Phonon Dispersions Of Nonmagnetic Bcc Iron At High Pressures From Ab Initio Molecular Dynamics And Harmonic Ensemble Lattice Dynamics

Valeria Itzel Arteaga Muniz
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PHONON DISPERSIONS OF NONMAGNETIC BCC IRON AT HIGH PRESSURES
FROM AB INITIO MOLECULAR DYNAMICS AND HARMONIC ENSEMBLE
LATTICE DYNAMICS

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PHONON DISPERSIONS OF NONMAGNETIC BCC IRON AT HIGH Pressures
FROM AB INITIO MOLECULAR DYNAMICS AND HARMONIC ENSEMBLE
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by

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THESIS
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The University of Texas at El Paso
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of the Requirements
for the Degree of

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Abstract

Numerous computational and experimental studies on the crystal structure of metals near the melt line, indicate the body-centered cubic (bcc) structure can be favored over other crystal phases at lower temperatures [1]-[4] and even in cases in which other crystal structures are thermodynamically more stable, bcc may nucleate first from the melt, at rapid cooling rates [5]. Iron (Fe) is a polymorph metal, with a bcc ferromagnetic structure at ambient conditions. Even though the phase diagram of Fe is well known at relatively low pressures, there is currently no consensus on the crystal structure of Fe below the melt line at pressures relevant to Earth’s inner core conditions and at the inner core boundary (ICB), regions at which the hexagonal-closed-packed structure has been found to be the most stable phase from static [6] and dynamic experiments [7]. Current disagreements between experimental observations, and computational calculations can be attributed to the dynamical stability of other structures prior to melting. In this work, the stability of the bcc structure of Fe at pressures in the range of 140-300 GPa is studied by computing the temperature dependent phonon dispersions of the non-magnetic bcc phase of Fe since at these high pressures the atomic magnetic moments can safely be taken to be zero [8]. The temperature-dependent phonon frequencies are calculated employing quantum molecular dynamics (QMD) and a recently developed lattice-dynamics approach, called Harmonic Ensemble Lattice Dynamics (HELD) [9] that allows the computation of the temperature-dependent interatomic force constants needed to obtain the phonon dispersions. While non-magnetic bcc Fe is known to be unstable at low temperatures, we show that temperature is key in mechanically stabilizing the bcc structure at high pressures and that regular quasi-harmonic lattice dynamics fail to capture the correct phonon dispersions and tetragonal distortions. The phase diagram obtained by means of these lattice dynamics calculations as well as observed trends in the temperature-dependent phonon frequencies will be presented.


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Iron (Fe) is one of the most common elements on the planet, and its discovery changed the course of history. It is a versatile material with a wide range of applications, primarily in the metallurgical industry. Now we know that the benefits of steel to early man and modern civilizations are due to the polymorphism of Fe, which is uncommon in other materials. Fe also plays an important role in the planetary sciences, as the one of the main constituents of the Earth’s core [9]. Although it is well known that Fe prevails in the inner core, knowledge of the arrangement of the atoms at such conditions remains a challenge.

The stable phase of Fe at room temperatures and pressures has a body-centered cubic (bcc, \(\alpha\) phase) crystal structure, in which spins are organized to produce a ferromagnetic state. The spins take random orientations above the Curie temperature (1043 K) and the total magnetic moment in the system is zero. It undergoes the first structural transition from the \(\alpha\) to the \(\gamma\) structure, which is face-centered cubic, at around 1185 K. (fcc). Another bcc structure (\(\delta\)) reappears at 1667 K before melting at 1811 K. Around 10 GPa and 0 K, the magnetism is suppressed and a transition to a hexagonal closed-packed structure (hcp, \(\epsilon\)) takes place. The phase diagram in this relatively low pressure regime is shown in Fig. 1.1.
The aforementioned transformations can be understood in the framework of Thermodynamics. The stable phase of a material at temperature $T$ is the one that minimizes the Helmholtz free energy.

In 1978 Alexander and McTague [1] proposed that, from very general symmetry considerations, the bcc crystal structure was favored near the meltline in some of the transition metals. Starting from that premise, a lot of work has been done to study possible bcc stabilization before melt in several materials over the periodic table. In 2010, Hernandez and Rodriguez-Prieto [24] analyzed that for Lithium (Li) by calculating the melting temperature of the bcc and fcc structures in a range of pressure from around 8 to 30 GPa, and their findings suggested that there must exist a narrow region of stability of the bcc separating the fcc from the liquid. In 2017, Lu et. Al., [31] studied the hcp-bcc transition in Beryllium (Be), and showed that even though the material assumes a hcp structure at relatively low pressures, the bcc structure is dynamically stabilized with increasing temperature by evaluation of the free energy between the two structures. Their proposed phase diagram is shown in Fig. 1.2.
In 2019, Xian et. Al., [44] investigated as well the hcp-bcc transition for the same material but at higher temperatures and pressures. By a correct incorporation of anharmonicity from MD and a direct study of the lattice dynamics, they demonstrated that even though hcp structure is energetically more favorable in a particular regime at high pressures, the bcc structure was stable in a wide range of pressure. In 2021, Sadigh et. Al. [37], studied non-equilibrium processes during solidification in Copper (Cu) which in its solid phase takes the fcc structure. Using large-scale molecular dynamics and large cooling, they were able to observe that Cu re-solidifies in the bcc structure just before the meltline and that this structure grows outside of the region of its thermodynamic stability.

As a result, lattice vibrations in crystals must be properly incorporated and studied. The theory of lattice dynamics provides a model to evaluate the vibrations in crystalline
structures. One of the main steps in any lattice dynamics calculations has to do with the correct computation of the interatomic force constants (IFC) of the material that allow to obtain information to assess lattice instability, e.g. through phonon dispersions. There are methods that incorporate finite temperature effects such as the temperature dependent effective potential (TDEP) [23], in which sets of displacements and forces from molecular dynamics are used to fit the coefficients in an effective lattice dynamical Hamiltonian. The method used in this work, harmonic ensemble lattice dynamics (HELD), also provides a framework to investigate the dynamics of the lattice by using forces and atomic displacements from molecular dynamics. One of its functionalities lies in computing sets of best-fits temperature-dependent force constants at each snapshot of the MD simulation, allowing the computation of instantaneous IFC, and the obtention of a heatmap that shows the phonon dispersions at all steps in the simulation.

This work will use Fe as a benchmark to investigate the lattice vibrations of the bcc structure at pressures around that of the Earth’s core in which the magnetic moment is suppressed by such high pressures [40]. In the pressure-temperature regime studied here, the ε (hcp) phase is known to be the most stable phase from static compression experiments [41], and from static laser-heated diamond anvil cell [4]. The high pressure melting curve and phase diagram of Fe has been studied using shock waves by Refs. [12] ([7] in Fig. 1.3), [45] ([5] in Fig. 1.3). Laser-heated diamond anvil cell experiments have also assisted the calculation of the melting curve for Fe at high pressures [10] ([8] in Fig. 1.3). As can be seen from Fig. 1.3, there is an enormous discrepancy between the meltlines and melting points at the inner core boundary (ICB) (330 GPa) from the above references. In order to better understand this uncertainty in the experimental results for the meltline and melting point at the ICB, several work has been done in the theoretical side with e.g. ab initio coexistence simulations [3] ([14] in Fig. 1.3) and with Monte Carlo free-energy simulations [39] ([15] in Fig. 1.3).
The dynamical stability of other structures prior to melting may be one of the causes of the huge discrepancy in the melting temperatures \[11\] reported by the different methods mentioned above. While nonmagnetic Fe is known to be mechanically unstable at low temperatures and pressures \[22\], there is currently no experimental evidence that a nonmagnetic bcc phase can thermodynamically be stable at high pressures near the meltline. In this work, we will use Ab initio molecular dynamics simulations based on Density Functional Theory (DFT), coupled with HELD to obtain temperature-dependent frequencies that allow the evaluation of the phonon dispersions in order to understand how temperature and pressure stabilize mechanically the bcc structure at the Earth’s core conditions.

