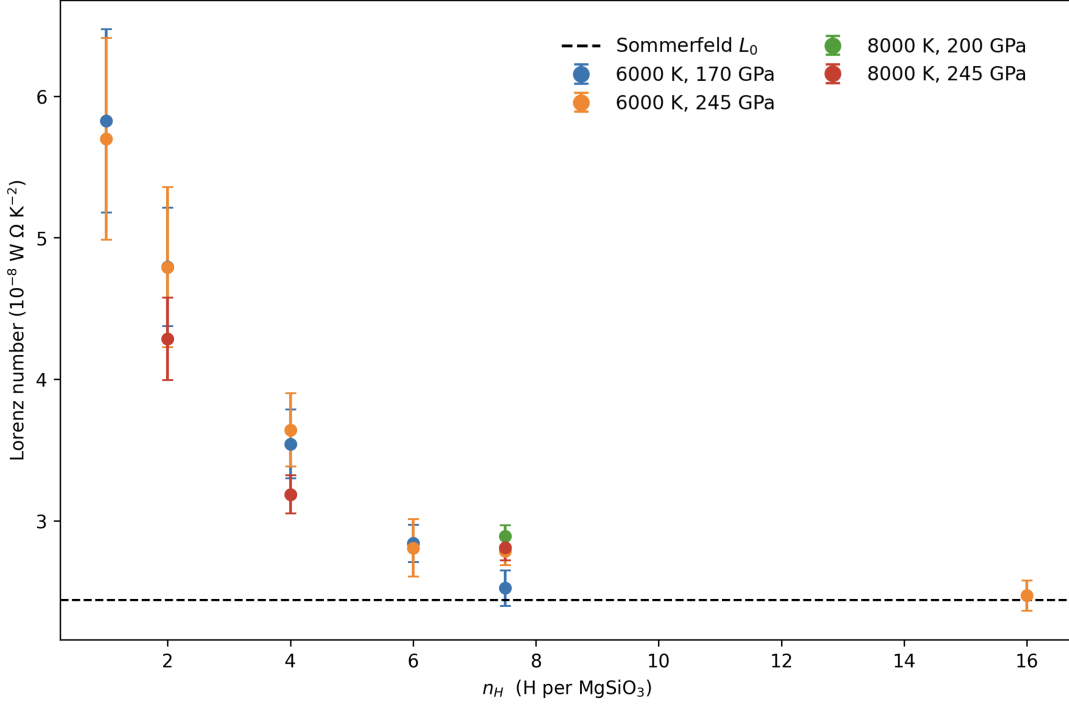


Figure 4.5: Lorenz number of hydrogen-bearing MgSiO₃ liquids as a function of hydrogen content. Symbols show the zero-frequency Lorenz number obtained by extrapolating $L(\omega) = k_{\text{el}}(\omega)/[\sigma_{\text{el}}(\omega)T]$ for individual Kubo–Greenwood snapshots and averaging the resulting intercepts. Error bars show the standard error of the snapshot mean. The horizontal dashed line marks the Sommerfeld value, $L_0 = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$. Increasing hydrogen content systematically drives the Lorenz number toward L_0 , consistent with increasingly metal-like electronic transport.

Together, the density-of-states and transport calculations provide complementary evidence that hydrogen substantially changes the electronic character of the silicate liquid. Increasing hydrogen content raises $g(E_F)$ and σ_{el} , while simultaneously driving the Lorenz number toward the Sommerfeld value. These trends are collectively consistent with increasingly metal-like electronic transport as hydrogen is incorporated into the liquid.

4.3.4 Global Pressure–Temperature–Composition Fit

The Kubo–Greenwood calculations provide conductivities at discrete values of pressure, temperature, and composition. A planetary interior, however, samples a continuous range of thermodynamic conditions. To evaluate transport properties along radial interior profiles, we fit the calculated zero-frequency conductivities with continuous pressure–temperature–composition functions. These global fits combine an empirical pressure–temperature dependence with a quadratic hydrogen-composition prefactor. The functional forms are used as empirical parameterizations of the calculated transport properties over the sampled range of conditions, rather than as unique microscopic models for the conduction mechanism.

For the electronic electrical conductivity, we use

$$\sigma_{\text{el}}(n_{\text{H}}, P, T) = (a_0 + a_1 n_{\text{H}} + a_2 n_{\text{H}}^2) T^{-1} \exp \left[-\frac{E_{\sigma} + PV_{\sigma}}{RT} \right], \quad (4.17)$$

where n_{H} is the number of hydrogen atoms per MgSiO_3 formula unit, P is pressure, T is temperature, and R is the gas constant. The coefficients a_0 , a_1 , and a_2 describe the hydrogen-composition dependence. The parameters E_{σ} and V_{σ} control the empirical temperature and pressure dependence of the fit. Although these parameters have the units of an energy scale and a volume, respectively, we do not interpret them as diagnostic of a specific microscopic transport mechanism.

The best-fit parameters for the electrical-conductivity model are

Table 4.1: Best-fit parameters for the electronic electrical conductivity model in Equation 4.17.

Parameter	Value	Uncertainty
a_0	1.0282×10^9	7.5764×10^8
a_1	2.0811×10^9	5.6055×10^8
a_2	2.1569×10^8	8.7821×10^7
E_σ	$170.972 \text{ kJ mol}^{-1}$	$6.311 \text{ kJ mol}^{-1}$
V_σ	$0.007764 \text{ cm}^3 \text{ mol}^{-1}$	$0.016529 \text{ cm}^3 \text{ mol}^{-1}$

The fit captures the main trends in the calculated conductivity data, with $R^2 = 0.9914$ and a reduced chi-squared value of $\chi_\nu^2 = 0.949$. The positive coefficients in the hydrogen-composition prefactor reflect the strong increase in conductivity with hydrogen content. The fitted pressure coefficient is small compared with its uncertainty, consistent with the weak isothermal pressure dependence of σ_{el} over the range sampled.

Figure 4.6 shows the behavior of the fitted $\sigma_{\text{el}}(n_{\text{H}}, P, T)$ model across representative pressure-temperature conditions. The main panel compares calculated conductivities with model curves evaluated as a function of hydrogen content at selected pressures. The inset shows an observed-versus-predicted comparison for the same global fit.

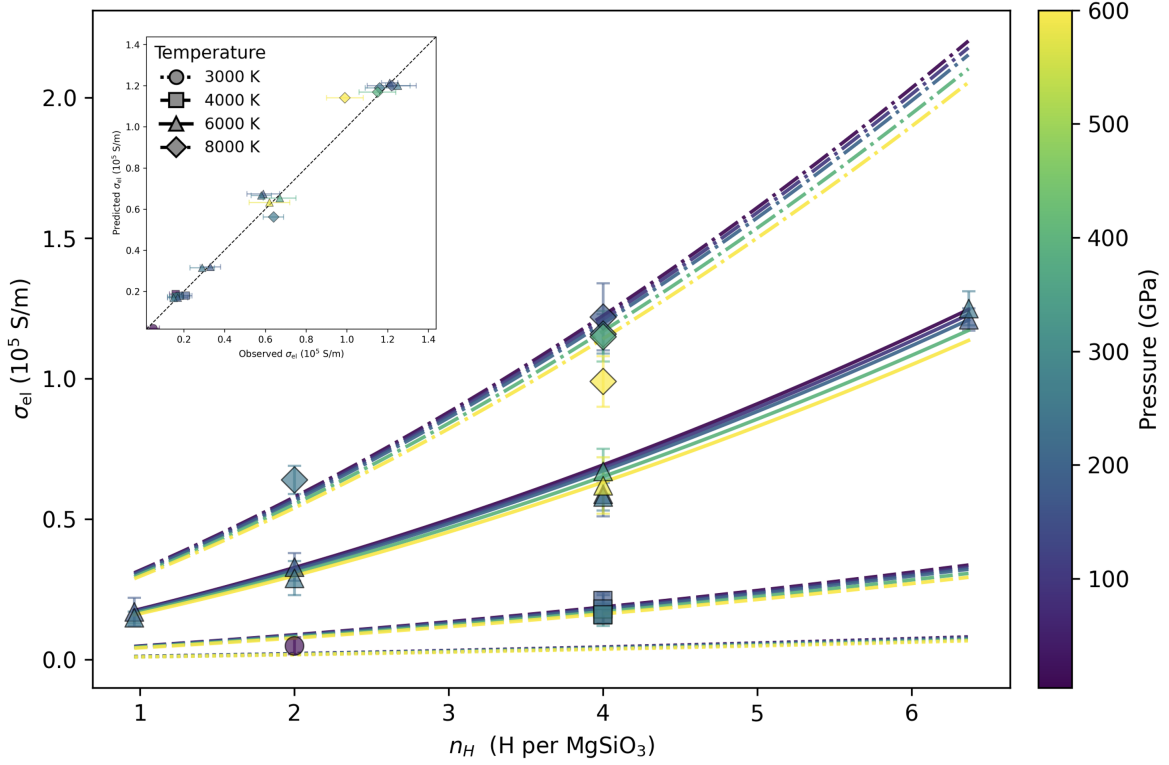


Figure 4.6: Global pressure–temperature–composition fit for the electronic electrical conductivity. The main panel shows model curves from Equation 4.17 evaluated across hydrogen content for representative pressures and temperatures, with calculated Kubo–Greenwood conductivities shown for comparison. Color indicates pressure and marker shape indicates temperature. The inset compares observed and predicted conductivities; the dashed line indicates perfect agreement.

We fit the electronic thermal conductivity with an analogous empirical expression,

$$k_{\text{el}}(n_H, P, T) = (b_0 + b_1 n_H + b_2 n_H^2) T \exp \left[-\frac{E_k + PV_k}{RT} \right]. \quad (4.18)$$

Here, b_0 , b_1 , and b_2 describe the hydrogen-composition dependence of the thermal-conductivity prefactor. The parameters E_k and V_k control the empirical temperature and pressure dependence of the thermal-conductivity fit. The different temperature prefactor reflects the

functional form used to represent the calculated k_{el} values, but the fitted parameters should again be interpreted as parameterization coefficients rather than as a unique microscopic model for electronic heat transport.

The best-fit parameters for the thermal-conductivity model are

Table 4.2: Best-fit parameters for the electronic thermal conductivity model in Equation 4.18.

Parameter	Value	Uncertainty
b_0	7.1513×10^{-3}	3.5115×10^{-3}
b_1	5.4984×10^{-3}	1.8148×10^{-3}
b_2	8.3052×10^{-5}	3.0195×10^{-4}
E_k	$131.650 \text{ kJ mol}^{-1}$	$5.001 \text{ kJ mol}^{-1}$
V_k	$0.025068 \text{ cm}^3 \text{ mol}^{-1}$	$0.015208 \text{ cm}^3 \text{ mol}^{-1}$

The electronic thermal-conductivity fit gives $R^2 = 0.9922$ and a reduced chi-squared value of $\chi_\nu^2 = 3.336$, indicating that the same general pressure–temperature–composition structure captures the main behavior of heat transport in the hydrogen-bearing silicate liquids. As in the electrical conductivity fit, the positive linear composition coefficient reflects the increase in electronic transport with hydrogen content. The fitted pressure coefficient is larger for k_{el} than for σ_{el} , consistent with the somewhat stronger pressure sensitivity seen in the thermal-conductivity data.

Figure 4.7 shows the corresponding global fit for k_{el} . The main panel compares calculated thermal conductivities with model curves evaluated as a function of hydrogen content at selected pressures. The inset shows the observed-versus-predicted comparison for the thermal-conductivity model.

