Thermal properties of materials from first principles

Olle Hellman
To my father
Abstract

In the search of clean and efficient energy sources intermediate temperature solid oxide fuel cells are among the prime candidates. What sets the limit of their efficiency is the solid electrolyte. A promising material for the electrolyte is ceria. This thesis aims to improve the characteristics of these electrolytes and help provide thorough physical understanding of the processes involved. This is realised using first principles calculations.

The class of methods based on density functional theory generally ignores temperature effects. To accurately describe the intermediate temperature characteristics I have made adjustments to existing frameworks and developed a qualitatively new method. The new technique, the high temperature effective potential method, is a general theory. The validity is proven on a number of model systems.

Other subprojects include low-dimensional segregation effects, adjustments to defect concentration formalism and optimisations of ionic conductivity.


För att bättre beskriva material vid höga temperaturer har jag utvecklat en ny metodik. Det är en allmän metod för att bestämma termodynamiska potentialer, som jag bekräftar med flera exempel. Andra projekt har ämnats åt segregationseffekter i lågdimensionella system, förbättringar av den formalism som används för att beskriva defekter och optimering av jonledningsförmåga i ceriumdioxid.
Preface

This work was carried out in the theoretical physics group at Linköping university between 2007 and 2012. There are a number of people whom I could not have done this without. First and foremost I would like to thank my supervisor, Sergei Simak, for imparting knowledge and enduring support during my forays further and further away from the initial goals, and my secondary supervisor Igor Abrikosov for his attempts at reining me in. I am grateful to Natalia Skorodumova for present and future collaborations and advice. I would like to thank my colleagues and friends in the Theoretical Physics and Computational physics groups for making the time spent at work seem nothing like a chore. I also want to thank my family for support, especially my sister for tirelessly proofreading incomprehensible manuscripts and min ömma moder for cookies.

Olle Hellman
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NOTATION

notation
\( a(\cdot) \) function
\( a[\cdot] \) functional
\( \{a\} \) set of all \( a \)
\( \bar{a} \) matrix
\( \hat{a} \) operator
\( a \) vector

operators
\( \hat{H} \) Hamiltonian operator \( \hat{H} = \hat{T} + V \)
\( \hat{T} \) kinetic energy operator

phonon formalism
\( \omega \) angular frequency
\( \mathbf{q} \) wave vector
\( \Phi \) force constant matrix

potentials
\( V_U \) LDA+U Coulomb potential
\( V_{\text{eff}} \) effective potential
\( V_{\text{ext}} \) exchange-correlation potential
\( V_H \) Hartree potential
\( V_{xc} \) exchange-correlation potential

thermodynamics
\( F \) Helmholtz free energy
\( G \) Gibbs free energy
\( S \) entropy
\( T \) temperature
\( U \) internal energy
\( V \) volume
\( \Lambda \) thermal De Broglie wavelength
\( \beta \) thermodynamic beta
\( Z \) partition function
\( p \) pressure

wavefunctions
\( \Psi \) many-body wavefunction
\( \phi \) single-particle wavefunction
\( \psi \) atomic-like orbitals
\( n \) electron density

masses
\( M \) mass of atom
\( m_e \) electron rest mass

coordinates
\( r \) Cartesian coordinate
\( \mathbf{R} \) lattice vector
\( \tau \) equilibrium position in the unit cell
\( \mathbf{u} \) displacement from equilibrium position
\( p \) momentum
\( v \) velocity
\( f \) force

energies
\( E_U \) LDA+U energy
\( E_H \) Hartree energy
\( T \) kinetic energy
\( E_t \) total energy
\( E_{xc} \) exchange-correlation energy

atomic number
\( h \) reduced Planck constant
\( e \) electron charge
\( k_B \) Boltzmann constant

constants
\( Z \)
ACRONYMS

bcc body centered cubic
BOMD Born-Oppenheimer molecular dynamics
DFT density functional theory
DMFT dynamical mean-field theory
fcc face centered cubic
GGA generalized gradient approximation
hcp hexagonal close packed
LDA local density approximation
MD molecular dynamics
PAW projector augmented wave
SOFC solid oxide fuel cells
TDEP temperature dependent effective potential method
The first rule of thermodynamics is you do not talk about thermodynamics.
INTRODUCTION

There is a global demand for clean and efficient energy sources. One such source could be intermediate temperature solid oxide fuel cells (SOFC). These devices produce electricity by directly oxidising fuel with no toxic by-products. The efficiency can be over 60% when generating electricity, and over 80% when the waste heat is taken care of. In figure 1.1 the operation of a SOFC is illustrated. The solid electrolyte that provides the conduction of oxygen ions is the primary bottleneck, both in terms of efficiency and cost. A substantial portion of the work in this thesis is devoted to the improvement and understanding of ceria-based electrolytes.