The structure of this thesis is as follows: In chapter 2, I will introduce a general overview of the concepts implemented for the methods used to study vibrations in crystals such as direct and reciprocal lattice, the implications of Bloch’s theorem, the Harmonic model, phonon thermodynamics, the quasiharmonic model, and finally anharmonicity. In Chapter
3. I describe the method we use for the computation of force constants used later to study lattice vibrations. In Chapter 4, a broad explanation of the solution to the electronic structure problem, which is the one implemented in the HELD method used in this thesis, is provided and detailed. In Chapter 5, the phonon dispersions of the high temperature bcc Fe are shown, and the phase diagram we mapped is displayed. In Chapter 6, I summarize the conclusions and findings.
Chapter 2

Lattice Dynamics and Anharmonicity: Fundamental Concepts

2.1 Direct and Reciprocal Space

An ideal infinite crystal consists of a unit or basis (in this case, individual atoms) located at the points where a Bravais lattice may appear. A Bravais lattice is an infinite, periodic array of atoms arranged so that the array is the same regardless of the point of view of the discrete points. Mathematically this lattice can be represented by a vector

\[ \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \] (2.1)

where \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_3 \) are three non-coplanar vectors called primitive vectors, that generate or span the lattice and \( n_1, n_2 \) and \( n_3 \) can range over all integers. Equation (2.1) can also be considered the ideal position of the atoms in the Bravais lattice when there is no thermal contribution to displace the atoms from equilibrium. There is some particular interest in crystal structures such as the body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal closed-packed (hcp), given that a lot of metals and materials resemble these phases in nature. However, for the sake of this work, we will focus our efforts to the bcc (delta) and fcc (gamma) phases of Fe, which are paramagnetic. In the case of a bcc structure, a particular choice of the primitive vectors is as follows

\[ \mathbf{a}_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}) \quad \mathbf{a}_2 = \frac{a}{2}(\hat{x} + \hat{z} - \hat{y}) \quad \mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}) \] (2.2)
In the case of fcc, the primitive vectors can be taken as

\[ a_1 = \frac{a}{2}(\hat{y} + \hat{z}) \quad a_2 = \frac{a}{2}(\hat{z} + \hat{x}) \quad a_3 = \frac{a}{2}(\hat{x} + \hat{y}) \]  

(2.3)

There is a specific choice of a volume of the Bravais lattice containing a single lattice point known as the primitive cell. One can write a primitive cell as a linear combination of the three primitive vectors \( a_1, a_2 \) and \( a_3 \) as

\[ \mathbf{r} = x_1 a_1 + x_2 a_2 + x_3 a_3 \]  

(2.4)

where the \( x_i \)'s vary from 0 to 1, which is the parallelepiped spanned by the three primitive vectors \( a_i \). One disadvantage of using the primitive cell convention is that it does not display the full symmetry of the Bravais lattice. To avoid the inconvenience, one can construct a primitive cell called the Wigner-Seitz cell, a region of space closer to a specific lattice point than any other region in the cell. Given the periodicity of the Bravais lattice specified in Eq. (2.1), there is a specific set of vectors \( \mathbf{K} \) that have the same periodicity as a set of Bravais points specified above that satisfy

\[ e^{i\mathbf{K} \cdot \mathbf{R}} = 1 \]  

(2.5)

for all \( \mathbf{R} \) in the Bravais lattice. Any vector \( \mathbf{k} \) in the reciprocal, or k-space, can be written as a linear combination of three reciprocal vectors \( b_1, b_2, b_3 \) as

\[ \mathbf{k} = k_1 b_1 + k_2 b_2 + k_3 b_3 \]  

(2.6)

The importance of the reciprocal space convention lies on the fact that the diffraction patterns used to visualize the crystal structure of materials is represented in this k-space.

### 2.2 Bloch’s Theorem

Given that ions in a crystal at 0K are arranged periodically, the potential felt by the atoms is also periodic, with \( \mathbf{R} \) being the interatomic distance

\[ U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}) \]  

(2.7)
for all Bravais vectors \( \mathbf{R} \). Given the numbers of particles composing a crystal and and its particle-particle interactions, finding the wavefunctions needed to obtain information of the system is a difficult task to do. By approximating the problem to an independent electron, one can model all those interactions with an effective one-electron potential \( U(\mathbf{r}) \). We are led thus to examine the Schrödinger equation for a single electron

\[
\hat{H}\psi = \left( \frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right)\psi = \varepsilon\psi \quad (2.8)
\]

As a consequence of the periodicity of the potential \( U(\mathbf{r}) \), the stationary states or wavefunctions (solutions to Eq. 2.8), follow the Bloch’s theorem that states that the eigenstates corresponding to the Hamiltonian displayed in 2.8 can be written in terms of plane waves times a function with the periodicity of the Bravais lattice [5] in the form

\[
\psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}) \quad (2.9)
\]

since \( u(\mathbf{r} + \mathbf{R}) = u(\mathbf{r}) \) it follows

\[
\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r}) \quad (2.10)
\]

for every \( \mathbf{R} \) in the Bravais lattice.

### 2.3 Harmonic Model

The theory reviewed in the previous sections was restricted to a static model, where atoms are confined to their equilibrium Bravais points. However, when temperature effects arise in a material, the particles start to vibrate out of their equilibrium positions, and these vibrations give rise to interesting properties. A good approximation to start dealing with the dynamics is the harmonic model. In this section, we will use the Born-von Kármán model that assumes that the atoms or ions (nuclei) in a crystalline structure interact with each other via massless springs, to which ends periodic boundary conditions are applied to solve the set of linear equations that arise. The instantaneous position of an atom \( k \) in a unit cell \( l \) that deviates from its equilibrium position by \( \mathbf{u}_{lk} \) is given by [18]
\[ \vec{R}_{lk}(t) = \vec{r}_l + \vec{r}_k + \vec{u}_{lk}(t) \] (2.11)

The displacement vector \( \vec{u}_{lk} \) is labeled by Cartesian components \( u_{\alpha k} \), where \( \alpha = \{x, y, z\} \).

The potential energy of the system is \( \Phi \) is a function of the instantaneous displacements of the atoms and can be Taylor expanded about the equilibrium positions of the atoms, i.e., '. The expansion of the potential is of the following form:

\[ \Phi = \Phi_0 + \sum_{\alpha l k} \Phi_{\alpha l k} u_{\alpha l k} + \frac{1}{2} \sum_{\alpha l k} \sum_{\beta l' k'} \Phi_{\alpha \beta l k l' k'} u_{\alpha l k} u_{\beta l' k'} + \ldots \] (2.12)

where the coefficients are the derivatives of the potential with respect to the thermal displacements \( u_{\alpha l k} \)

\[ \Phi_{\alpha l k} = \frac{\partial \Phi}{\partial u_{\alpha l k}} \bigg|_0 ; \quad \Phi_{\alpha \beta l k l' k'} = \frac{\partial^2 \Phi}{\partial u_{\alpha l k} \partial u_{\beta l' k'}} \bigg|_0 \] (2.13)

The subscript 0 means that the derivatives are evaluated in \( \vec{u}_{lk}(t) = 0 \). The coefficient \( \Phi_{\alpha l k} \) above is the negative of the force acting on the \( \alpha \)-direction of atom \( k \) in the \( l \) cell at equilibrium. In the equilibrium configuration, however, the force of any atom should vanish \([33]\) and hence

\[ \Phi_{\alpha l k} = 0 \] (2.14)

In the Harmonic Approximation terms up to the one in Eq. 2.12 are considered. The second term in Eq. 2.13 can be written in matrix form as

\[ \Phi_{lk,lkr} = \begin{bmatrix} \phi_{xx} & \phi_{xy} & \phi_{xz} \\ \phi_{yx} & \phi_{yy} & \phi_{yz} \\ \phi_{zx} & \phi_{zy} & \phi_{zz} \end{bmatrix} \] (2.15)

where the elements are the force constants in the different orthogonal directions. The equations of motion in vectorial form and with the matrix given above are then

\[ m_k \ddot{u}_{lk}(t) = -\sum_{l' k'} \Phi_{lk l' k'} \vec{u}_{l' k'}(t) \] (2.16)
Applying boundary conditions, we assume solutions of the form of plane waves of the form

\[ \bar{u}_{l\kappa k_j}(t) = \frac{1}{\sqrt{m_k}} \bar{e}_{kj}(\bar{k})e^{i(\bar{k} \bar{r}_i - \omega_{kj} t)} \]  

(2.17)

where \( \bar{k} \) denotes a wavevector in the reciprocal space, \( \bar{e}_{kj}(\bar{k}) \) is a polarization vector, \( \omega_{kj} \) is the angular frequency and the index \( j \) labels specific branches. By substituting the plane wave anzats in the equations of motion, we obtain the problem is reduced to the eigenvalue problem [18]

\[ D(\bar{k})\bar{e}_j(\bar{k}) = \omega^2_{k,j}(\bar{k})\bar{e}_j \]  

(2.18)

where \( D(\bar{k}) \) is known as the dynamical matrix, and the elements are Fourier transforms of the force constant matrix. All the polarization vectors have been placed in a single vector \( \bar{e}_j(\bar{k}) \) that runs over all orthogonal directions and all the number of atoms in the cell. The frequencies \( \omega_{k,j} \) can be found by diagonalizing the dynamical matrix.