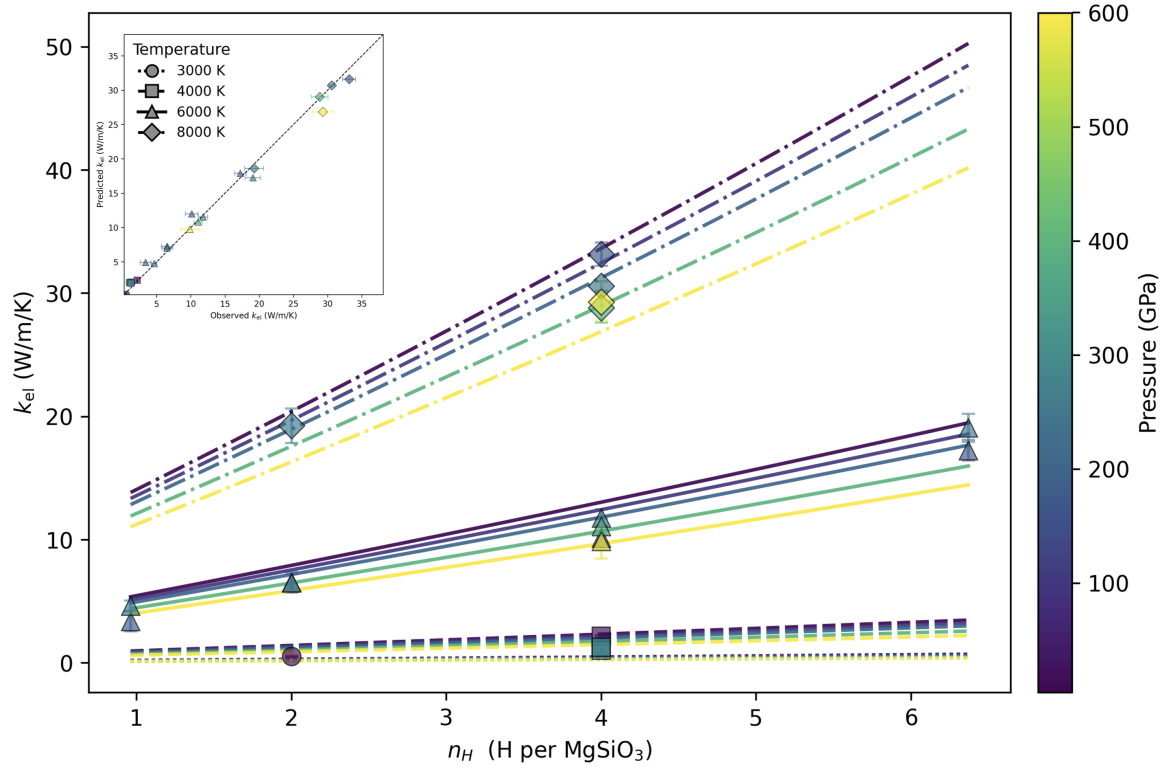


Figure 4.7: Global pressure–temperature–composition fit for the electronic thermal conductivity. The main panel shows model curves from Equation 4.18 evaluated across hydrogen content for representative pressures and temperatures, with calculated k_{el} values shown for comparison. Color indicates pressure and marker shape indicates temperature. The inset compares observed and predicted thermal conductivities; the dashed line indicates perfect agreement.

These empirical parameterizations provide the material-property bridge between the first-principles simulations and the planetary models. In the next section, we evaluate Equations 4.17 and 4.18 along radial pressure–temperature profiles for a representative sub-Neptune interior.

4.4 Conductivity Profiles in a Model Sub-Neptune

The empirical conductivity parameterizations described above provide continuous functions $\sigma_{\text{el}}(P, T, n_{\text{H}})$ and $k_{\text{el}}(P, T, n_{\text{H}})$ that can be evaluated along a planetary interior profile. To assess whether the calculated conductivities are large enough to matter for planetary dynamos, we apply these fits to a representative sub-Neptune interior model generated with PlanetLab. This step translates the first-principles material-property calculations into radial transport-property profiles that can be used in the magnetic Reynolds number calculation below.

The representative planet considered here has a mass of approximately $6 M_{\oplus}$ and consists of a hydrogen-rich envelope overlying a molten, hydrogen-bearing silicate interior. In the PlanetLab model, the top of the molten interior occurs at a pressure of several GPa, corresponding to the base of the atmosphere/envelope and the outer boundary of the condensed interior. The model provides radial profiles of pressure, temperature, density, and radius, $P(r)$, $T(r)$, $\rho(r)$, and r . As in Chapter 3, we treat the molten interior as compositionally well mixed, so the hydrogen abundance used in the conductivity parameterizations is constant with radius.

The planetary model reports the hydrogen abundance as a mass fraction, whereas the conductivity fits use

$$n_{\text{H}} = \frac{N_{\text{H}}}{N_{\text{Si}}}, \quad (4.19)$$

the number of hydrogen atoms per MgSiO_3 formula unit. For a hydrogen mass fraction w_{H} , this conversion is

$$n_{\text{H}} = \frac{w_{\text{H}} M_{\text{MgSiO}_3}}{m_{\text{H}}(1 - w_{\text{H}})}, \quad (4.20)$$

where M_{MgSiO_3} is the molar mass of MgSiO_3 and m_{H} is the molar mass of hydrogen. This

converted value of n_{H} is then held fixed throughout the molten region.

At each radial point, we evaluate the electronic electrical conductivity using

$$\sigma_{\text{el}}(r) = \sigma_{\text{el}}[P(r), T(r), n_{\text{H}}], \quad (4.21)$$

and similarly evaluate the electronic thermal conductivity,

$$k_{\text{el}}(r) = k_{\text{el}}[P(r), T(r), n_{\text{H}}]. \quad (4.22)$$

The electrical conductivity profile is the direct material-property input to the dynamo calculation. The same radial structure is also combined with thermodynamic quantities from the $\text{MgSiO}_3\text{--H}$ lookup table, including the thermal expansivity $\alpha(P, T, n_{\text{H}})$ and heat capacity $C_P(P, T, n_{\text{H}})$, which enter the buoyancy-flux scalings used below.

Figure 4.8 shows the resulting radial electrical-conductivity profile. The electronic conductivity is largest in the deep, hot interior and decreases outward toward the top of the molten region. This depth dependence follows directly from the conductivity trends in Section 4.3: temperature and hydrogen content strongly increase σ_{el} , while the isothermal pressure dependence is comparatively weak. Because the hydrogen abundance is fixed throughout the well-mixed molten interior, the radial variation in σ_{el} is controlled primarily by the pressure–temperature structure of the planet. The deep interior is therefore the most electrically conducting part of the molten region, whereas the cooler outer portion has lower conductivity and is more susceptible to Ohmic diffusion.

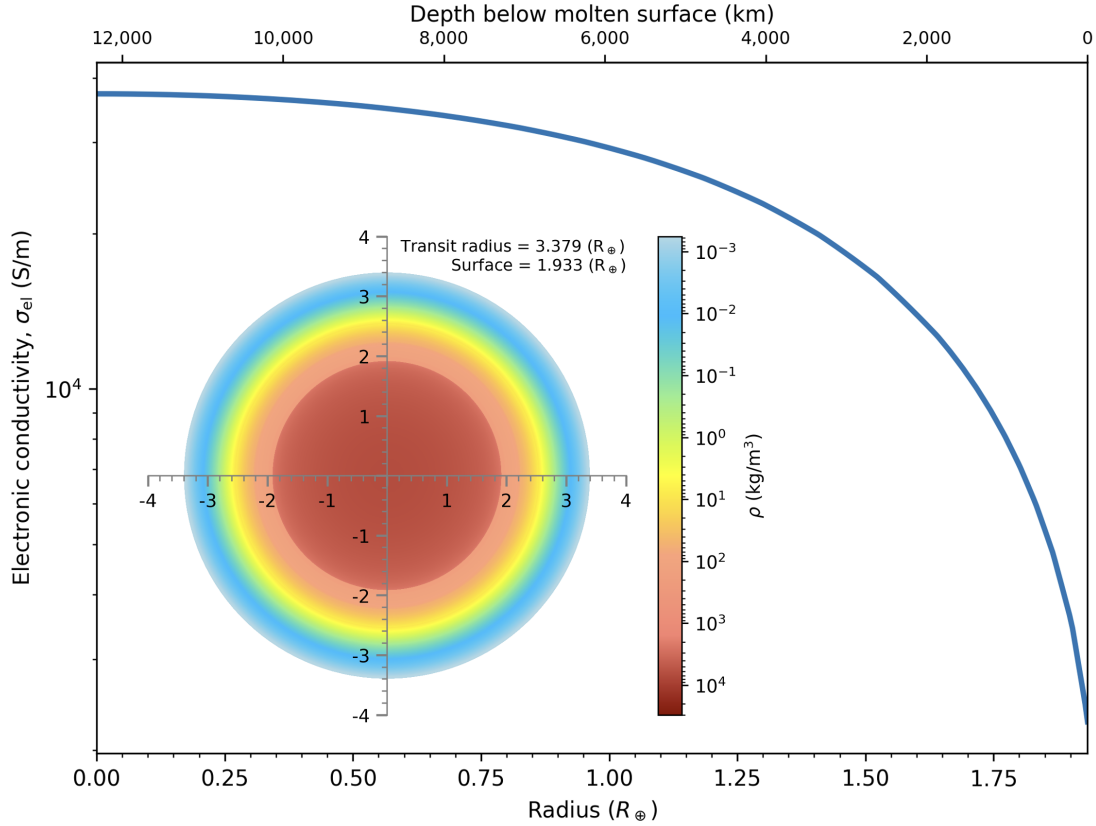


Figure 4.8: Electronic electrical-conductivity profile for a representative hydrogen-bearing MgSiO_3 sub-Neptune interior. The fitted pressure–temperature–composition conductivity model is evaluated along the PlanetLab radial profile, $\sigma_{\text{el}}(r) = \sigma_{\text{el}}[P(r), T(r), n_{\text{H}}]$. Conductivity is highest in the deep, hot interior and decreases outward toward the top of the molten region.

4.5 Dynamo Feasibility

4.5.1 Magnetic Reynolds Number and Conducting-Shell Feasibility

We evaluate dynamo feasibility using the magnetic Reynolds number, which measures the competition between magnetic induction and Ohmic diffusion. In terms of the magnetic diffusivity, $\lambda = 1/(\mu_0\sigma)$, the magnetic Reynolds number is

$$Rm = \frac{UL}{\lambda} = \mu_0 \sigma UL, \quad (4.23)$$

where $\mu_0 \approx 4\pi \times 10^{-7} \text{ H m}^{-1}$ is the magnetic permeability of free space, σ is the electrical conductivity, U is a characteristic convective velocity, and L is a characteristic length scale of the conducting, convecting fluid.

There is no single universal magnetic Reynolds number for dynamo onset. Values near $Rm \sim 40$ – 50 are commonly associated with self-sustained dynamo action in relatively thick spherical-shell calculations (Christensen and Aubert, 2006; Léorat and Nore, 2008). More recent thin-shell magma-ocean simulations find dynamo onset at somewhat larger values, $Rm \sim 70$ – 80 , and enter a strong-field regime at approximately $Rm \sim 85$ – 130 (Schaeffer et al., 2025). We therefore compare our results with reference values of $Rm = 40$, 70 , and 130 , and use $Rm = 130$ as a conservative strong-field benchmark rather than as a universal critical value for dynamo onset.

For giant planets and sub-Neptunes, electrical conductivity may vary smoothly with depth and the appropriate magnetic length scale is therefore not uniquely defined (Wulff et al., 2025). Depending on the induction problem and the internal flow geometry, possible choices include the thickness of a convecting region or a conductivity scale height. We use Rm as a feasibility diagnostic and ask: how much conducting depth is required for a shell within the molten interior to reach a dynamo-relevant magnetic Reynolds number?

For the fiducial sub-Neptune model considered here, the molten interior has $n_{\text{H}} = 1.1790$, corresponding to $X_{\text{H}} = 0.1908$ and $1.170 \text{ wt\% H}$. The top of the molten interior is located at $R_{\text{molten}} = 1.9334 R_{\oplus}$, and the intrinsic luminosity is $L_{\text{int}} = 2.144 \times 10^{15} \text{ W}$. We adopt a 10-day rotation period for the fiducial rotating case.

For each trial shell-base radius r , we define an outer conducting shell extending from r to the top of the molten interior. Its thickness is

$$L(r) = R_{\text{molten}} - r. \quad (4.24)$$

Moving inward therefore corresponds to progressively increasing the thickness of the candidate conducting shell. The fiducial magnetic Reynolds number associated with each shell base is

$$Rm(r) = \mu_0 \sigma_{\text{el}}(r) U(r) L(r), \quad (4.25)$$

where $\sigma_{\text{el}}(r)$ is the local electronic conductivity at the shell-base radius. Our calculation does not average the electrical conductivity through the entire shell: the local conductivity at each trial depth is combined with the total shell thickness $L(r)$. This construction is intended as a shell-thickness feasibility diagnostic rather than a self-consistent variable-conductivity dynamo calculation.

4.5.2 Convective Velocity Estimates

The other major uncertainty in Equation 4.23 is the characteristic convective velocity. We estimate velocities from the buoyancy flux of the molten interior. The intrinsic heat flux is

$$F_{\text{int}} = \frac{L_{\text{int}}}{4\pi R_{\text{molten}}^2}. \quad (4.26)$$

For the radial Rm feasibility calculation, the buoyancy flux is evaluated from the local thermodynamic state at each trial shell base,

$$I_b(r) = g(r) F_{\text{int}} \frac{\alpha(r)}{\rho(r) C_P(r)}, \quad (4.27)$$

where g is gravity, ρ is density, α is thermal expansivity, and C_P is heat capacity. The quantities $\alpha(P, T, n_{\text{H}})$ and $C_P(P, T, n_{\text{H}})$ are evaluated from our MgSiO₃-H thermodynamic lookup table along the same PlanetLab radial profile used to calculate the conductivity.

Because the convective dynamics of a sub-Neptune magma ocean are uncertain, we consider several velocity scalings. A free-fall estimate,

$$U_{\text{FF}} = (I_b L)^{1/3}, \quad (4.28)$$

provides an optimistic upper bound. A thermal-wind scaling,

$$U_{\text{ThW}} = \left(\frac{I_b^2 L}{2\Omega} \right)^{1/5}, \quad (4.29)$$

accounts for rotational constraint, where $\Omega = 2\pi/P_{\text{rot}}$. We therefore treat the thermal-wind velocity as the preferred rotating estimate and the free-fall velocity as an optimistic upper bound.

4.5.3 Conducting-Shell Magnetic Reynolds Number

Figure 4.9 shows the magnetic Reynolds number as the base of the candidate conducting shell is moved progressively inward. The magnetic Reynolds number generally increases with conducting-shell thickness because L increases and the deeper material is hotter and more electrically conductive.

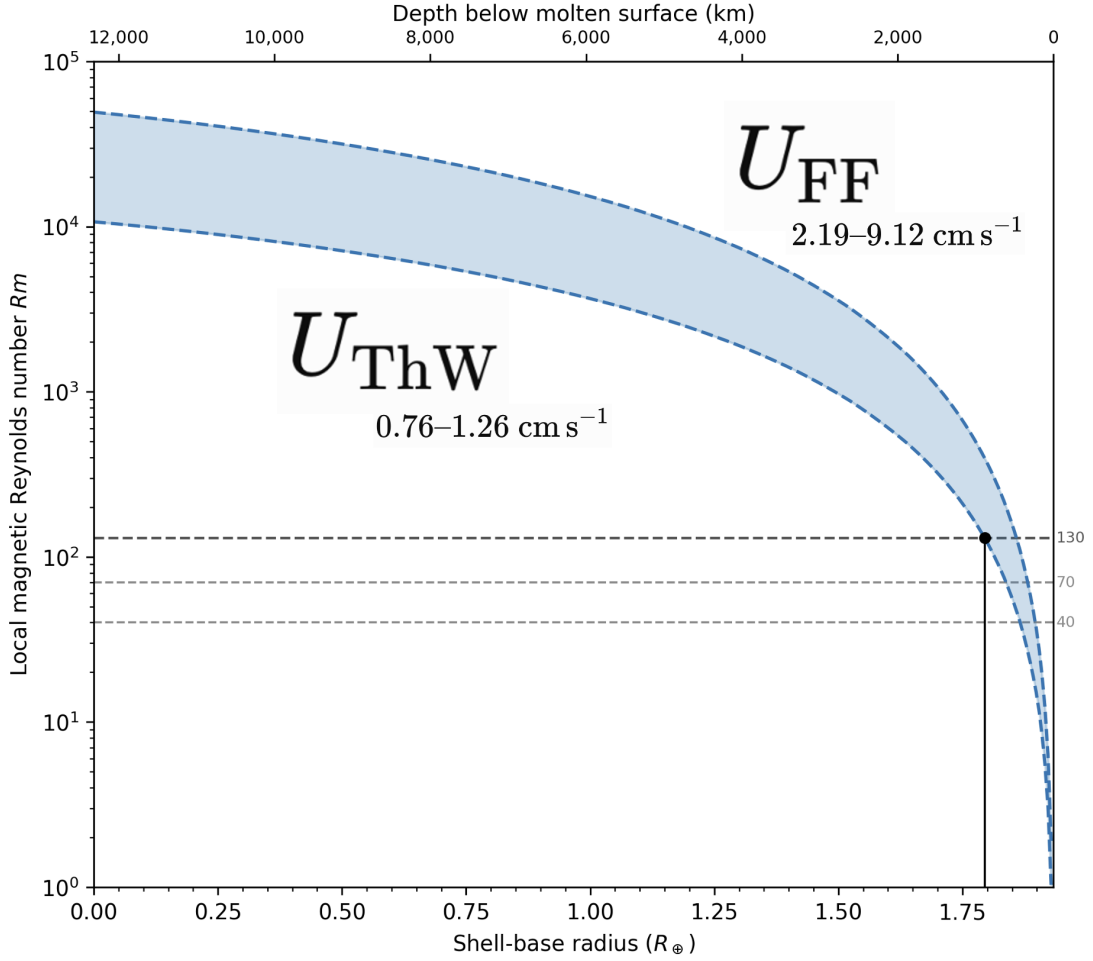


Figure 4.9: Magnetic Reynolds number as a function of depth below the top of the molten interior for the representative sub-Neptune model. Each depth defines the base of an outer conducting shell extending from r to R_{molten} , with thickness $L = R_{\text{molten}} - r$. The fiducial calculation uses the local electronic conductivity and local buoyancy flux at the shell base. Horizontal lines show the reference values $Rm = 40$, 70 , and 130 .

For the fiducial 10-day rotation case, the thermal-wind velocity scaling reaches $Rm = 40$, 70 , and 130 once the conducting shell reaches thicknesses of approximately 502 , 721 , and 1059 km, respectively. The $Rm = 130$ crossing occurs at a pressure of approximately 53 GPa. The more optimistic free-fall scaling reaches the same reference values at shell thicknesses of

approximately 263, 372, and 540 km, respectively.

Only about 10^3 km of conducting depth is required to reach the conservative strong-field benchmark. Importantly, the 1059 km crossing is not interpreted as a physical boundary within the planet. The modeled $\text{MgSiO}_3\text{--H}$ interior is continuous, molten, and assumed to be convecting; no phase boundary or stable layer is imposed at this depth. The calculation therefore establishes a minimum conducting-shell thickness required to reach a specified Rm , rather than uniquely determining the radial extent of the dynamo.

At the opposite geometrical limit, the entire molten interior can be treated as a single connected conducting region. Its radial extent is approximately 12,318 km. As a sanity check, we calculate a bulk magnetic Reynolds number for this full molten region using several effective conductivities. With the thermal-wind velocity and the conductivity at the top of the molten region, the most conservative treatment gives $Rm \simeq 600$. Harmonic- and volume-averaged conductivities give values of approximately 2.9×10^3 and 4.7×10^3 , respectively.

4.5.4 Magnetic-Field Strength Estimate

The Rm calculation establishes whether a conducting shell can plausibly support magnetic induction, but it does not determine the volume over which magnetic-field generation occurs. We therefore evaluate magnetic field strength as a function of assumed active-shell thickness. For each shell-base radius r , the source region is taken to be the same outer shell used in the Rm calculation,

$$r \leq r' \leq R_{\text{molten}}. \quad (4.30)$$

For the field-strength calculation, the energetics of this extended region are represented using a volume average of the complete buoyancy factor,

$$I_{b,\text{src}} = F_{\text{int}} \left\langle \frac{g\alpha}{\rho C_P} \right\rangle_{\text{src}}. \quad (4.31)$$

This differs deliberately from the local buoyancy treatment used to locate the Rm crossing. A local state is useful for the radial feasibility diagnostic, whereas the field-strength calculation describes the energetics of an extended source volume.

For each source geometry, the thermal-wind and free-fall scalings are used to estimate the characteristic fluid velocity. The corresponding convective heat-flux proxy is

$$q_c(r) = \frac{2C_P(r)\rho(r)^2U^3}{P(r)\alpha(r)}, \quad (4.32)$$

and q_0 denotes its value at the top of the active source region. The magnetic-field strength is then estimated using a convective-power scaling for convection-driven dynamos (Christensen and Aubert, 2006; Christensen et al., 2009),

$$\frac{B_{\text{dyn}}^2}{2\mu_0} = cf_{\text{ohm}} \langle \rho \rangle^{1/3} (Fq_0)^{2/3}, \quad (4.33)$$

where B_{dyn} is the characteristic field strength in the active source region, c is an empirical scaling constant, f_{ohm} is the fraction of convective power lost to Ohmic dissipation, $\langle \rho \rangle$ is the mean density of the source region, and F is a radial structure factor accounting for variations in density, heat flux, and characteristic convective and thermal length scales through the source region. We use $c = 0.63$ and $f_{\text{ohm}} = 1$ as fiducial values.

Because $q_c \propto U^3$ while $B_{\text{dyn}} \propto q_0^{1/3}$ for a fixed source geometry, the predicted field strength scales approximately linearly with the adopted velocity. The thermal-wind and free-fall estimates therefore define the lower and upper bounds, respectively, of the field-strength envelopes shown below.

Because every source region considered in the outer-shell calculation extends to R_{molten} , the external field is attenuated outward from the top of the molten interior. We relate

the characteristic dynamo field to its dipole component through $f_{\text{dip,B}} = B_{\text{dip,dyn}}/B_{\text{dyn}}$, and adopt $f_{\text{dip,B}} = 1/(2\sqrt{2})$. Assuming that this dipole component decays as r^{-3} outside the field-generating region,

$$B_{\text{dip,1bar}} = f_{\text{dip,B}} \left(\frac{R_{\text{molten}}}{R_{\text{1bar}}} \right)^3 B_{\text{dyn}}. \quad (4.34)$$

The conversion from B_{dyn} to $B_{\text{dip,dyn}}$ accounts for the fraction of the characteristic dynamo field represented by the dipole component, while the $(R_{\text{molten}}/R_{\text{1bar}})^3$ term describes the geometric attenuation of that dipole field to the 1-bar radius. The large difference between the molten-interior radius and the 1-bar radius therefore substantially reduces the magnetic-field amplitude at the observable planetary radius.

Figure 4.10 shows the resulting field strength as a function of active-shell base radius, or equivalently active-shell thickness. The thermal-wind $Rm = 130$ crossing defines a conservative minimum-shell endmember. For this approximately 1059 km-thick shell, the predicted internal field is approximately 14–44 G, where the range spans the thermal-wind and free-fall field-strength scalings. After dipole attenuation to the 1-bar radius, the corresponding field is approximately 1.3–4.1 G.

The $Rm = 130$ shell is not, however, required to be the full dynamo source region. As the shell base is moved inward, progressively more of the molten interior participates in the field-strength calculation. The limiting case at the innermost shell base corresponds to the entire molten interior. In this full-molten-interior limit, the predicted internal field increases to approximately 19–90 G and the corresponding 1-bar dipole field is approximately 1.8–8.4 G. The lower edge of each range corresponds to the preferred rotating thermal-wind estimate, while the free-fall scaling provides an optimistic upper bound.