### 2.4 Monoatomic Chain of Atoms; Normal Modes

![Equilibrium positions of ions located at na. The gray dots depict the out-of-equilibrium positions that the ions can take](image)

(2.1)

We will review a particular case of the above mentioned problem of vibrations in the crystal. Consider a linear chain of ions with mass \( M \) separated a distance \( a \), so that the Bravais
vectors are $\mathbf{R} = na$ as in figure 2.1. Now let $u(na)$ be the displacement from the equilibrium position $na$. Assuming just neighboring atoms interact, the potential energy due to this interaction is governed by

$$U^{\text{harm}} = \frac{1}{2} K \sum_n [u(na) - u([n + 1]a)]^2$$

(2.19)

$K$ being the force constant for this problem. By using Hooke’s law, the equations of motion have the form

$$M \ddot{u}(na) = -\frac{\partial U^{\text{harm}}}{\partial u(na)} = -K[2u(na) - u([n - 1]a) - u([n + 1]a)].$$

(2.20)

A usual trick for long finite chains is to join the two ends back together with other springs interacting with the internal ions. This particular choice is called the Born-von Kármán boundary conditions. If the ions occupy sites $a, 2a, ..., Na$, then the periodic boundary condition is

$$u([N + 1]a) = u(a); \quad u(0) = u(Na).$$

(2.21)

We know that the solution to the harmonic equation has the form of sinusoidal waves [15], hence, we expect the solution of the system to be in the form of traveling waves of the form

$$u(na, t) \propto e^{i(kna - \omega t)},$$

(2.22)

where $k$ is any wavevector, and $\omega$ is the angular frequency. Applying periodic boundary conditions to Eq. 2.9,

$$e^{ikNa} = 1$$

(2.23)

which implies

$$k = \frac{2\pi}{a} \frac{n}{N}$$

(2.24)

$n$ being an integer. Substituting 2.19 in 2.16, we have

$$-M\omega^2 e^{i(kna - \omega t)} = -K \left[2 - e^{-ika} - e^{ika}\right] e^{i(kna - \omega t)}$$

$$= -2K(1 - \cos ka)e^{i(kna - \omega t)}.$$  

(2.25)
It follows from here that

$$\omega(k) = 2\sqrt{\frac{K}{M}} |\sin \frac{1}{2} ka|.$$  \hspace{1cm} (2.26)

Figure 2.2 depicts the dispersion relation $\omega(k)$ given in Eq. 2.24.

Figure 2.2: Dispersion relation for a one-dimensional monoatomic chain of ions

In the long wavelength limit, one can take $k \rightarrow 0$ to find a linear dependence on $\omega$ to $k$

$$\omega = \left( a \sqrt{\frac{K}{M}} \right) |k|.$$  \hspace{1cm} (2.27)

which allows to calculate the wave velocity $c = \frac{\omega}{k}$ equivalent to the sound velocity in the crystal

$$c = \frac{\omega}{k} = a \left( \sqrt{\frac{K}{m}} \right).$$  \hspace{1cm} (2.28)

Because of this similarity to the sound velocity, the dispersion in Figure 2.2 is known as an acoustic mode.
2.5 Phonons and Thermodynamics

The previous sections described a classical model that studies vibrations in crystals and connects the symmetry in a lattice with the normal modes of vibration of the crystal and the forces that drive those vibrational modes. However, even though it helps to get an insight into what happens in materials, it is not an entirely correct theory because it does not include temperature. One evidence of this is the heat capacity. In the expansion of the potential energy, the $\Phi_0$ is the binding energy, and the following term describes the interaction of a system of three-dimensional independent harmonic oscillators. Thus, the specific heat of a system of $N$ atoms with $3N$ harmonic oscillators is, under the harmonic approximation

$$C_V = T \left. \frac{\partial S}{\partial T} \right|_V = 3N k_B$$

(2.29)

which is the Dulong and Petit limit and tells that is independent of temperature. However, experiments show that $C_v \to 0$ as $T \to 0$. This result indicates a need for other theories to correctly account for quantized vibrations that occur at small temperatures called phonons. Assuming now a quantum harmonic oscillator (QHO), in which vibrations are quantized with frequency $\omega_i$, the specific heat of $N$ independent QHO the following form

$$C_V = 3N k_B \left( \frac{\hbar \omega_i}{k_B T} \right)^2 \frac{\exp \left( \frac{\hbar \omega_i}{k_B T} \right)}{\left[ \exp \left( \frac{\hbar \omega_i}{k_B T} \right) - 1 \right]^2}$$

(2.30)

and $C_V \to 0$ as $T \to 0$, and at high temperatures recovers the constant value in Eq. 2.29. This implies then that lattice vibrations are quantized, and the quantum of vibrational energy is called a phonon. So analogous to photons, the particles of light, the particles of vibrational waves or vibrational modes are called phonons. It is common then to interchange between the particle and wave description, and usually vibrations in crystals are called phonons. Following this quantum description, the partition function for $3N$ independent QHO, with energies $\varepsilon_i$

$$Z_N = \prod_{i}^{3N} \frac{e^{-\beta \varepsilon_i/2}}{1 - e^{-\beta \varepsilon_i}}$$

(2.31)
and the free energy

\[ F_{\text{vib}} = \frac{1}{2} \sum_{i}^{3N} \varepsilon_i + k_B T \sum_{i}^{3N} \ln \left(1 - e^{-\beta \varepsilon_i}\right) \]  

(2.32)

From the derivative of the free energy with respect to the temperature \( T \), we can obtain the entropy arising from the vibrations or phonons,

\[ S_{\text{vib}} = k_B \sum_{i}^{3N} \left[ -\ln \left(1 - e^{-\beta \varepsilon_i}\right) + \frac{\beta \varepsilon_i}{e^{\beta \varepsilon_i} - 1} \right] \]  

(2.33)

For computational purposes, sometimes writing the vibrational entropy in terms of the phonon density of states (DOS) is often used \[18\]

\[ S_{\text{vib}}(T) = 3k_B \int_{0}^{\infty} g(\varepsilon) \left[ (n(\varepsilon) + 1) \ln(n(\varepsilon) + 1) - n(\varepsilon) \ln(n(\varepsilon)) \right] d\varepsilon \]  

(2.34)

with

\[ n(\varepsilon_i, T) = \frac{1}{e^{\beta \varepsilon_i} - 1} \]  

(2.35)

the Planck distribution that dictates the distribution of the quantos.

### 2.6 Quasiharmonic Approximation

The quasiharmonic approximation considers the harmonic approximation to treat the lattice dynamics at \( T=0K \). However, the temperature-dependent effects are incorporated by considering the effects of thermal expansion in a lattice. This theory assumes that the phonon modes should be volume dependent. One important thermodynamic relation that can be derived from this volume dependent incorporation is the phonon mode Gruneisen parameter

\[ \gamma_i = - \left. \frac{\partial \ln \omega_i}{\partial \ln V} \right|_T \approx - \frac{V \Delta \omega_i}{\omega_i \Delta V} \]  

(2.36)

defined in terms of the volume \( V \), and the phonon frequency \( \omega_i \). This mode gives information at the microscopic level of the vibrations in the crystal. A more commonly used
thermodynamic relation can be obtained by averaging this mode or from thermodynamic relations and its known as simply the Gruneisen parameter

$$\gamma = \frac{\alpha K_T}{C_v \rho} = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_S$$

(2.37)

where $K_T$ is the isothermal Bulk modulus, $\alpha$ the isothermal volume expansion, $C_v$ the heat capacity at constant volume and $\rho$ the atomic density. From thermodynamic relations as well, the thermal pressure at a particular $T$ can be expressed in terms of the Gruneisen parameter as

$$P_{th} = \gamma \frac{C_v T}{V}$$

(2.38)

### 2.7 Anharmonic Theory

The quasiharmonic approximation provides a framework to compute properties such as thermal expansion by incorporating the volume dependence of the phonon frequencies that are not well described by the harmonic approximation. However, even though it corrects some effects in the harmonic approximation, it still treats phonons as independent particles that do not interact. Because of this, the thermal conductivity predicted by this model and the harmonic model is infinite [18], and it does not indicate the shortening of phonon lifetimes.
Anharmonicity is the appropriate treatment of lattice vibrations at high temperatures. Demonstrations of anharmonic effects involve experiments on the interactions of two phonons to produce a third phonon at a frequency $\omega_3 = \omega_1 + \omega_2$ [27]. These processes are caused by third-order terms in the expansion of the potential energy of the crystal. Physically, the presence of one phonon causes a periodic elastic strain that modulates the crystal’s elastic constant in space and time. A second phonon feels the modulation of the elastic constant and is then scattered to produce a third phonon.

Retention of additional terms in expression 2.12 is needed for a more physical explanation of the interatomic interactions. However, the dimensionality of the coefficients for the force constants makes the calculations unfeasible. A qualitatively explanation of how to introduce anharmonic effects on a system was proposed by Hooton [26] supporting the Born-von Kármán model of lattice dynamics he claims that in a strongly anharmonic system (see Fig. 2.3, left, solid line), the harmonic potential is not a good fit anymore (dotted line), but as atoms vibrate and visit wider regions in space, a harmonic fit to the average positions and mean-square deviation is a good approximate (dashed line) [26].
The majority of modern methods that exist to account for anharmonicity in solids, follow Hooton’s idea and fit a potential to an average position and mean-square deviation. Since methods such as molecular dynamics are not restricted to harmonic forces, large-amplitude displacements can be sampled to allow the investigation of anharmonicity [18]. In this work, we will assess the anharmonicity of Fe at high temperatures using a newly developed model called Harmonic Ensemble Lattice Dynamics. Even though the force constants are calculated within the harmonic approximation, anharmonicity is inherently taken from molecular dynamics simulations.
Chapter 3

Harmonic Ensemble Lattice Dynamics

We can now obtain properties of materials in their ground state thanks to the advent of approximation theories like density functional theory. Calculating material properties at finite temperatures, however, remains a challenge. The quasiharmonic approximation (QHA) allows one to compute material properties by introducing a volume dependency of phonon frequencies while assuming a temperature-independent potential energy surface. However, although it analyzes some systems effectively, it fails to do so for anharmonic systems.

We offer a new way to explore phonon dispersions of materials at finite temperatures, because anharmonicity is intrinsically incorporated in molecular dynamics simulations. The methodology is explained in this Chapter.

3.1 Models

The Harmonic Ensemble Lattice Dynamics (HELD) method uses the Born-von Karman approach revised in Chapter 2 and treats the lattice dynamics within the harmonic approximation. Following the notation described in [14], the instantaneous position of the \( kth \) atom in the unit cell \( l \) that deviates by \( u^{a}_{\ell k} \) from its equilibrium position in the \( a \) direction is

\[
\vec{R}^{a}_{\ell k} = \vec{r}^{a}_{\ell k} + \vec{u}^{a}_{\ell k}
\]  

(3.1)
\[ \Phi = \Phi_0 + \sum_{a} \Phi_{0}^{a} u_{\ell k}^{a} + \frac{1}{2} \sum_{a} \sum_{b} \Phi_{\ell k}^{ab} u_{\ell k}^{a} u_{\ell k}^{b} + \ldots \] (3.2)

where

\[ \Phi_{\ell k}^{a} = \frac{\partial \Phi}{\partial u_{\ell k}^{a}}|_{0} ; \quad \Phi_{\ell k}^{ab} = \frac{\partial^{2} \Phi}{\partial u_{\ell k}^{a} \partial u_{\ell k}^{b}}|_{0} ; \quad \Phi_{\ell k}^{abc} = \frac{\partial^{3} \Phi}{\partial u_{\ell k}^{a} \partial u_{\ell k}^{b} \partial u_{\ell k}^{c}}|_{0} \] (3.3)

\( a, b, c \) stand for the three different orthogonal directions \( x, y, z \). HELD considers terms up to the second derivative to incorporate interactions up to the harmonic approximation. The solutions to the equations of motion for the system described above are wave-like and have an associated frequency \( \omega \) and polarization. After solving the equations, the problem is reduced to find the following eigenvalues

\[ \tilde{D}(\bar{k}) \tilde{e}_{s}(\bar{k}) = \omega_{k,s}^{2} \tilde{e}_{s}(\bar{k}) , \] (3.4)

where the elements of the dynamical matrix \( \tilde{D}(\bar{k}) \) are the submatrices \( \tilde{D}_{\kappa \kappa'}(\bar{k}) \), which are the Fourier transforms of force constant matrices \( \Phi_{\ell k \ell' k'} \).
3.2 Force Constants

In order to finding the elements of the dynamical matrix in Eq. 3.4, HELD assumes a supercell of n atoms with periodic boundary conditions interacting in a pair-wise manner. Then, the interaction between atoms $i$ and $j$ can be represented by a matrix of force constants

$$D_{ij} = \begin{bmatrix} xx & xy & xz \\ yx & yy & yz \\ zx & zy & zz \end{bmatrix},$$

(3.5)

where the rows and columns represent the orthogonal directions $x, y$ and $z$. Each element of the matrix corresponds to two different directions $a$ and $b$, where $a, b \in \{x, y, z\}$. The element $[ab]_{ij}$ of the matrix $D_{ij}$ describes how the $b_j$ component of the displacement $\vec{P}_j$ of $j$ from its ideal lattice position $\vec{p}$ (written in $\ell_\ell$ notation as $\vec{r}_\ell$) changes the force $F_{i,a}$ exerted on particle $i$ in the $a$ direction \[14\], so

$$-\vec{F}_{ij} = D_{ij} \vec{P}_j$$

(3.6)

and

$$-F_{i,a} = \sum_{j,b} ([ab]_{ij} b_j) .$$

(3.7)

and is described in Fig. 3.2.

Figure 3.2: Pairwise interactions as described by the Born-von Kármán model
Table 3.1: Canonical ideal lattice position $\vec{p}$ of atom $j$ and force constant matrix $D_{ij}$ between pair of atoms $i$ (located at the origin) and $j$ in the zeroth (0NN) through fifth (5NN) coordination shell for the BCC crystal structure [14]

<table>
<thead>
<tr>
<th></th>
<th>0NN</th>
<th>1NN</th>
<th>2NN</th>
<th>3NN</th>
<th>4NN</th>
<th>5NN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\vec{p}$</td>
<td>$\frac{1}{2}a[0, 0, 0]$</td>
<td>$\frac{1}{2}a[1, 1, 1]$</td>
<td>$\frac{1}{2}a[2, 0, 0]$</td>
<td>$\frac{1}{2}a[0, 2, 2]$</td>
<td>$\frac{1}{2}a[3, 1, 1]$</td>
<td>$\frac{1}{2}a[2, 2, 2]$</td>
</tr>
</tbody>
</table>

$\begin{bmatrix}
\alpha_0 & 0 & 0 \\
0 & \alpha_0 & 0 \\
0 & 0 & \alpha_0 \\
\end{bmatrix}$

$\begin{bmatrix}
\alpha_1 & \beta_1 & \beta_1 \\
\beta_1 & \alpha_1 & \beta_1 \\
\beta_1 & \beta_1 & \alpha_1 \\
\end{bmatrix}$

$\begin{bmatrix}
\alpha_2 & 0 & 0 \\
0 & \beta_2 & 0 \\
0 & 0 & \beta_2 \\
\end{bmatrix}$

$\begin{bmatrix}
\alpha_3 & 0 & 0 \\
0 & \beta_3 & \gamma_3 \\
0 & \gamma_3 & \beta_3 \\
\end{bmatrix}$

$\begin{bmatrix}
\alpha_4 & \gamma_4 & \gamma_4 \\
\gamma_4 & \beta_4 & \delta_4 \\
\gamma_4 & \delta_4 & \beta_4 \\
\end{bmatrix}$

$\begin{bmatrix}
\alpha_5 & \beta_5 & \beta_5 \\
\beta_5 & \alpha_5 & \beta_5 \\
\beta_5 & \beta_5 & \alpha_5 \\
\end{bmatrix}$

Figure 3.3: Nearest neighbors in a bcc lattice. The red, green, blue and magenta are the first, second, third and fourth nearest neighbors with respect to the black atom site [43].

Symmetry concerns affect the values of the elements in the $D_{ij}$ matrix, so some of them vanish or are equal to others. For a bcc cell, the nearest neighbors up to the fourth one are depicted in Fig. 3.3, and the force constants up to the fifth coordination shell are shown in Table 3.1. Since interatomic forces and positions are obtained from molecular dynamics (MD) runs, the code applies two transformation procedures to the matrix $D_{ij}$ to account
for the accommodation of specific MD outputs:

\[
[x, y, z] \rightarrow [y, x, z] \quad \Rightarrow \quad \begin{bmatrix} xx & xy & xz \\ yx & yy & yz \\ zx & zy & zz \end{bmatrix} \quad \begin{bmatrix} x & y & z \end{bmatrix} \quad \begin{bmatrix} yx & xy & xz \\ xx & yy & yz \\ zx & zy & zz \end{bmatrix} \quad \begin{bmatrix} y & x & z \end{bmatrix}
\]

\[R_1 \leftrightarrow R_2, \quad C_1 \leftrightarrow C_2\]  \hspace{1cm} (R1)

and

\[
[x, y, z] \rightarrow [-x, y, z] \quad \Rightarrow \quad \begin{bmatrix} xx & xy & xz \\ yx & yy & yz \\ zx & zy & zz \end{bmatrix} \quad \begin{bmatrix} -xx & -xy & -xz \\ -yx & yy & yz \\ -zx & zy & zz \end{bmatrix} \quad \begin{bmatrix} xx & -xy & -xz \\ -yx & yy & yz \\ -zx & zy & zz \end{bmatrix}
\]

\[R_1 \rightarrow R_1, \quad C_1 \rightarrow C_1\]  \hspace{1cm} (R2)

where \(R_1, R_2\) are rows and \(C_1, C_2\) are columns. After applying rules \(R1\) and \(R2\), the components of the force exerted on particle \(i\) by particles in, e.g., the fourth coordination shell are:

\[
-F_{i,x}^{4NN} = \alpha_4 x_{[3,1,1]} + \gamma_4 y_{[3,1,1]} + \gamma_4 z_{[3,1,1]} + \ldots + \beta_4 x_{[1,1,-3]} + \gamma_4 y_{[1,1,-3]} - \gamma_4 z_{[1,1,-3]}
\]

\[
-F_{i,y}^{4NN} = \gamma_4 x_{[3,1,1]} + \beta_4 y_{[3,1,1]} + \delta_4 z_{[3,1,1]} + \ldots + \gamma_4 x_{[1,1,-3]} + \beta_4 y_{[1,1,-3]} - \delta_4 z_{[1,1,-3]} \]  \hspace{1cm} (3.8)

\[
-F_{i,z}^{4NN} = \gamma_4 x_{[3,1,1]} + \beta_4 y_{[3,1,1]} + \beta_4 z_{[3,1,1]} + \ldots - \gamma_4 x_{[1,1,-3]} - \beta_4 y_{[1,1,-3]} + \alpha_4 z_{[1,1,-3]}
\]

In Eq. 3.8, each Greek letter represents a force constant, and the \(x, y, z[1,2,3]\) indicates a displacement in one of the orthogonal directions, with \([1,2,3]\) implying that the displacement is about the lattice ideal position \(\vec{p} = \frac{1}{2}a[1,2,3]\), with atom \(i\) at the origin.