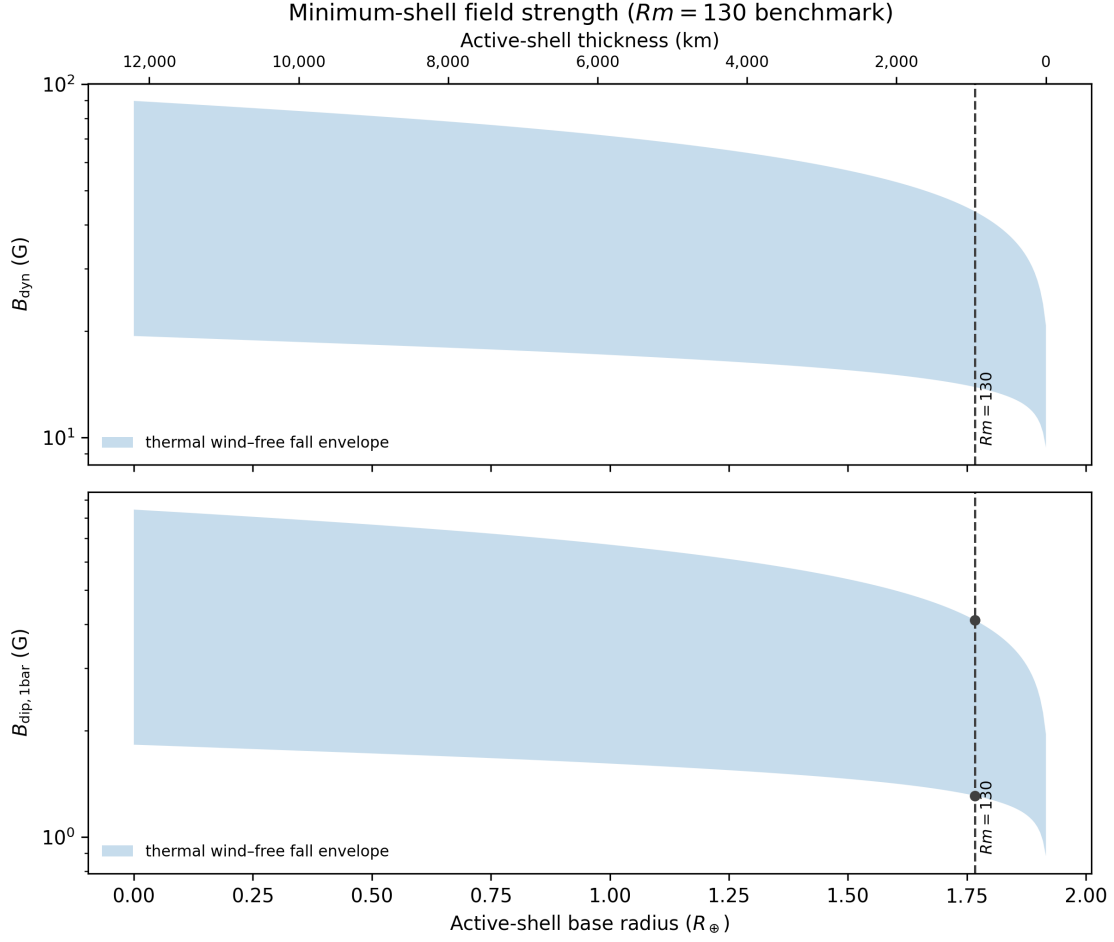


Figure 4.10: Predicted magnetic-field strength as a function of active-shell base radius for the representative sub-Neptune model. At each radius, the assumed dynamo source region is the outer molten shell extending from the shell base to R_{molten} . The shaded envelope spans the thermal-wind and free-fall velocity scalings. The $Rm = 130$ thermal-wind crossing marks the minimum-shell strong-field endmember, corresponding to a shell thickness of approximately 1059 km. The opposite, full-thickness limit corresponds to the entire molten interior participating in field generation. The upper panel shows the characteristic internal dynamo field, and the lower panel shows the corresponding dipole field attenuated to the 1-bar planetary radius.

4.6 Discussion

The calculations presented in this chapter suggest that hydrogen-bearing silicate liquids may represent an additional class of planetary dynamo material. Previous work has shown that silicate liquids can reach electrical conductivities relevant for dynamo action at sufficiently high pressure and temperature, and that composition can strongly modify those transport properties (Soubiran and Militzer, 2018; Stixrude et al., 2020; Dragulet and Stixrude, 2025). Here we find that hydrogen also modifies the electronic transport properties of MgSiO_3 liquid. Adding hydrogen increases the density of electronic states near the Fermi level and systematically increases the electronic electrical conductivity.

This result has important implications for miscible sub-Neptune interiors. If hydrogen and silicate become miscible at depth, the electrically conducting region of the planet is not limited to metallic hydrogen, an iron-rich core, or a thin basal magma ocean. Instead, a large fraction of the molten condensed interior may be a hydrogen-bearing silicate fluid with conductivity high enough for magnetic induction to compete with diffusion. In the representative PlanetLab models considered here, the radial conductivity profile increases inward because the deep interior is hotter and more compressed than the outer molten region. The conductivity therefore varies substantially with radius, reinforcing the need to treat σ_{el} as a depth-dependent material property rather than as a single characteristic value.

The magnetic Reynolds number calculations show that the outermost part of the molten interior is not necessarily sufficient to support strong magnetic induction. Although the entire condensed interior is molten in the model, the cooler outer portion has lower electrical conductivity. Moving inward towards the deeper parts of the planet increases both the local conductivity and the thickness of the conducting shell. For our fiducial 10-day rotation case, the thermal-wind velocity scaling reaches $Rm = 40$, 70, and 130 at conducting-shell thicknesses of approximately 502, 721, and 1059 km, respectively. We interpret the $Rm = 130$ crossing as a conservative minimum-shell strong-field endmember rather than as the location

of a sharp dynamo boundary.

This distinction is important because no phase boundary or stably stratified layer is imposed at the $Rm = 130$ crossing. The modeled MgSiO_3 -H interior is continuous, molten, and assumed to be convecting, so material deeper than the minimum shell may also participate in field generation. Treating the entire molten interior as a connected conducting region gives a bulk magnetic Reynolds number of approximately 600 even when the thermal-wind velocity is combined with the relatively low conductivity at the top of the molten region.

The predicted magnetic-field strength depends on how much of this molten interior is assumed to participate in dynamo generation. If only the minimum 1059-km-thick shell required to reach $Rm = 130$ is active, the predicted characteristic internal field is approximately 14–44 G, where the range spans the thermal-wind and free-fall velocity scalings. Dipole attenuation to the 1-bar radius gives approximately 1.3–4.1 G. At the opposite geometrical limit, allowing the entire molten interior to participate increases the predicted internal field to approximately 19–90 G and the corresponding 1-bar dipole field to approximately 1.8–8.4 G.

Although exoplanetary magnetic fields have not yet been measured unambiguously, several observational studies provide indirect constraints on their strengths. Ultraviolet transit observations of the Neptune-sized planet HAT-P-11b have been interpreted using magnetospheric models to imply an equatorial magnetic field of approximately 1–5 G (Ben-Jaffel et al., 2022). Stronger fields of approximately 20–120 G have been inferred for several hot Jupiters from chromospheric signatures of magnetic star–planet interactions (Cauley et al., 2019). Although these estimates are model dependent and the planets differ from the sub-Neptune interiors considered here, they provide a precedent for the gauss-level external fields predicted by our models.

One possible observational consequence of such a field is electron cyclotron maser radio emission. Radio auroral emission can provide a direct constraint on magnetic-field strength because the characteristic emission frequency is set by the local magnetic field at the emission

site (Brain et al., 2024), according to

$$\nu_c[\text{MHz}] \simeq 2.8B[\text{G}]. \quad (4.35)$$

Our calculations do not explicitly model the location or plasma conditions of the radio-emitting region. We therefore use $B_{\text{dip},1\text{bar}}$ as a reference field strength rather than assuming that the emission originates at the 1-bar level. The fiducial $Rm = 130$ thermal-wind boundary gives a 1-bar dipole field of approximately 1.3–4.1 G, corresponding to reference cyclotron frequencies of $\nu_c \approx 3.7\text{--}11$ MHz. If the entire molten interior participates in field generation, the corresponding reference range increases to approximately 5.1–24 MHz.

Because electron cyclotron maser emission is expected to originate in the upper atmosphere or magnetosphere, where the local magnetic field may differ from its value at 1 bar, these frequencies should not be interpreted as predictions of the observed emission frequency. For a dipolar field, the field strength decreases approximately as r^{-3} with distance from the planet, although the local field also depends on magnetic latitude and the geometry of the emitting region.

These frequencies straddle the approximate ~ 10 MHz terrestrial ionospheric cutoff, suggesting that space-based observations may be required to probe fields in this range. This comparison is therefore intended only as a frequency-accessibility check rather than a detectability prediction. A true detectability calculation would require additional modeling of the emission altitude and plasma environment, emitted radio power, stellar-wind interaction, magnetospheric size, beaming, plasma absorption, sky background, distance, and instrument sensitivity.

Several uncertainties remain. First, the conductivity model is calibrated over a finite range of pressure, temperature, and hydrogen content. Evaluating it in planetary regions outside the range of our simulations introduces extrapolation uncertainty. Because Rm is proportional to conductivity, any systematic error in σ_{el} directly affects the inferred mini-

mum conducting-shell thickness. Second, the convective velocity is uncertain. The range of field strengths reported here reflects different velocity and field-strength scaling assumptions, but these scalings are not a substitute for a full three-dimensional dynamo simulation of a compressible, radially stratified sub-Neptune magma ocean. Third, translating the characteristic dynamo field into an externally observable field requires assumptions about magnetic geometry. We adopt a fixed ratio between the dipole component and characteristic dynamo field, $f_{\text{dip,B}} = 1/(2\sqrt{2})$, and assume that the resulting dipole component decays as r^{-3} outside the field-generating region. The actual dipolarity of a silicate–hydrogen dynamo is not known. A more multipolar field would decay more rapidly with radius and could therefore produce a weaker large-scale field than estimated here.

The present calculations also focus on iron-free MgSiO_3 –H liquids in order to isolate the effect of hydrogen. This is a useful first step, but real sub-Neptune interiors may contain iron mixed into the silicate–hydrogen fluid, depending on the planet’s differentiation history and phase stability. Because iron enrichment strongly increases the electronic conductivity of silicate liquids in basal magma ocean calculations, even modest Fe incorporation could further enhance conductivity in the supercritical mixture (Dragulet and Stixrude, 2025). Future MgSiO_3 –Fe–H simulations will be needed to determine whether hydrogen and iron produce additive, competing, or coupled effects on the electronic density of states and transport properties.

Despite these limitations, the results show that supercritical hydrogen-bearing silicate liquids should be considered viable conducting materials in planetary interiors. The same miscibility that alters the density and equation of state of sub-Neptune interiors also changes their electronic transport properties. In this sense, magnetic fields provide a potential link between the chemical evolution of magma-ocean interiors and observable planetary properties. A natural next step is to apply the conductivity and dynamo workflow developed here to a broader population of sub-Neptune interior models in order to identify which combinations of mass, radius, hydrogen content, intrinsic luminosity, atmospheric thickness, and

dynamo-region depth are most favorable for observable magnetic fields.

4.7 Conclusions

In this chapter, we calculated the electronic transport properties of hydrogen-bearing MgSiO_3 liquids and evaluated their implications for magnetic-field generation in miscible sub-Neptune interiors. Using density-functional-theory molecular dynamics and Kubo–Greenwood post-processing, we determined the electronic electrical conductivity of supercritical MgSiO_3 –H liquids over a range of pressures, temperatures, and hydrogen concentrations. Static electronic-structure calculations on uncorrelated liquid snapshots were used to obtain frequency-dependent conductivity spectra, which were extrapolated to the DC limit relevant for magnetic induction and Ohmic diffusion.

The calculated conductivities show that temperature and hydrogen content are the dominant controls on electronic transport. At fixed hydrogen content, σ_{el} increases strongly with temperature, while the pressure dependence is comparatively weak over the range sampled. At fixed pressure and temperature, adding hydrogen systematically increases σ_{el} , in some cases by approximately an order of magnitude across the sampled composition range. Density-of-states calculations show that hydrogen redistributes electronic states toward the Fermi level and increases $g(E_F)$ in concert with the enhanced electrical conductivity. Increasing hydrogen content also drives the Lorenz number toward the Sommerfeld value, consistent with increasingly metal-like electronic transport. Together, these results show that hydrogen substantially modifies the electronic structure and transport properties of the silicate liquid.

We fit the calculated DC conductivities with continuous pressure–temperature–composition functions for both electronic electrical and thermal conductivity. These fits provide the material-property bridge between the first-principles simulations and planetary interior models. When evaluated along representative PlanetLab radial profiles, the electrical conductivity is highest in the deep, hot interior and decreases outward toward the top of the molten

region.

Combining the radial conductivity profile with buoyancy-flux velocity scalings shows that portions of the molten interior can exceed magnetic Reynolds number thresholds relevant for dynamo action. In the fiducial rotating case, the conservative $Rm = 130$ crossing occurs at a depth of 1059 km below the top of the molten interior. If only this minimum $Rm = 130$ shell participates in field generation, the predicted internal magnetic field is approximately 14–44 G and the attenuated 1-bar dipole field is approximately 1.3–4.1 G. Because the modeled molten interior is continuous and assumed to convect, the true source region could extend substantially deeper. In the limiting case in which the entire molten interior participates, the predicted fields increase to approximately 19–90 G internally and 1.8–8.4 G at the 1-bar radius.