Eq. 3.8 can be rewritten as

\[
-F_{i,a}^{4NN} = \alpha_4 u_{i,a}^a + \beta_4 u_{i,\beta_4}^a + \gamma_4 u_{i,\gamma_4}^a + \delta_4 u_{i,\delta_4}^a
\]

\[a = a_4\]  \hspace{1cm} (3.9)

where \(u_{i,a}^a\) is the sum of displacements to be multiplied by force constant \(\alpha_4\) to get the force along the direction \(a\) on particle \(i\) located at the origin due to displacements of particles in the fourth coordination shell about their ideal lattice positions. Corrections to the signs introduced by rules \(R1\) and \(R2\) are included in the \(u\) terms. The total force along \(a\) on particle \(i\) up to coordination shell \(NN\) is then

\[
-F_{i,a} = \alpha_0 u_{i,a_0}^a + \alpha_1 u_{i,a_1}^a + \ldots + \zeta_{NN} u_{i,\zeta_{NN}}^a
\]

\[a = a_4\]  \hspace{1cm} (3.10)
\( \zeta_{NN} \) being the final force constant matrix element of the last coordination shell \( NN \). Because the supercell’s total number of atoms is \( n \), the system of equations can be represented as a matrix product

\[
- \begin{bmatrix}
F_{1,x} \\
F_{1,y} \\
\vdots \\
F_{n,z}
\end{bmatrix} = \begin{bmatrix}
u_{1, a_0}^x & u_{1, a_1}^x & \cdots & u_{1, \zeta_{NN}}^x \\
u_{1, a_0}^y & u_{1, a_1}^y & \cdots & u_{1, \zeta_{NN}}^y \\
\vdots & \vdots & \ddots & \vdots \\
u_{n, a_0}^z & u_{n, a_1}^z & \cdots & u_{n, \zeta_{NN}}^z
\end{bmatrix} \begin{bmatrix}
\alpha_0 \\
\alpha_1 \\
\vdots \\
\zeta_{NN}
\end{bmatrix}
\] (3.11)

or in an abbreviated form,

\[
- \mathbf{\mathcal{F}} = \mathbf{C \mathcal{P}} .
\] (3.12)

In the method described in this section, the forces and displacements in Eq. 3.12, are obtained from molecular dynamics simulations, hence, the atoms will generally be out of their equilibrium positions. Since thermal disorder of the system affects the values of the pair force constants, \( \mathcal{P} \) is a vector of effective harmonic force constants. Suppose the size of the supercell is sufficiently large. In that case, the system will be overdetermined, and the force constants can be determined by computing the pseudoinverse of \( \mathbf{C} \), with \( \mathbf{\mathcal{P}} = -\mathbf{C}^{-1} \mathbf{\mathcal{F}} \), with the force constants being a best least-squares fit to the data. The next step is to find the elements of the dynamical matrix \( \mathbf{\tilde{D}(k)} \) as implemented by Parlinski.
Chapter 4

Ab initio Molecular Dynamics

4.1 Density Functional Theory: A Review

Materials are composed by nuclei and electrons, which interact via electrostatic Coulombic forces, giving rise to specific properties. The interaction at the quantum level between is governed by the Hamiltonian

\[ \hat{H} = -\sum_i^M \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_i^m \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_i^1 \sum_i^2 \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_i|} \]  

(4.1)

[28] where the upper case indices denote the nuclei coordinates and the lower case, the electronic coordinates. The first term in Eq. (4.1) corresponds hence to the kinetic energy of the nuclei-nuclei interaction, the second one is the kinetic energy associated with the electrons, the third one is the Coulombic interaction among the nuclei, the third one is associated with the Coulomb potential from the electrons and the last one is the Coulombic interaction between nuclei-electron.

The Born-Oppenheimer approximation allows us to treat the electronic and nuclei interactions separately by assuming that the nuclei is much heavier compared to the electrons, and hence, the electrons move much more faster than the nuclei. Hence, Eq. (4.1), can be written as

\[ \hat{H} = \hat{T} + \hat{V} + \hat{V}_{ext} \]  

(4.2)

where \( \hat{T} \) is the kinetic energy operator, \( \hat{V} \) is the potential energy operator of the electrons and \( \hat{V}_{ext} \) the corresponding potential energy operator of the nuclei. The knowledge of the system’s properties is reduced to solving the Schrödinger equation \[38\], i.e., finding the
wavefunction for
\[ \hat{H}\Psi_n(R, r) = E_n \Psi_n(R, r) \] (4.3)
where \( E_n \) are the energy eigenvalues and \( \Psi_n \) is the wavefunction. However, trying to solve it for an N-body system is an intractable problem, since the wave functions for a N-body system depend on at least \( 3N \) variables. There are methods and frameworks that can approximate the solution to the electronic density in the ground state and we will discuss the Kohn-Sham one for the sake of this work.

Since 1964, the two theorems [25] proposed by Hohenberg and Kohn laid the groundwork to tackle the parameterless solution to the above Hamiltonian by the introduction of density functional theory (DFT). In the first theorem, they propose that the external potential \( \hat{V}_{ext} \) is a unique functional of the electron density \( \rho(r) \), besides a constant [28], and therefore, the total energy must also be a unique functional of the electron density. The second theorem states that the true ground state electronic density corresponds to the electron density that minimizes the ground state of the functional. It follows that
\[ E[\rho(r)] = F[\rho(r)] + \int \rho(r)v_{ext}(r)dr \] (4.4)
where \( v_{ext}(r) \) is the external potential, \( E \) the total energy and \( F[\rho(r)] \) is a universal functional [28] independent of the external potential of the form
\[ F[\rho(r)] = \langle \Phi|\hat{T} + \hat{V}\rangle\Phi \] (4.5)
\( \Phi \) being the ground state wave function associated to the density \( \rho(r) \).

The formulation proposed by Hohenberg and Kohn although powerful, does not offer a way of computing the ground state density in practice. The problem at this point is the way to take the kinetic energy operator \( \hat{T} \) since its direct expression in terms of the electronic density is unknown. In 1965 Kohn and Sham [29] reformulated the problem of the system of interacting electrons to a fictitious non-interacting system of electrons, given that the wave function of such system is well known to be of the Slater determinant type. In this case, the kinetic energy of the system of non-interacting electrons (reference system)
is also known and has the form

\[ T_k = -\frac{\hbar^2}{2m} \sum_{i=1}^{\infty} f_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle \]  \hspace{1cm} (4.6)

where \( \varphi_i \) are the one-electron orbitals and \( f_i \) are the occupation numbers of such orbitals.

The problem is reduced thus to finding the electronic density of the fictitious system whose density must be the same as in the case of the interacting system. The corresponding ground state wave function associated to the electronic density for this problem, can be determined then by a determinant of single particle orbitals \( \varphi_i \). The conversion from the interacting to non-interacting system lies in the introduction of a exchange-correlation term in the universal functional that dictates the difference between the interacting and non-interacting systems

\[ F[\rho] = T_k[\rho] + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} d\text{dr}d\text{r'} + \tilde{E}_{\text{XC}}[\rho] \]  \hspace{1cm} (4.7)

where the first term corresponds to the kinetic energy of the non-interacting system, and the second one is the Hartree-Fock Coulombic interaction potential. With this in mind one can find the one-particle wave functions by solving

\[ \hat{H}_{KS} \varphi_i(r) = \epsilon_i \varphi_i(r) \]  \hspace{1cm} (4.8)

in an iterative fashion. The remaining problem is to device accurate approximations for the exchange correlation term.