These field strengths imply electron cyclotron cutoff frequencies of approximately 3.7–24 MHz for the fiducial model and are very close to the approximate terrestrial ionospheric cutoff. A full observational prediction would require additional modeling of radio emission, plasma propagation, stellar-wind coupling, beaming, and telescope sensitivity.

Overall, these results indicate that hydrogen-bearing silicate liquids can reach conductivities high enough to be relevant for planetary dynamos. In miscible sub-Neptune interiors, the same supercritical magma ocean that controls the planet’s density structure may also provide a deep conducting region capable of generating magnetic fields. Future work should extend these calculations to Fe-bearing MgSiO_3 –H mixtures, fully dynamical simulations, and broader populations of sub-Neptune interior models.

CHAPTER 5

Miscibility and Differentiation in Sub-Neptune Interiors

5.1 Introduction

Sub-Neptunes are among the most abundant planets identified in the current exoplanet census, yet their interior structures remain poorly constrained. Some models interpret these planets as volatile-rich bodies with substantial water-bearing interiors (e.g., Fortney et al., 2007; Zeng et al., 2019). Other models describe them as rocky planets with molten or partially molten interiors beneath H₂-rich primary atmospheres (Chachan and Stevenson, 2018; Bean et al., 2021). These pictures can produce similar bulk masses and radii, illustrating why the material properties and phase equilibria of candidate interior components are essential for interpreting sub-Neptune structure.

In the hydrogen-envelope picture, percent-level H₂ atmospheres can strongly affect planetary radii and thermal evolution. Dense H₂-rich envelopes insulate the underlying rocky interior and can allow magma oceans to persist for Gyr timescales, depending on the planet’s cooling and atmospheric loss history (Ginzburg et al., 2016; Misener and Schlichting, 2022; Rogers et al., 2024b). Atmospheric observations also motivate considering chemical interaction between H₂ envelopes and molten rocky interiors. Several sub-Neptune spectra have been interpreted in terms of atmosphere–magma–ocean exchange, including cases where high mean molecular weight, metal enrichment, or low C/O ratios may reflect equilibration between a hydrogen-rich envelope and an underlying magma ocean (Shorttle et al., 2024; Ahrer

et al., 2025; Benneke et al., 2024; Felix et al., 2025). These observations do not uniquely determine the interior structure, but they support the idea that the outer envelope and condensed interior may exchange material and should be considered as a coupled chemical system.

Super-Earths provide an additional motivation for understanding the condensed interiors of sub-Neptunes. Super-Earths may be the stripped descendants of sub-Neptunes that lost their primordial H_2 envelopes (Rogers et al., 2024a). In that case, the interior structures of super-Earths may retain information about earlier magma-ocean and hydrogen-envelope stages (Bean et al., 2021). However, the extent to which these bodies preserve properties of their sub-Neptune progenitors is unknown.

Recent work suggests that the boundary between a sub-Neptune magma ocean and its overlying atmosphere may be more than a simple physical interface. The surface of the magma ocean may also correspond to a phase boundary in the $\text{MgSiO}_3\text{--H}_2$ system, where a fully miscible supercritical silicate–hydrogen fluid exsolves into coexisting silicate-rich and hydrogen-rich phases (Markham et al., 2022; Young et al., 2024a; Gilmore and Stixrude, 2026; Rogers et al., 2025). In this picture, the binodal, or solvus, defines the outer boundary of the miscible condensed interior. Interior to this boundary, hydrogen can behave as a chemical component of the molten silicate interior as well as a component of the overlying envelope.

The previous two chapters focused on the thermodynamic properties of this supercritical $\text{MgSiO}_3\text{--H}_2$ fluid. However, silicate and hydrogen are only part of the chemical system relevant to sub-Neptune interiors. Rocky planets are expected to contain substantial iron, and many interior models assume that this iron segregates into a dense metallic core overlain by a silicate mantle. This assumption follows naturally from terrestrial planet structure, where metal–silicate differentiation provides the basic framework for understanding planetary interiors. For sub-Neptunes, the persistence of an Earth-like metal core may depend on whether Fe-rich and silicate-rich liquids remain stable as separate phases under high-pressure,

high-temperature, hydrogen-rich conditions.

Several physical processes may inhibit complete metal–silicate differentiation even when sufficient iron is present. Equilibration between Fe-rich metal, silicate, and hydrogen-rich envelopes can introduce significant light elements into the metal phase (Schlichting and Young, 2022). These effects can reduce metal–silicate density contrasts and may allow Fe-rich droplets to become neutrally buoyant or remain entrained within deep magma oceans (Young et al., 2024a; Lichtenberg, 2021).

The nature of the condensed interior directly affects how sub-Neptune bulk densities are interpreted. If hydrogen is retained in a miscible silicate–metal interior, then less of the planet’s density deficit must be attributed to the outer H_2 envelope alone (Kite et al., 2019; Schlichting and Young, 2022). At the same time, stellar Fe/Mg/Si ratios and observations of polluted white dwarfs suggest that rocky exoplanet building blocks can be consistent with the formation of Earth-like Fe-rich metal fractions (Adibekyan et al., 2021; Doyle et al., 2019; Trierweiler et al., 2023). This moves the problem beyond iron availability alone and toward the pressure–temperature conditions and chemical environment that control whether iron remains separated from silicate and hydrogen.

In this chapter, we treat the $\text{MgSiO}_3\text{--Fe--H}_2$ system as a phase-stability problem in which each pair of components provides a different constraint on the full mixture. The first part of this chapter is heavily based on (Young et al., 2025) in which we describe the construction of a ternary $\text{MgSiO}_3\text{--Fe--H}_2$ phase diagram model for sub-Neptune interiors. We review the binary phase relations that form the basis of the model and describe how they are extrapolated into ternary composition space. We then describe the two-phase DFT-MD approach used to test whether initially distinct liquids persist, broaden, or mix and apply them to $\text{MgSiO}_3\text{--H}_2$ and $\text{MgSiO}_3\text{--Fe}$ binaries. Finally, we present preliminary two-phase tests of the $\text{MgSiO}_3\text{--Fe--H}_2$ ternary system.

5.2 Phase Relations of the $\text{MgSiO}_3\text{--Fe--H}_2$ System

For a closed system with fixed bulk composition, pressure, and temperature, the equilibrium state is found by minimizing the molar Gibbs free energy, $\hat{G}$. We use the molar Gibbs free energy of mixing, $\Delta\hat{G}_{\text{mix}}$, to determine whether one or more phases are stable at specified conditions and to identify the compositions of any coexisting phases.

The shape of $\Delta\hat{G}_{\text{mix}}$ determines whether a mixture is stable as a single homogeneous phase or lowers its free energy by separating into two coexisting phases. In binary composition space, the binodal, or solvus, defines the compositions of coexisting phases at thermodynamic equilibrium. The spinodal lies inside the binodal and marks the region where the free-energy surface has negative curvature, so that infinitesimal composition fluctuations grow spontaneously and drive phase separation. The region between the binodal and spinodal is metastable: a homogeneous phase can persist there, but two-phase coexistence is favored at equilibrium.

The $\text{MgSiO}_3\text{--Fe--H}_2$ ternary model is built from three bounding binary systems: $\text{MgSiO}_3\text{--H}_2$, $\text{MgSiO}_3\text{--Fe}$, and Fe--H_2 . Each binary captures a different part of the phase-stability problem. The $\text{MgSiO}_3\text{--H}_2$ binary constrains the miscibility of silicate and hydrogen. The $\text{MgSiO}_3\text{--Fe}$ binary constrains the stability of Fe-rich and silicate-rich liquids. The Fe--H_2 binary constrains the incorporation of hydrogen into Fe-rich liquid. Together, these binary relations define the thermodynamic basis for the ternary $\text{MgSiO}_3\text{--Fe--H}_2$ model. We discuss each in detail below.

5.2.1 $\text{MgSiO}_3\text{--H}_2$

The $\text{MgSiO}_3\text{--H}_2$ binary describes the phase relation between silicate melt and hydrogen. At lower temperatures, silicate-rich and H_2 -rich phases can coexist, but at sufficiently high pressure and temperature, the miscibility gap closes and the system forms a single supercritical silicate–hydrogen fluid. We adopt the subregular mixing model described in Gilmore

and Stixrude (2026). Fitting the Gibbs free energy of mixing to their DFT-MD simulations results in the expression

$$\begin{aligned}\Delta\hat{G}_{\text{mix}} = & [L_{\text{CB}}x + L_{\text{BC}}(1-x)]x(1-x) \left(1 - \frac{T}{\tau} + \frac{P}{\pi}\right) \\ & + RT [x \ln x + (1-x) \ln(1-x)].\end{aligned}\tag{5.1}$$

Here, L_{CB} and L_{BC} are asymmetric binary interaction parameters, and x is the mole fraction of H_2 along the binary join. The first term describes nonideal mixing, while the second term is the ideal configurational entropy of mixing. In this formulation, the excess molar enthalpy of mixing is

$$\Delta\hat{H}_{\text{excess}} = [L_{\text{CB}}x + L_{\text{BC}}(1-x)]x(1-x).\tag{5.2}$$

The temperature and pressure dependence of the nonideal contribution are parameterized by τ and π , respectively. The adopted fit parameters are $L_{\text{CB}} = 622000 \text{ J mol}^{-1}$, $L_{\text{BC}} = -4950 \text{ J mol}^{-1}$, $\tau = 4800 \text{ K}$, and $\pi = -35 \text{ GPa}$ (Gilmore and Stixrude, 2026).

5.2.2 $\text{MgSiO}_3\text{--Fe}$

The $\text{MgSiO}_3\text{--Fe}$ binary constrains the stability of Fe-rich and silicate-rich liquids. Direct free-energy calculations and experiments for $\text{MgSiO}_3\text{--Fe}$ are limited (Badro et al., 2018; Shakya et al., 2024), so our ternary model uses the better-characterized MgO--Fe system as a proxy for the metal–silicate interaction. Previous first-principles work shows that molten MgO and Fe become increasingly miscible at high pressure and temperature (Wahl and Militzer, 2015). A recent study by Insixiengmay and Stixrude (2025) on the miscibility of MgO in liquid Fe presented a regular solution model describing the system,

$$\begin{aligned}\Delta\hat{G}_{\text{mix}} = & L_{\text{AC}}(T, P)x(1-x) \\ & + RT [x \ln x + (1-x) \ln(1-x)],\end{aligned}\tag{5.3}$$

where

$$L_{AC} = L_{CA} = 240000 - 28T(\text{K}) + 1116P(\text{GPa}) \quad (5.4)$$

in J mol^{-1} . In the ternary model, this interaction parameterization is used as an approximation for the MgSiO_3 –Fe binary.

This approximation is necessary because the available thermodynamic constraints are stronger for MgO –Fe than for MgSiO_3 –Fe. However, it also introduces uncertainty into the ternary model. The MgSiO_3 –Fe two-phase simulation described below provides a direct check on whether MgSiO_3 and Fe are miscible at a condition where the MgO –Fe proxy predicts one-phase behavior.

5.2.3 Fe–H₂

The Fe–H₂ binary constrains the incorporation of hydrogen into Fe-rich liquid. The binary relation for this system is taken from experimental and first-principles constraints on hydrogen solubility in liquid Fe.

At relatively low pressure and temperature, Fe-rich melt coexists with H₂ gas (San-Martin and Manchester, 1990). At higher pressure and temperature, experiments and first-principles calculations indicate that hydrogen becomes increasingly soluble in liquid Fe. Tagawa et al. (2021) measured the distribution coefficient for hydrogen between molten Fe metal and molten silicate,

$$D_{\text{H}} = \frac{[H]_{\text{metal}}}{[H]_{\text{silicate}}}, \quad (5.5)$$

from 3100 to 4600 K and 30 to 60 GPa. They found that D_{H} increases from near unity at $T < 3000$ K to 10 at 3000 K and 30 GPa, and to 30 at 4000 K and 60 GPa. Yuan and Steinle-Neumann (2020) similarly found from *ab initio* calculations that D_{H} increases from

near unity at 0 GPa to approximately 100 at 40 GPa. These constraints imply that hydrogen solubility in Fe-rich liquid increases strongly with pressure.

An additional constraint comes from lower-pressure parameterizations of hydrogen solubility in molten Fe. The compilations of Zhang (2007) and Jiang et al. (2011) give

$$\ln(x_{\text{H}}) = -4.423 - \frac{4009 \text{ K}}{T} + \frac{1}{2} \ln \left(\frac{P_{\text{H}_2}}{1 \text{ bar}} \right). \quad (5.6)$$

This relation is used to constrain the metal-rich limb of the Fe–H₂ binodal at the lowest pressure–temperature conditions relevant to the magma-ocean/envelope boundary.