### 4.2 Exchange-correlation Term

The general form of the exchange-correlation energy term is

\[ \tilde{E}_{\text{XC}}[\rho] = \int \rho(r)\bar{\epsilon}_{\text{XC}}[\rho(r)] d\text{r} \]  \hspace{1cm} (4.9)

where \( \bar{\epsilon}_{\text{XC}}[\rho(r)] \) is an average of the energy density. Commonly, \( \tilde{E}_{\text{XC}}[\rho(r)] \) is written in terms of the XC hole as where the XC hole, \( \tilde{\rho}_{\text{XC}}(r,r') \), as

\[ \bar{\epsilon}_{\text{XC}}[\rho] = \frac{1}{2} \int \tilde{\rho}_{\text{XC}}(r,r') \frac{d\text{dr'}}{|r-r'|} \]  \hspace{1cm} (4.10)
where $\tilde{\rho}_{XC}(r,r')$ is a fictitious charge depletion due to exchange and correlation effects coming from the Pauli exclusion principle and the Coulombic interactions [28]. Functionals try to model expression 4.9 by managing the XC hole in several ways and the first one appeared in the Hohenberg and Kohn original DFT paper [25], the Local Density Approximation (LDA). There are other common types of functionals that model the XC energy term such as Generalized Gradient Approximation (GGA), meta-Generalized Gradient Approximation(meta-GGA), hybrid functionals and non-local functionals. Frequently the exchange correlation term is divided in exchange and correlation energy densities. Within the LDA approximation, a commonly used correlation term is the one parametrized by Perdew and Zunger (1981) [36]. As for the GGA’s case, a common XC functional (or at least the one we will be using for the sake of this work) is the one developed by Perdew, Burke and Ernzerhof (1996) [34].

4.3 Pseudopotentials

The external potential $V_{ext}$ dictates the interactions of the electrons and nuclei. Electrons can be divided into valence, which are the outer-most electrons and can create chemical bonds, and core electrons which are strongly bound to the nuclei and can be treated as frozen orbitals [28]. Given that the core electrons do not actively participate in chemical bonding, their corresponding degrees of freedom can be eliminated by replacing the atomic nuclei with an effective point-like nucleus of charge $Z_N = Z + Z_{\text{core}}$, where $Z_{\text{core}}$ is the charge from the core electrons. This effective charge represents the nucleus and the core electrons together, significantly reducing the number of electrons treated and the number of the basis set. It is important to remark that the interaction between the core electrons and nuclei is not just the single Coulombic interaction in $V_{ext}$, but there is also a contribution from the screening of the nuclear charge by the core electrons.
4.4 Basis Set

Studying the electronic structure problems within the Kohn-Sham formulation requires a way to represent the wavefunction of one-electron orbitals. The first step is to expand the one-electron wavefunctions as basis set of orbitals $|\phi_i\rangle$

$$\varphi_j(r) = \sum_{\alpha=1}^{M} c_{j\alpha} \phi_\alpha(r) \quad (4.11)$$

where $j$ labels the wavefunction or band, the $\varphi_j$ are the single particle Kohn-Sham wavefunctions, $c_{j\alpha}$ are the coefficients of the expansion of $j$. The wavefunctions are solution to the Schrödinger equation, and thus they depend on energy values of the system that are the eigenvalues $\epsilon_j$. In crystalline structures in general, given the periodicity of the structure and thus of the potential, the Bloch’s theorem reviewed in previous chapters ensures that the wavefunction can be represented as a linear combination of function that ensures the periodicity of the cell. In that sense, Eq. 4.11 can be represented as

$$\varphi_j^{(k)}(r) = e^{ikr} \sum_{\alpha=1}^{M} c_{j\alpha}^{(k)} \phi_\alpha(r) = \sum_{\alpha=1}^{M} c_{j\alpha}^{(k)} \phi_\alpha^{(k)}(r) \quad (4.12)$$

where $k$ represents a vector in the Brillouin zone, and the basis functions are

$$\phi_\alpha^{(k)}(r) = e^{ikr} \phi_\alpha(r) \quad (4.13)$$

The periodicity mentioned above followed by the Bloch’s theorem allows then to naturally use plane waves as a basis set. Plane waves are solution to the Schrödinger equation, and in regions where the potential is nearly constant, a single plane wave is needed to solve the problem. However, in regions of the nuclei, the potential is no longer constant and a linear expansion of plane waves is required. Any periodic function in real space can be expressed as a Fourier transform of a function in reciprocal space.

$$u_k(r) = \int e^{ig^r} \tilde{u}_k(g) \, dg \quad (4.14)$$
with However, given the periodicity of such function only specific values of \( g = G \), with \( G \) the reciprocal lattice vectors are allowed and Eq. 4.12 can be written as

\[
\varphi_j^{(k)}(r) = e^{i k \cdot r} \sum_{G=0}^{\infty} C_{jk}(G) \phi_G(r) 
\]  

(4.15)

with

\[
\phi_G(r) = \frac{1}{\sqrt{\Omega}} e^{i G \cdot r} 
\]  

(4.16)

### 4.5 Ab initio Molecular Dynamics

Classical molecular dynamic (MD) provide trajectories of particles by integrating Newton’s equations of motion. The workflow is to set the interaction potential and the geometry of the system, and assign initial velocities and positions for the particles. After this, the forces are calculated as a gradient of the interatomic potential, and the equations of motion are integrated (e.g. Verlet algorithm) to obtain the time trajectories. The particle’s positions and velocities are updated, and information such as temperature, pressure and energy is stored, and the procedure is repeated for a desired number of steps. The method is the workhorse to studying vibrational material behavior. If a small time step is used in the integration of the equations of motion and a good enough force field describes the interactions between the particles, the methodology can be very accurate. Satisfying the second requirement is challenging since some empirical potentials used do not fully capture quantum behavior characteristic of atomic interactions.

In order to solve the above issue, more accurate methods have been proposed. One of them involves the calculation of the forces directly from the electronic structure. The forces for the classical nuclei degrees of freedom that are needed to sample trajectories over the phase space can be obtained by means of the Hellman-Feynman theorem [17] that states that the variation of the electronic energy with respect to a parameter \( \lambda \) can be expressed as the expectation value of the variation of the electronic Hamiltonian [28]:
\[
\frac{\partial \varepsilon_n(\lambda)}{\partial \lambda} = \left\langle \Phi_n(\mathbf{R}) \left| \frac{\partial \hat{h}_v(\lambda)}{\partial \lambda} \right| \Phi_n(\mathbf{R}) \right\rangle 
\]
for a specific value of \( \lambda = \mathbf{R}_I \),
\[
M_I \frac{d^2 \mathbf{R}_I(t)}{dt^2} = -\frac{\partial}{\partial \mathbf{R}_I} \left\langle \Phi(\mathbf{R}) \left| \hat{h}_v(\mathbf{R}) \right| \Phi(\mathbf{R}) \right\rangle - \frac{\partial V_{nm}(\mathbf{R})}{\partial \mathbf{R}_I}
\]
where,
\[
\hat{h}_v(\mathbf{R}, \mathbf{r}) = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 - e^2 \sum_{l=1}^{P} \sum_{i=1}^{N} \frac{Z_l}{|\mathbf{R}_l - \mathbf{r}_l|} + \frac{e^2}{2} \sum_{l=1}^{N} \sum_{j \neq l}^{N} \frac{1}{|\mathbf{R}_l - \mathbf{r}_j|}
\]
and,
\[
V_{nm}(\mathbf{R}) = \frac{e^2}{2} \sum_{l=1}^{P} \sum_{j \neq l}^{P} \frac{Z_l Z_j}{|\mathbf{R}_l - \mathbf{R}_j|}
\]
A feasible approach to compute those forces is to solve the electronic structure problem for the ground state e.g. with the Kohn-Sham formalism in the nuclear degrees of freedom. In that case we have
\[
\left\langle \Phi(\mathbf{R}) \left| \hat{h}_v(\mathbf{R}) \right| \Phi(\mathbf{R}) \right\rangle = E_{KS}[\rho](\mathbf{R})
\]
\[
= T_R[\rho] + \frac{1}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{XC}[\rho]
\]
\[
+ \sum_{l=1}^{P} \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r} - \mathbf{R}_l) d\mathbf{r} + \frac{1}{2} \sum_{l=1}^{P} \sum_{j \neq l}^{P} \frac{Z_l Z_j}{|\mathbf{R}_l - \mathbf{R}_j|}
\]
and the force obtained by deriving the above, noting that the only non-vanishing terms are the last two terms
\[
\mathbf{F}_l = -\frac{\partial E_{KS}[\rho](\mathbf{R})}{\partial \mathbf{R}_l}
\]
\[
= -\int \rho(\mathbf{r}) \frac{\partial v_{\text{ext}}(\mathbf{r} - \mathbf{R}_l)}{\partial \mathbf{R}_l} d\mathbf{r} + \sum_{j \neq l}^{P} \frac{Z_l Z_j \mathbf{R}_l - \mathbf{R}_j}{|\mathbf{R}_l - \mathbf{R}_j|^3}
\]
The integration of the above equations is know as first-principles or ab initio molecular dynamics and allows us to obtain the trajectories of particles over the phase space. In the Born-Oppenheimer molecular dynamics (BOMD) scheme, the system is ensured to remain in the Born-Oppenheimer potential energy surface throughout the propagation, with the electronic subsystem always in the ground state \[28\] and the equations needed to find the wavefunction \( \Phi(\mathbf{R}) \) are solved in each timestep of the simulation.
Chapter 5

Results

5.1 Equilibrium Parameters

Equilibrium calculations were performed for spin-polarized and non-spin-polarized bcc Fe as implemented in Quantum Espresso. Energy minimization was performed for each of the sets for different volumes, and the Birch-Murnaghan equation of state [8]:

\[
E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[ \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right]^3 B'_0 + \left[ \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V_0}{V} \right)^{\frac{3}{2}} \right] \right\}
\] (5.1)

was fitted to the data for both PBE [34] and PBEsol [35] functionals. In Eq. 5.1, \(V\) is a particular volume, \(V_0\) is the equilibrium volume, \(B_0\) is the Bulk modulus, and \(B'_0\) is the Bulk modulus prime.

In the case of the PBE functional the details of the calculations were selected based on convergence criteria with respect to the kinetic energy cutoff and the k-points. The optimum value for the kinetic energy cutoff was selected to be 71 Ry, and the charge density cutoff was set to be 496 Ry. The k-point mesh for the spin and non-spin-polarized calculations was 20x20x20. For the PBEsol functional the kinetic energy cutoff was set to 40 Ry, the cutoff for the charge density to 320 Ry and the convergence threshold for self-consistency was set to 1e-8 Ry. In the case of the spin-polarized calculation, a 25x25x25 k-point mesh was used, whereas for the non-spin-polarized calculation a 30x30x30 mesh was selected by a convergence criteria.

From the equations of state shown in Fig. 5.1, we obtained the lattice parameter, Bulk modulus, and Bulk modulus prime shown in Table 5.1 for the PBE functional.
Figure 5.1: Energy minimization curves for spin-polarized Fe and non-spin-polarized Fe at 0K using GGA functionals. The energy per atom for the two functionals was shifted to the experimental cohesive energy of Fe (4.28 eV/atom) [16]

Table 5.1: Equilibrium parameters of Fe as given by PBE

<table>
<thead>
<tr>
<th></th>
<th>Spin-polarized</th>
<th>Non-spin-polarized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter (Å)</td>
<td>2.83</td>
<td>2.77</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>187.44</td>
<td>256.91</td>
</tr>
<tr>
<td>Bulk modulus prime</td>
<td>4.98</td>
<td>4.63</td>
</tr>
</tbody>
</table>

The experimental lattice parameter for ferromagnetic Fe is 2.853 Å [19] and the bulk modulus is 168 GPa [27]. The percent errors between the theoretical and experimental values of the lattice parameter and bulk modulus are 0.8% and 11.57%, respectively.

Equilibrium values at 0 K for spin-polarized and non-spin-polarized Fe were also calculated using a PBE for solids functional [35] and can be found in 5.2. We can see that the lattice parameter obtained by means of the PBEsol functional, has an absolute error of 2.21
% compared with the experimental of 2.853 Å [19], but this issue has been encountered several times and has been reported in the literature as well [19]. The experimental Bulk modulus for bcc Fe is 168 GPa [27], and the percent error between this value and the one obtained theoretically by means of PBEsol is 111.81%.

Table 5.2: Equilibrium parameters of Fe as given by PBEsol

<table>
<thead>
<tr>
<th></th>
<th>Spin-polarized</th>
<th>Non-spin-polarized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter (Å)</td>
<td>2.79</td>
<td>2.76</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>355.84</td>
<td>461.24</td>
</tr>
<tr>
<td>Bulk modulus prime</td>
<td>3.11</td>
<td>1.86</td>
</tr>
</tbody>
</table>

A study of the equations of state for both functionals was performed for pressure as a function of volume to compare the values with experimental results e.g. [7], [6]. The results for both functionals can be found in Fig. 5.2.

Figure 5.2: EOS of pressure as a function of reduced volume for the PBE and PBEsol functionals - bcc magnetic Fe
The PBE functional is in good agreement with the results from Bancroft [6] and Barker [7] at relatively low pressures, i.e., in regions where the alpha phase is stable (below 15 GPa) before the epsilon (hcp) transition.

5.2 Phonon Dispersions for Spin-polarized and Non-spin-polarized bcc Fe at Relatively Low Pressures

Lattice dynamics of spin-polarized and non-spin-polarized bcc Fe were studied at relatively low pressures to understand the importance of magnetism stabilizing the bcc structure at relatively low pressures and temperatures. For the spin-polarized case, a 4x4x4 supercell of bcc Fe with 128 atoms was simulated using Quantum Espresso under the Born-Oppenheimer approximation to perform NVT molecular dynamics. The exchange-correlation interactions were modeled using a PBE for solids functional [35]. For this particular case, the optimum values for the kinetic energy and charge density cutoff were kept, so the kinetic energy cutoff was set to 40 Ry, the cutoff for the charge density to 320 Ry and the convergence threshold for self-consistency was set to 1e-4 Ry. The temperature of the system was controlled using a stochastic velocity rescaling thermostat [13] and set at 1043 K, the Curie temperature for Fe. For the thermostat, some test were run and it was found that the optimum parameter to achieve convergence of the temperature or thermalization, was nraise = 20. The volume of the simulation was picked to be the equilibrium value as obtained by doing energy minimization and fitting a Birch-Murnaghan equation of state as shown in 5.1, leading to a thermal pressure of approximately 7 GPa.
Figure 5.3: 
Phonon dispersions at particular steps of a MD simulation for spin-polarized Fe

Fig. 5.3 depicts the relation between the frequency $\omega_k$ and a wavevector $\vec{k}$ for the spin-polarized case. A total of 153 phonon dispersions were calculated and then aggregated. The top figure shows the aggregate of all the steps of the simulation. The lighter colors indicate areas where most of the dispersions are located. Darker or more diffuse colors indicate places where the dispersions per step wiggle more. The bottom figure in 5.3 displays the dispersions for just 50 steps of the simulation starting at step 100. We are interested in looking at steps almost at the end of the simulation to ensure that the system has reached thermodynamic equilibrium. The frequencies in the G-N direction can be compared by those obtained in Ref. [22] by Heine et al. in which the frequency for the longitudinal mode is of the order of 8.5 THz for Heine’s paper and ours is around 10.5 THz, around a 20% higher. In general, the structure of the dispersions is the same in both works. The interatomic force constants calculated using HEED follow Gaussian distributions for particular nearest neighbors, as shown in Fig. 5.2.
Figure 5.4: Distributions of the forces constants for 900 steps in the simulation of spin-polarized Fe at 1043 K. For some of the directions of the nearest neighbors, the distributions are Gaussian.
In Fig. 5.5, phonon dispersions for the non-spin-polarized system are shown. Opposite to the magnetic calculations, the nonmagnetic were computationally cheaper to achieve, and we obtained 1000 steps, each of them one femtosecond long. The top figure shows dispersions for all the steps simulated. The middle picture displays 100 dispersions starting at step 100 of the simulation. The last plot in Fig. 5.5 shows 100 dispersions starting at step 900 of the simulation.

Figure 5.5: Phonon dispersions at particular steps of a MD simulation for non-spin-polarized Fe

In Fig. 5.5, phonon dispersions for the non-spin-polarized system are shown. Opposite to the magnetic calculations, the nonmagnetic were computationally cheaper to achieve, and we obtained 1000 steps, each of them one femtosecond long. The top figure shows dispersions for all the steps simulated. The middle picture displays 100 dispersions starting at step 100 of the simulation. The last plot in Fig. 5.5 shows 100 dispersions starting at step 900 of the simulation.
We can observe that this particular system is unstable, as indicated by the low transverse (TA1) acoustic mode in the G-N high symmetry direction crossing to the negative part of the frequency axis. This particular anharmonic behavior of the TA1 mode is characteristic of bcc systems and was also predicted by Ref. [22] in their study of nonmagnetic Fe at high temperatures. Moreover, the positive modes for this nonmagnetic system are even considerably softened than those where magnetism is considered.

The distributions of the force constants for 900 steps in the simulation are displayed in Fig. 5.6
Figure 5.6: Distributions of the forces constants for 900 steps in the simulation of nonmagnetic Fe at 1043 K. For some of the directions of the nearest neighbors, the distributions are Gaussian.
5.3 Nonmagnetic Fe at High Temperatures

We studied the stability of the nonmagnetic bcc phase near the melt line at pressures of around 10 GPa. In order to cover the desired pressure-temperature range, simulations were performed and initialized from the last atomic configurations that were thermalized from a classical simulation on LAMMPS. For each set of volumes and temperatures, around 200 steps were calculated, each of them one femtosecond long. For these calculations, a simple PBE functional was used as pseudopotential with the kinetic energy cutoff as 71 Ry, and the charge density cutoff was set to be 496 Ry. The thermalization information can be found in Figs. 5.7 and 5.8.
Figure 5.8: Thermalization graphs of pressure and temperature as a function of step of the simulation corresponding to a volume of 2.76 Å and temperatures of 1700, 1850 and 1950 K

The phonon dispersions for this runs were generated to obtain information regarding the stability of nonmagnetic Fe near the meltine and the bcc-fcc transition boundary and are shown in 5.9.