The Fe–H₂ binary is represented with a pressure-dependent subregular solution model,

$$\begin{aligned} \Delta \hat{G}_{\text{mix}} = & [L_{\text{AB}}x + L_{\text{BA}}(1 - x)] x(1 - x) \\ & + RT [x \ln x + (1 - x) \ln(1 - x)], \end{aligned} \quad (5.7)$$

where

$$L_{\text{AB}} = 138000 - 9500P(\text{GPa}) \quad (5.8)$$

and

$$L_{\text{BA}} = 17000 - 9500P(\text{GPa}) \quad (5.9)$$

in J mol^{−1}, and x is the mole fraction of H₂ along the Fe–H₂ join.

5.3 Two-Phase Simulation Strategy

A central part of this chapter involves testing whether compositionally distinct liquids remain separated or mix under sub-Neptune interior conditions. To do this, we use two-phase first-principles molecular dynamics simulations. In these calculations, two initially distinct fluids

are placed in direct contact within a single simulation cell and allowed to evolve under DFT forces. The subsequent evolution of the interface provides a direct test of phase behavior at the pressure, temperature, and bulk composition of the simulation.

This approach is useful because phase stability can be difficult to infer from a homogeneous starting configuration alone. A system initialized as a single mixed fluid may remain mixed over finite simulation times even if a separated state would be stable, particularly when nucleation barriers are large. A two-phase initial condition instead begins with a possible coexistence geometry already present. The simulation can then be used to ask whether the initial interface persists, broadens, or disappears. Complete mixing indicates that the imposed two-phase geometry is not stable on the simulation timescale, whereas persistent compositional contrast suggests either stable coexistence or slow approach toward equilibrium.

The two-phase simulations in this chapter follow the general protocols used in previous first-principles phase-coexistence studies (Insixiengmay and Stixrude, 2025; Gilmore and Stixrude, 2026; Gupta et al., 2024). Individual phases are first equilibrated independently at the target temperature and approximately matched pressure. The equilibrated configurations are then combined into an elongated supercell with the initial interface normal to the z direction. Periodic boundary conditions produce two planar interfaces. The combined system is then evolved at fixed temperature and volume, allowing the initially distinct regions to mix, maintain an interface, or evolve toward a different two-phase configuration.

5.3.1 Initial Conditions

The two-phase simulations are initialized by placing two independently equilibrated fluids in contact within a single simulation cell. For each test, the separate fluids are first prepared at the same target temperature and at approximately matched pressures. The equilibrated configurations are then combined into an elongated supercell with the initial interface normal to the z direction. Periodic boundary conditions produce two planar interfaces between the

initially distinct regions. This setup follows the general phase-coexistence approach used in previous first-principles simulations of liquid interfaces (Insixiengmay and Stixrude, 2025; Gupta et al., 2024; Gilmore and Stixrude, 2026).

The simulations presented here are targeted tests of phase behavior rather than complete mappings of the relevant phase diagrams. In each case, the initial two-phase geometry is used to test whether an imposed compositional interface persists, broadens, or disappears over the simulation time. Complete first-principles mapping of the binary and ternary phase relations would require a much larger suite of simulations spanning pressure, temperature, and composition. The calculations in this chapter instead focus on diagnostic state points that can be compared directly with the predicted phase relations described below.

5.3.2 Phase Interfaces

For simulations that maintain two compositionally distinct regions, the interface can be described using a Gibbs dividing surface. This surface provides a geometric way to separate the two regions and to track whether the initial interface persists, broadens, or disappears with time. Following the general approach used for coarse-grained liquid interfaces (Willard and Chandler, 2010), the atomic positions are converted into a smoothed density field, and the dividing surface is defined as the surface where that density field reaches a specified reference value.

For the $\text{MgSiO}_3\text{--H}_2$ binary simulations, we use oxygen as a tracer of the silicate-rich liquid. Oxygen is abundant in MgSiO_3 and nearly absent from the H_2 -rich region, making it a useful species for locating the silicate–hydrogen interface. The smoothed oxygen density field is constructed from the instantaneous atomic positions, and the dividing surface is defined as the surface where the oxygen density is equal to one half of the bulk oxygen density in the silicate-rich liquid. The interface position is then averaged over the selected portion of the trajectory.

The presence or absence of a stable dividing surface is a useful qualitative diagnostic of phase behavior. In a simulation that remains two-phase, the oxygen density continues to define a persistent boundary between silicate-rich and hydrogen-rich regions. In a simulation that becomes fully miscible, oxygen and hydrogen become distributed throughout the simulation cell, and the oxygen density no longer separates the system into two distinct regions.

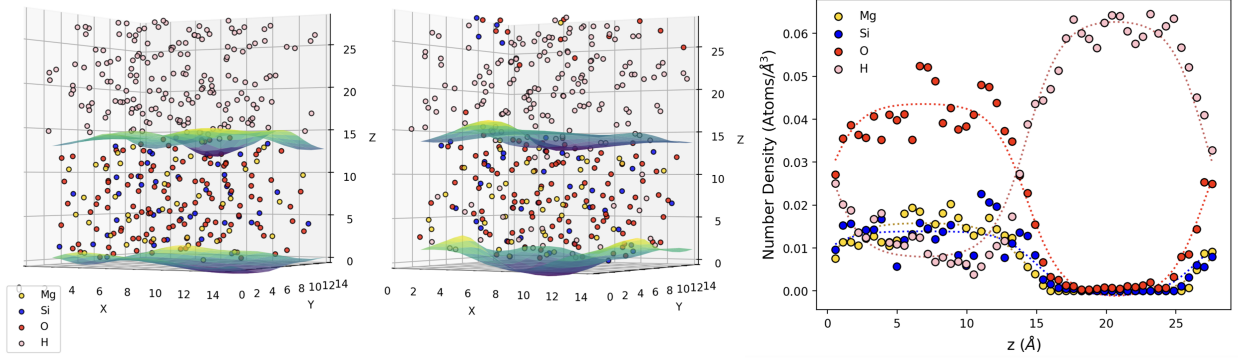


Figure 5.1: Example interface analysis for the $\text{MgSiO}_3\text{--H}_2$ two-phase simulation at 3000 K and 2.5 GPa. Left and center: atomic configurations with Gibbs dividing surfaces determined from the smoothed oxygen density field. Right: species-resolved number-density profiles along the direction normal to the interface. The Gibbs dividing surface provides a geometric representation of the $\text{MgSiO}_3\text{--H}_2$ boundary, while the density profiles quantify the compositional contrast between the silicate-rich and H_2 -rich regions.

A second way to quantify two-phase behavior is to compute one-dimensional density profiles normal to the initial interface. This approach follows the standard treatment of diffuse liquid interfaces, in which the density changes smoothly between two plateau values across an interfacial region (Widom, 1982; Xiao and Stixrude, 2018). For each atomic species i , we compute the number density as a function of position along the z direction,

$$\rho_i(z) = \langle \rho_i(z, t) \rangle, \quad (5.10)$$

where the angle brackets indicate a time average over a selected portion of the trajectory. The instantaneous density is

$$\rho_i(z, t) = \sum_{k \in i} \delta[z - z_k(t)], \quad (5.11)$$

where $z_k(t)$ is the position of atom k of species i along the z axis. In practice, the cell is divided into thin slabs, and the density is computed by binning atoms by their z coordinate and averaging over time.

For slab-like two-phase geometries, we fit the species-resolved density profiles with a hyperbolic tangent form,

$$\rho_i(z) = \rho_{i,\text{off}} + \frac{\rho_{i,\text{on}} - \rho_{i,\text{off}}}{2} \left[\tanh\left(\frac{z - z_0 + w/2}{\delta}\right) - \tanh\left(\frac{z - z_0 - w/2}{\delta}\right) \right]. \quad (5.12)$$

Here, $\rho_{i,\text{on}}$ and $\rho_{i,\text{off}}$ are the plateau number densities of species i inside and outside the selected region, z_0 is the center of the slab, w is the slab width, and δ is the characteristic interfacial width. The two hyperbolic tangent terms describe the two sides of the slab, corresponding to the two interfaces created by periodic boundary conditions.

This fitting procedure provides two useful diagnostics. First, the plateau densities estimate the compositions of the two regions away from the interface. Second, the parameter δ provides a measure of interface broadening. In a miscible simulation, the plateau densities on the two sides of the cell should become increasingly similar with time. In a simulation that maintains two phases, the plateau densities should remain distinct, although the interface may broaden as the system evolves.

5.4 Binary Two-Phase Tests

The binary phase relations described above provide the thermodynamic basis for the MgSiO_3 – Fe-H_2 ternary model. Selected two-phase DFT-MD simulations provide direct checks on key

parts of this framework. For each binary test, the pressure, temperature, and bulk composition of the simulation are shown on the corresponding predicted phase diagram, with the simulated composition marked by a pink point. The initial and final simulation snapshots are then used to test whether the imposed two-phase geometry persists or disappears. In this way, the figures compare the predicted phase behavior directly with the outcome of the first-principles simulation.

In this section, I describe the binary two-phase simulations used to test the $\text{MgSiO}_3\text{--H}_2$ and $\text{MgSiO}_3\text{--Fe}$ joins. No new Fe--H_2 simulations were performed for this chapter; the Fe--H_2 relation is constrained from the literature as described in Section 5.2.3.

5.4.1 $\text{MgSiO}_3\text{--H}_2$ Two-Phase Tests

The $\text{MgSiO}_3\text{--H}_2$ binary was tested using two two-phase DFT-MD simulations chosen to sample conditions on opposite sides of the predicted $\text{MgSiO}_3\text{--H}_2$ binodal. Both simulations were initialized with adjacent MgSiO_3 melt and an H_2 -rich region. The bulk hydrogen abundance was approximately 4 wt%, corresponding to a composition near the crest of the predicted binodal. This system has been described in detail in Gilmore and Stixrude (2026) and the results of our limited testing agree with their findings.

At 3000 K and 2.5 GPa, the simulated bulk composition lies within the predicted two-phase field (Figure 5.2). The initial condition contains a silicate-rich liquid in contact with an H_2 -rich region. Over the course of the simulation, the two regions remain compositionally distinct. The persistence of a silicate-rich region and an H_2 -rich region is consistent with the predicted immiscibility of the $\text{MgSiO}_3\text{--H}_2$ mixture at this state point. In this case, the oxygen density continues to define a persistent silicate-rich region, and the Gibbs dividing surface analysis provides a way to track the location of the interface.

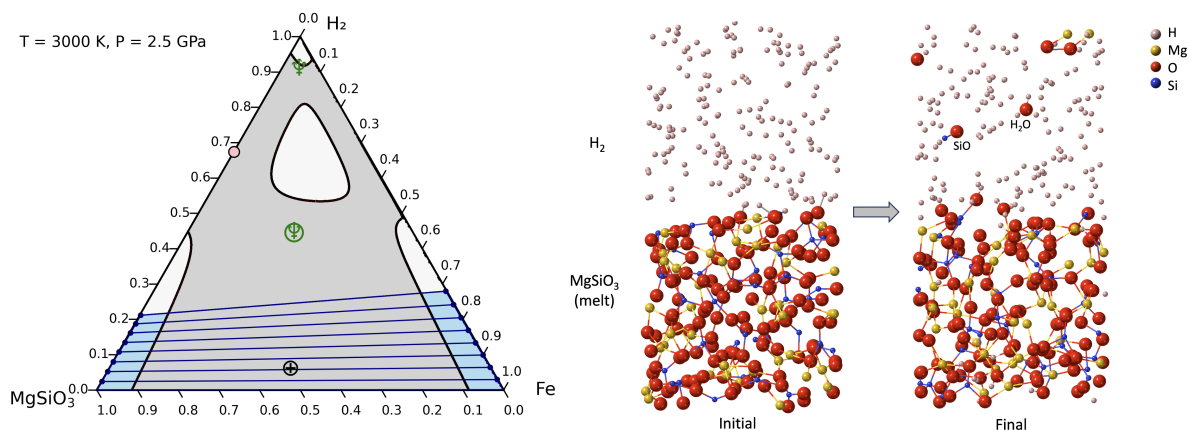


Figure 5.2: Binary test of the $\text{MgSiO}_3\text{--H}_2$ phase relation at 3000 K and 2.5 GPa. The predicted phase diagram is shown with the simulated bulk composition marked by a pink point. Initial and final DFT-MD snapshots show that the MgSiO_3 -rich and H_2 -rich regions remain compositionally distinct over the simulation time, consistent with the predicted two-phase field.