From the heatmaps in Fig. 5.9, we see that the bcc structure contains a good number of negative modes in several of the high symmetry directions. We attribute this to the fact that at such conditions, the magnetic moment of Fe is still important to stabilize the bcc structure at high temperatures and relatively low pressures, as predicted by [22]. We then conclude that we need an accurate description of the magnetic spins to stabilize Fe at high temperatures.
Figure 5.9: Phonon dispersions of the high-temperature non magnetic Fe. The volumes are 2.755 and 2.76 Å, and the temperatures vary from 1700 K, 1850 and 1950 K.
5.4 Phonon Dispersions at Earth Core-like Conditions

Using HELD, we studied the dispersion relations for bcc nonmagnetic Fe at pressures near the inner core of the Earth to test the stability of nonmagnetic bcc at such conditions. Ab initio molecular dynamics data was generated to cover the desired range of pressure and temperature. The simulations performed were carried out in the NVT ensemble, using a PBE functional with a PAW pseudopotential, as implemented in Quantum Espresso. The kinetic energy cutoff was selected to be 71 Ry, and the charge density cutoff was set to be 496 Ry. The temperature was controlled using a stochastic velocity rescaling thermostat, and similarly, the parameter of the thermostat nraise was set to 20 in general. The simulations were initiated from the ideal lattice configurations and run for 200 steps, each of them 1 femtosecond long. The thermalization graphs for each of the volumes 2.49, 2.39 and 2.36 Å can be found in Figs. 5.10, 5.11, 5.12.
Figure 5.10: Temperature and pressure as a function of the step for the QMD simulation runs for the 2.49 Å volume. All of the simulations were run for a total of 200 steps, with a timestep 1 femtosecond long.
Figure 5.11: Temperature and pressure as a function of the step for the QMD simulation runs for the 2.39 Å volume. All of the simulations were run for a total of 200 steps, with a timestep 1 femtosecond long.
Figure 5.12: Temperature and pressure as a function of the step for the QMD simulation runs for the 2.36 Å volume. All of the simulations were run for a total of 200 steps, with a timestep 1 femtosecond long.
The phonon dispersions averages of the simulations were also obtained by taking 50 random steps from the last 0.1 picosecond of the simulation. Such averages are displayed in Figs. 5.13, 5.14 and 5.15 for the three different volumes.

Figure 5.16: Heat maps for the 2.49 Å volume. For each temperature, the top figure contains the aggregate of all steps in the simulation, whereas the bottom one is an aggregate of the last 100 steps.
Figure 5.13:
Averaged dispersion relations for 50 random steps taken within the last 0.1 picoseconds of the simulation for 2.49 Å volume.
Figure 5.14:
Averaged dispersion relations for 50 random steps taken within the last 0.1 picoseconds of the simulation for 2.39 Å volume.
Figure 5.15:
Averaged dispersion relations for 50 random steps taken within the last 0.1 picoseconds of the simulation for 2.36 Å volume.
Figure 5.17: Heat maps for the 2.39 Å volume. For each temperature, the top figure contains the aggregate of all steps in the simulation, whereas the bottom one is an aggregate of the last 100 steps.
Figure 5.18:
Heat maps for the 2.36 Å volume. For each temperature, the top figure contains the aggregate of all steps in the simulation, whereas the bottom one is an aggregate of the last 100 steps.

Overall, from the thermalization graphs we see how by increasing the temperature by keeping the volume constant, the pressure increases, which is expected from thermal pressure. For most of the volumes, the frequencies at the N point and in the 2/3 of the G-H direction, tend to lower with lowering the temperature. This indicates that the stabilization of bcc occurs by increasing the temperature in the system.

In general, by increasing the pressure, the temperature at which the bcc phase becomes
stable increases too, in agreement with the results from Ref. [11]. The N-point is one of the points of main interest from the phonon dispersion curves, since in that direction the frequencies become imaginary for some ranges of pressure and temperature, the effect that temperature has on the transverse acoustic mode of lowest energy (TA2) is more dramatic. In order to understand more on the temperature-volume dependence of the modes at N, isochores and isotherms for the different volumes and temperatures were calculated, and are shown in Fig. 5.19
Figure 5.19: Phonon frequencies for the isochores (up) and isotherms (down)

From the isochores at constant volume, we see that in general the three phonon branches tend to increase in energy with increasing temperature. However, the TA2 modes have a steeper slope in general, indicating that their dependence on temperature is more sensitive than for the TA1 and longitudinal modes. From the isotherms, we observe the strong
dependence on pressure of the frequencies of the longitudinal mode, denoted with open squares. Increasing the pressure in the system results in a strong increase in the frequencies for this mode. The TA1 mode marked with open circles is almost invariant to pressure, whereas the TA2 mode in general softens with decreasing the volume.

With the results from the averaged dispersions we mapped the stability of nonmagnetic bcc Fe at high pressures and temperatures, which is the main result of this thesis. The phase diagram mapped in this work is shown in Fig. 5.20.

Figure 5.20: Map of stability of nonmagnetic bcc Fe at high temperatures and pressures. Meltline is from Ref. [4]

The meltline is from the most recent EOS from Ref. [4].
Chapter 6

Conclusions and Discussion

We used a recently developed method called harmonic ensemble lattice dynamics (HELD) that computes temperature-dependent interatomic force constants that are required to obtain phonon dispersions to study the stability of bcc Fe.

Using this implementation, we mapped the stability of bcc nonmagnetic Fe at different conditions by means of finite temperature lattice dynamics with Ab initio molecular dynamics based on DFT. At relatively low pressures, the phonon dispersions of nonmagnetic bcc Fe show negative frequencies, indicating the structure is unstable at such conditions. This is in accordance with the results from [22] that indicate that a correct description of the magnetism must be properly incorporated in order to stabilize bcc Fe even above the Curie temperature. However, in the regime of high temperature, at Earth core pressures, the magnetic moment of Fe is suppressed by the high pressure [42], [40], so we can treat Fe as nonmagnetic. We showed that the bcc nonmagnetic phase of Fe could be mechanically stable at high temperatures and pressures in the range of the Earth core. Also, as the pressure in the system increases, the temperature at which bcc becomes stable is also higher, in agreement with the findings in Refs. [32] [11].

In the case of the unstable sets of volume-temperature, we observe some features appearing in particular high symmetry directions in k-space in the dispersion relations. The first feature is captured in the $\Gamma$ to N direction by the low transverse phonon $T_{21/2}(110)$. This branch is the more anharmonic, meaning that from the heat maps is the most ”diffuse” one, and the one that becomes negative at lower temperatures. The second feature comes in the H-P direction, particularly at $L2/3(111)$, when at particular pressures and temperatures that mode crosses the frequency axis into the negative region.
The features mentioned above are of great importance and have been reported in other bcc metals such as Zr, Ti, La and Hf [21], [20] transforming the bcc to other crystalline structure. In Ti and Zr, for example, the anomaly in the [110] direction is attributed to the $T_{11/2}(110)$ phonon displacing neighboring (110) planes in the [-110] direction. This lattice vibration coupled with long wave shears (-112)[-110] squeezes the bcc octahedron into a regular hcp one when lowering the temperature in such systems [20]. It is also important to note the remarkable dependence of this mode with the temperature. We can see that in general, from the averaged dispersion plots, this branch softens considerably by decreasing the temperature in the system.

In the case of the anomaly in the [111] direction, the longitudinal mode L exhibits a dip at $k = 2/3$ of the path. The atomic displacements attributed to this phonon have a particular crystallographic meaning in the bcc structure; two of the three neighboring (111) planes move towards each other while every third one remains at rest. A new structure $\omega$ is obtained when two (111) planes collapse. This transition is observed in all the group 4 metals under high pressure [20].

Even though the longitudinal mode at [111] exhibits softening with temperature, the softening of the T2A mode is larger in the [110] direction, particularly, the N-point. This is the reason why we studied in more detail the dependence on the frequencies with respect to pressure and temperature at that particular k-point in the Brillouin zone.

From the isochores and isotherms we observe that the longitudinal and particularly the low transverse acoustic mode are the ones more affected by temperature and pressure at the N-point. In general, with increasing the pressure in the system, the longitudinal mode increases in energy, as observed by [32]. By looking at the isochores, we noted that the TA2 phonon mode is the more sensitive with respect to temperature, indicating that temperature might be responsible for mechanically stabilizing this mode.

In summary, we found that nonmagnetic bcc Fe might be stabilized by the high temperatures at pressures of the core of the Earth. A more rigorous analysis is required in order to understand if the bcc structure becomes thermodynamically stable with respect
to other phases such as hcp, for instance. The thermodynamic stabilization of this phase could explain the huge discrepancies between the several experimental [12], [10], [45], [41], [4], and theoretical [2], [3], [39] predictions of the melting temperatures by hinting the possible stabilization of the bcc structure at such conditions.
References


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After finishing her MS degree, she will be joining The Ohio State University in Fall of 2022 to pursue her Ph.D. in Physics and work in the area of computational condensed matter physics.

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