At 4000 K and 3.5 GPa, the simulated bulk composition lies in the predicted one-phase field (Figure 5.3). In contrast to the lower-temperature case, the initially separated MgSiO_3 and H_2 regions mix into a single fluid over the course of the simulation. The loss of a persistent interface is consistent with the predicted miscibility of the mixture at this state point. Because the oxygen density no longer separates the simulation cell into distinct silicate-rich and hydrogen-rich regions, a stable Gibbs dividing surface cannot be identified at late times.

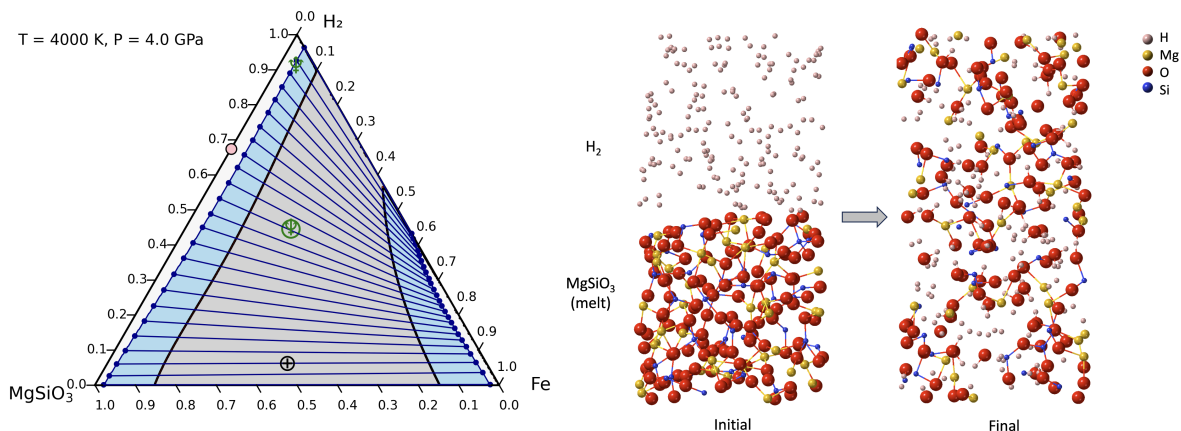


Figure 5.3: Binary test of the $\text{MgSiO}_3\text{--H}_2$ phase relation at 4000 K and 3.5 GPa. The predicted phase diagram is shown with the simulated bulk composition marked by a pink point. Initial and final DFT-MD snapshots show that the initially separated MgSiO_3 -rich and H_2 -rich regions mix into a single fluid, consistent with the predicted one-phase field.

Together, these two simulations bracket the predicted $\text{MgSiO}_3\text{--H}_2$ miscibility boundary. The lower-temperature case preserves compositional separation, whereas the higher-temperature case becomes fully mixed. This agreement between the predicted phase fields and the simulation outcomes supports the use of the $\text{MgSiO}_3\text{--H}_2$ binary relation in the ternary phase model.

5.4.2 $\text{MgSiO}_3\text{--Fe}$ Two-Phase Test

The $\text{MgSiO}_3\text{--Fe}$ binary was tested with one direct two-phase DFT-MD simulation at 9000 K and 60 GPa. This calculation was designed to evaluate whether the MgO--Fe mixing model can be used as a first-order proxy for $\text{MgSiO}_3\text{--Fe}$ at high pressure and temperature. The simulated state point lies in the predicted one-phase region of the adopted MgO--Fe -based phase relation (Figure 5.4).

The initial configuration consists of liquid MgSiO_3 in contact with liquid Fe. Over the

course of the simulation, the initially distinct MgSiO_3 -rich and Fe-rich regions mix into a single fluid. The disappearance of the imposed interface is consistent with the predicted miscibility of the mixture at this pressure and temperature. Because no persistent interface remains, no Gibbs dividing surface or plateau-density contrast is analyzed for this case.

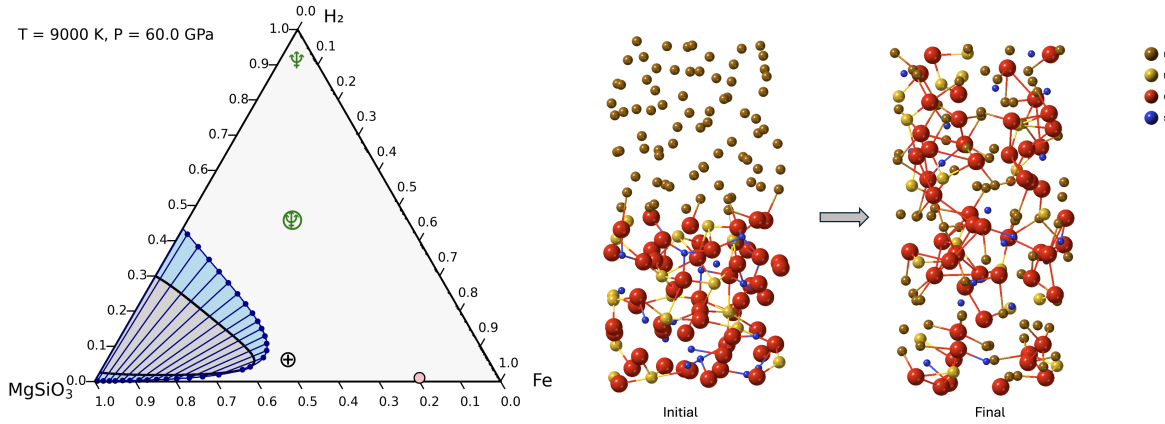


Figure 5.4: Binary test of the MgSiO_3 -Fe phase relation at 9000 K and 60 GPa. The predicted phase diagram is shown with the simulated bulk composition marked by a pink point. Initial and final DFT-MD snapshots show that the initially separated MgSiO_3 -rich and Fe-rich regions mix into a single fluid, consistent with the predicted one-phase field.

This test does not determine the full MgSiO_3 -Fe phase diagram. A complete binary free-energy surface would require simulations over a broader range of pressures, temperatures, and compositions. However, the result provides an important consistency check: MgSiO_3 and Fe become miscible at a condition where the adopted MgO -Fe proxy also predicts one-phase behavior. This supports using the MgO -Fe relation as a first-order approximation for the MgSiO_3 -Fe join in the high-pressure, high-temperature regime sampled here. It also provides a bridge to the ternary MgSiO_3 -Fe- H_2 simulations, where Fe-H liquid and MgSiO_3 liquid are placed in direct contact and allowed to react and mix.

5.5 Preliminary Ternary Two-Phase Tests

The binary tests described above provide checks on the bounding phase relations used to construct the $\text{MgSiO}_3\text{--Fe--H}_2$ ternary model. The next step is to test the full ternary system directly. These calculations are more difficult to interpret than the binary tests because the predicted coexisting phases in the ternary system are not pure endmembers. Instead, the ternary phase diagrams predict coexisting Fe-rich, silicate-rich, and H-bearing liquids whose compositions are set by tie lines on the Gibbs free-energy surface. A direct first-principles test therefore requires choosing an initial two-phase geometry that is simple enough to construct while still sampling the ternary composition space of interest.

For these preliminary ternary tests, we initialize the simulations using one equilibrated Fe–H liquid and one equilibrated MgSiO_3 liquid. These two fluids are prepared separately at the same target temperature and approximately matched pressure before being joined into a single elongated supercell. The resulting simulation is ternary in bulk composition because the combined cell contains MgSiO_3 , Fe, and H, but the initial geometry consists of an Fe–H-rich region in contact with a silicate-rich region. This construction is a practical simplification of the full ternary coexistence problem. The equilibrium ternary phase diagram predicts coexisting compositions that may each contain all three components, but those coexisting compositions are not known *a priori* from first-principles simulations. Starting from Fe–H and MgSiO_3 liquids provides a controlled way to test whether an imposed metal-rich/silicate-rich interface persists, broadens, or disappears.

We performed two preliminary ternary two-phase simulations at different pressure–temperature conditions. In each case, the bulk composition of the combined simulation cell is plotted on the predicted $\text{MgSiO}_3\text{--Fe--H}_2$ ternary phase diagram. The first simulation samples a higher-temperature, higher-pressure condition closer to the predicted miscible or near-miscible regime. The second samples a lower-temperature, lower-pressure condition closer to the predicted two-phase region. The goal of these calculations is not to determine equilibrium

coexistence compositions directly, but to evaluate whether the initially imposed Fe–H-rich and MgSiO_3 -rich regions remain separated or evolve toward a single mixed fluid.

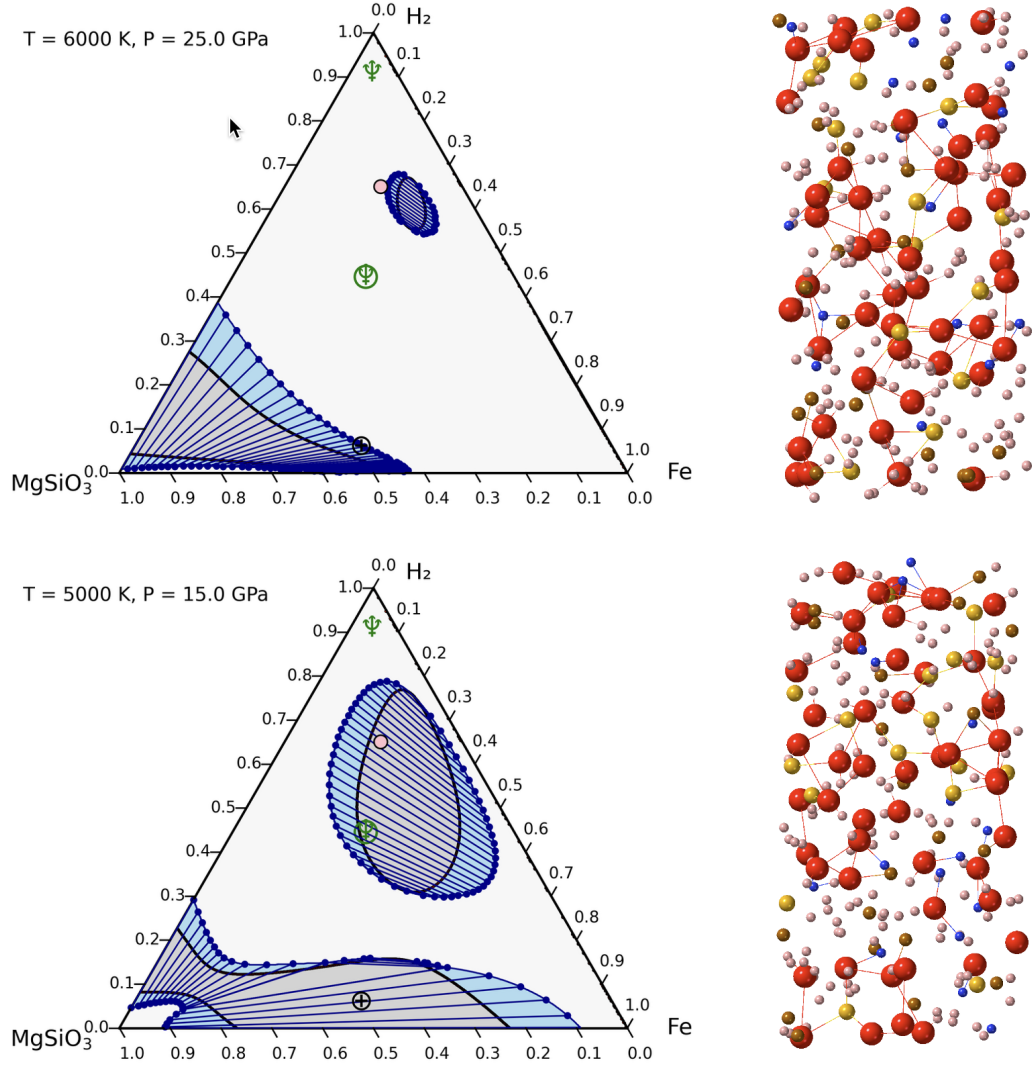


Figure 5.5: Preliminary ternary two-phase tests in the MgSiO_3 –Fe– H_2 system. Left: predicted ternary phase diagrams at the pressure and temperature of each simulation, with the simulated bulk composition marked by a pink point. Right: representative final atomic configurations from the corresponding DFT-MD simulations.

Visual inspection of the final configurations suggests that both ternary simulations erode

the initially imposed two-phase geometry. In the higher-temperature, higher-pressure simulation, the initially Fe–H-rich and MgSiO₃-rich regions lose compositional contrast rapidly and approach a more homogeneous mixed state. In the lower-temperature, lower-pressure simulation, the loss of contrast is slower, and remnants of the initial Fe-rich and silicate-rich regions remain visible over the same general stage of the run. However, this lower-T/P case also does not preserve a sharply defined, persistent interface. A stable Gibbs dividing surface could not be robustly identified because the two sides of the simulation cell became too compositionally similar. We therefore interpret both ternary tests as exhibiting near-miscible or evolving one-phase behavior on the simulated timescale, with the lower-T/P case approaching that state more slowly.

5.5.1 Density Profiles and Finite-Time Mixing Diagnostics

To quantify the compositional contrast seen in the ternary simulations, we apply the species-resolved density-profile analysis described above. For each simulation, we compute number-density profiles along the z direction and fit them with the hyperbolic tangent form in Equation 5.12. Here we focus on the cumulative 0–3000 timestep window, corresponding to 1.5 ps of simulation time, so that the two simulations can be compared over the same interval.

The tanh fits provide plateau densities for each species on the two sides of the simulation cell, as well as an estimate of the width of the transition between them. For the ternary tests, we use the fitted plateau densities to define a finite-time density-contrast ratio,

$$D_i = \frac{\rho_{i,\text{rich}}}{\rho_{i,\text{poor}}}, \quad (5.13)$$

where $\rho_{i,\text{rich}}$ and $\rho_{i,\text{poor}}$ are the larger and smaller fitted plateau densities for species i in the selected time window. This quantity is not intended to be an equilibrium partition coefficient. Instead, it provides a compact measure of how much compositional contrast remains between

the initially distinct regions. Values of D_i near unity indicate that species i is distributed relatively uniformly through the cell, while larger values indicate stronger concentration of that species in one region. Large values of D_i should be interpreted cautiously because they can result from very small fitted densities in the species-poor region, especially for species with small atom counts.

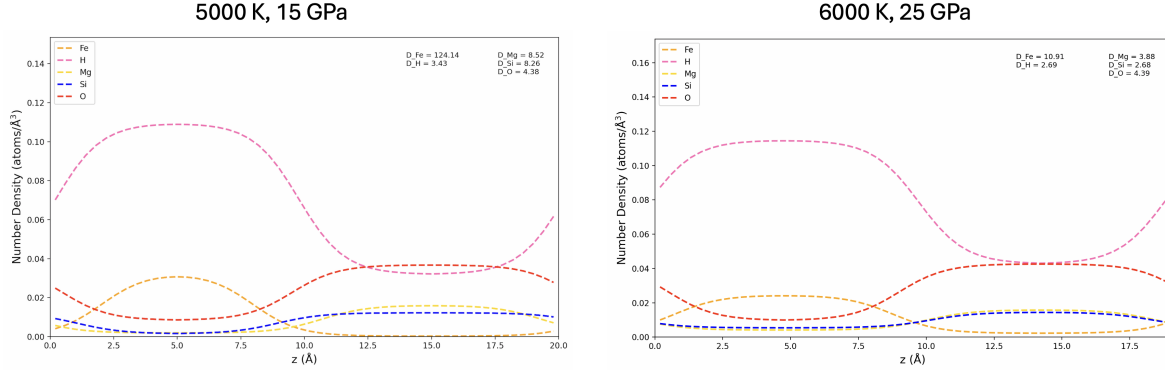


Figure 5.6: Hyperbolic tangent fits to species-resolved number-density profiles for the preliminary ternary $\text{MgSiO}_3\text{--Fe--H}_2$ simulations, evaluated over the cumulative 0–3000 timestep window (1.5 ps). The fits are used to compare finite-time compositional contrast between the initially Fe–H-rich and MgSiO_3 -rich regions. The higher-temperature, higher-pressure simulation shows lower density contrast for Fe, H, Mg, and Si, consistent with more rapid approach toward a mixed state.

The fitted profiles show that the higher-temperature, higher-pressure simulation is more mixed at 1.5 ps than the lower-temperature, lower-pressure simulation. The clearest differences appear in Fe, H, Mg, and Si. For Fe, the fitted interfacial width increases from 5.94 Å in the low-T/P simulation to 8.04 Å in the high-T/P simulation, while the density-contrast ratio decreases from $D_{\text{Fe}} = 124$ to $D_{\text{Fe}} = 10.9$. The large value of D_{Fe} in the low-T/P simulation reflects the very small fitted Fe density in the Fe-poor region and should not be interpreted as an equilibrium partition coefficient. Instead, it indicates that Fe remains more strongly concentrated on one side of the simulation cell over this finite time window. The

lower value of D_{Fe} and the broader fitted Fe interface in the high-T/P case indicate greater Fe transport away from the initially Fe-rich region.

Hydrogen also becomes more uniformly distributed in the high-T/P case, with D_{H} decreasing from 3.43 to 2.69. The silicate cations show an even stronger response: D_{Mg} decreases from 8.52 to 3.88, and D_{Si} decreases from 8.26 to 2.68. These changes indicate that the initially MgSiO_3 -rich region loses compositional contrast more rapidly in the higher-temperature, higher-pressure simulation. Oxygen shows the weakest sensitivity to pressure and temperature, with $D_{\text{O}} = 4.38$ in the low-T/P simulation and $D_{\text{O}} = 4.39$ in the high-T/P simulation.

Our density-profile analysis supports the qualitative impression from the final simulation states. Over the first 1.5 ps, both ternary simulations lose compositional contrast, but the higher-temperature, higher-pressure simulation does so more rapidly. The lower-temperature, lower-pressure simulation retains larger finite-time density contrasts, especially for Fe, Mg, and Si, but the inability to define a robust Gibbs dividing surface suggests that this contrast does not correspond to a sharply defined equilibrium two-phase interface. Instead, both simulations appear to be evolving toward near-miscible or one-phase behavior on the simulated timescale.

5.5.2 Discussion and Future Work

These preliminary ternary simulations provide useful tests of the predicted phase behavior, but they do not yet determine equilibrium ternary coexistence compositions. The initial two-fluid geometry is a simplified representation of the full ternary phase diagram, and the starting compositions are not expected to lie exactly on the equilibrium tie lines. If a simulated bulk composition lies deep in a predicted two-phase region, the precise choice of starting fluids may be less important because the mixture should retain or develop compositional contrast. Near a binodal or near-miscible regime, however, the finite simulation time and the initial geometry may strongly influence the observed behavior.

Finite-size effects are also important. The number of Fe and Mg atoms in the current simulations is small, so the fitted plateau densities can be sensitive to individual atomic motions. The interfaces also occupy a significant fraction of the simulation cell, and periodic boundary conditions couple the two interfaces. These limitations make it difficult to determine whether a slowly mixing simulation has reached a true two-phase equilibrium state or is still evolving toward a homogeneous fluid. In the present simulations, the lack of a robust Gibbs dividing surface provides an additional indication that the apparent finite-time compositional contrast should not be interpreted as a well-defined equilibrium interface.

For these reasons, we interpret the ternary simulations as preliminary, finite-time tests of the phase diagram rather than as a complete validation of the ternary model. The present results suggest that both ternary simulations evolve toward near-miscible or one-phase behavior on the simulated timescale. The higher-temperature, higher-pressure case mixes more rapidly, while the lower-temperature, lower-pressure case retains stronger finite-time compositional contrast but does not preserve a clearly defined Gibbs dividing surface. Longer trajectories and larger simulation cells will be needed to determine whether the apparent compositional contrast continues to decay, whether any long-lived two-phase state emerges, and whether the final compositions approach the tie lines predicted by the ternary phase diagram.

A more robust test of the ternary phase diagram will likely require methods that extend beyond direct DFT-MD alone. One promising direction is the use of DFT-trained machine-learning interatomic potentials, which could make it possible to simulate larger cells and longer trajectories while retaining a connection to first-principles energetics. Such simulations would allow the interfaces to be better separated from their periodic images, provide larger plateau regions for measuring coexisting compositions, and make it possible to test whether the long-time compositions converge toward a homogeneous composition or toward the tie lines predicted by the thermodynamic model. In this way, the present DFT-MD calculations provide a starting point for future larger-scale simulations that can more rigorously

evaluate the $\text{MgSiO}_3\text{--Fe--H}_2$ phase diagram.

5.6 Conclusions

In this chapter, we examined the phase stability of the $\text{MgSiO}_3\text{--Fe--H}_2$ system as a model for hydrogen-bearing, iron-bearing magma oceans in sub-Neptune interiors. The motivation for this work is that standard differentiated interior models assume an Fe-rich core separated from a silicate mantle, while recent models of sub-Neptune interiors suggest that silicates, hydrogen, and iron may interact chemically under the relevant pressure–temperature conditions. Whether Fe-rich and silicate-rich liquids remain separated or become miscible has direct implications for the density, composition, and evolution of the condensed interior.

We first reviewed the thermodynamic framework used to construct the ternary phase diagram. The model is based on the Gibbs free energy of mixing and is built from three bounding binary systems: $\text{MgSiO}_3\text{--H}_2$, $\text{MgSiO}_3\text{--Fe}$, and Fe--H_2 . The $\text{MgSiO}_3\text{--H}_2$ relation describes the transition between a miscible supercritical silicate–hydrogen fluid and coexisting silicate-rich and hydrogen-rich phases. The $\text{MgSiO}_3\text{--Fe}$ relation is approximated using the better-constrained MgO--Fe system, and the Fe--H_2 relation is constrained by experimental and first-principles studies of hydrogen solubility in Fe-rich liquid. Together, these binary relations define the ternary Gibbs free-energy surface used to predict one-phase and two-phase regions, spinodals, binodals, and tie lines.

We then described two-phase DFT-MD simulations as direct tests of selected phase relations. The $\text{MgSiO}_3\text{--H}_2$ binary simulations bracket the predicted binodal: the lower-temperature case remains separated, while the higher-temperature case becomes fully mixed. The $\text{MgSiO}_3\text{--Fe}$ binary simulation becomes miscible at a condition where the MgO--Fe proxy predicts one-phase behavior, providing a useful consistency check on the approximation used in the ternary model. These binary tests support the qualitative phase relations used as the basis for the $\text{MgSiO}_3\text{--Fe--H}_2$ phase diagram.

Finally, we presented preliminary ternary two-phase simulations in which an Fe–H liquid and an MgSiO_3 liquid are placed in contact. These tests are more difficult to interpret than the binary simulations because the predicted coexisting ternary phases are not pure endmembers and the equilibrium tie-line compositions are not known *a priori* from first-principles simulations. Nevertheless, the simulations provide a useful first test of whether the initial Fe-rich and silicate-rich character of the cell is retained or erased. Both ternary simulations lose compositional contrast over the first 1.5 ps of simulation time. The higher-temperature, higher-pressure simulation mixes more rapidly, while the lower-temperature, lower-pressure simulation retains larger finite-time density contrasts but does not preserve a robust Gibbs dividing surface. These results suggest that both tested conditions are near miscible or evolving toward one-phase behavior on the simulated timescale.

The ternary results remain preliminary. The current simulations are limited by short run times, small numbers of Fe and Mg atoms, and finite-size effects associated with the two interfaces in a periodic cell. The density-contrast ratios extracted from hyperbolic tangent fits should therefore be interpreted as finite-time diagnostics of mixing, not as equilibrium partition coefficients. A more complete test of the ternary phase diagram will require longer trajectories, larger simulation cells, and additional compositions chosen relative to the predicted binodals, spinodals, and tie lines.

Despite these limitations, the simulations presented here provide an initial first-principles test of the idea that metal, silicate, and hydrogen may become increasingly miscible under sub-Neptune interior conditions. The results support a picture in which the persistence of an Earth-like Fe-rich core is not determined by iron abundance alone, but also by the pressure, temperature, hydrogen content, and phase stability of the surrounding magma ocean. These findings motivate further first-principles exploration of MgSiO_3 –Fe– H_2 liquids and provide a thermodynamic foundation for understanding whether sub-Neptune interiors remain differentiated or evolve toward chemically mixed condensed interiors.

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