We have based our work on *ab initio* calculations. It is a class of theoretical methods where the input is the fundamental laws of physics and no assumptions or empirical models are made. When practically using these techniques, some approximations have to be introduced. Temperature effects, for example, are usually ignored or crudely treated. This is often an appropriate approximation, the operational temperatures for most materials are around room temperature where the finite temperature effects are small. However, the operational temperatures of SOFC...
are 800–1000°C. In this range the temperature effects cannot be ignored.

During the project we realised that the theoretical framework for dealing with temperature effects, in particular thermodynamic stabilities, was not up to par. There was a host of pre computer-era work extensively detailing how to theoretically treat temperature effects. We sidetracked a bit from the initial task and developed a thorough formalism to accurately determine finite temperature properties using state-of-the-art methods, bridging the gap between formal theory and practical implementation. This has lead to a qualitatively new way of determining relevant thermodynamic potentials.

Other than temperature, we have faced other issues when it comes to first principles calculations. The scales are limited. In size, we can simulate features up to a few Ångström and in time we talk about picoseconds at most. To extend our reach we extract parameters from first principles calculations and build models on a relevant scales. We have used this approach to study low-dimensional segregation effects as well as seeking to explain the general behaviour of the ionic conductivity in ceria.

Outline of thesis

In chapter 2 I outline the basics of first principles calculations. Chapter 3 deals with lattice dynamics. I then proceed to discuss molecular dynamics in chapter 4. In chapter 5 I describe the novel temperature dependent effective potential method. The final two chapters, 6 and 7 deal with the Monte-Carlo method and crystal defects respectively. The papers and the authors contributions are presented at the end.
At the turn of the 20th century, the development of a theoretical framework describing matter on the microscopic scale was in full swing. In 1926, Erwin Schrödinger formulated his famous equation, which if solved allows us to describe any physical system at the atomic scale. It opened up the possibility to model a system without any empirical parameters. This class of calculations are called first principles calculations.

**Density functional theory**

Ideally, to investigate a system of $N$ electrons and $M$ nuclei, we begin with the Schrödinger equation:

$$\hat{H}\Psi = E\Psi$$

(2.1)

where

$$\Psi = \Psi(r_1, \ldots, r_N, r_1^1, \ldots, r_M^N)$$

(2.2)

is a wavefunction that depends on the position of all electrons $\{r\}$ and nuclei $\{r^n\}$. The Hamiltonian takes this form:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \frac{\hbar^2}{2} \sum_k \frac{\nabla_k^2}{M_k} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

$$+ \frac{1}{2} \sum_{k \neq l} \frac{Z_k Z_l}{|r_k^1 - r_l^1|} - \sum_{i,k} \frac{eZ_k}{|r_i - r_k^1|} - \sum_{i,k} \frac{eZ_k}{|r_i - r_k^1|}.$$  

(2.3)

The resulting equations can only be exactly solved for the simplest of systems. To solve it we successively apply layers of approximations, hopefully maintaining physical relevance. The first step is to separate the nuclei and the electronic degrees of freedom. This is the Born-Oppenheimer approximation. The nuclei terms will enter as a constant. We are left with

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_{i,k} \frac{eZ_k}{|r_i - r_k^1|}.$$  

(2.4)

This is still too complex to solve. In 1964 Hohenberg and Kohn formulated the density functional theory (DFT). The central idea is to replace the many-body problem in equation 2.4 with an equation for the electron density. The density, with its dependence on three spatial coordinates, will implicitly contain the electronic degrees of freedom. Their original formulation contains two theorems stating this is possible:

(I) In this thesis I do not discuss the issues of relativistic quantum mechanics and accordingly do not address the relativistic Dirac equation.
The unknown parts are the kinetic and exchange-correlation energy functionals. There were some early attempts at approximating the kinetic energy functional, originating from Thomas-Fermi theory.\textsuperscript{60,22} It approximated the kinetic energy to that of a uniform electron gas of the same density. For that specific case the theory is exact, but it fails to predict bonding and thus the existence of molecules. It was later corrected by von Weizsäcker\textsuperscript{63} but this formulation was overbinding. Orbital free density functional theory has been an active field of research ever since, with numerous functionals suggested. Unfortunately none of these have been as robust as the Kohn-Sham theory and have limited practical applications.

1. The potential $V_{\text{ext}}$ is determined uniquely by the ground state density $n$, up to an arbitrary constant.

2. Any external potential has a universal total energy functional $F_{\text{HK}}$. The exact ground state density minimizes the total energy functional $E_i[n]$.

The Hohenberg-Kohn functional is defined as

$$F_{\text{HK}}[n] = E_i[n] - \int V_{\text{ext}}[n]ndr,$$

(2.5)

where $E_i[n]$ is the total energy functional. This functional exists, but the explicit form is unknown.\textsuperscript{21} The Kohn-Sham equations,\textsuperscript{41} formulated in 1965, provide the framework wherein the electronic structure problem in the density functional formulation becomes solvable. Here we follow the reasoning in Eshrig.\textsuperscript{20}

The Kohn-Sham ansatz is to replace the real electrons with non-interacting quasiparticles that produce the correct ground state density, and gather all the unknown terms in one term called exchange and correlation. The universal functional now takes the form

$$F_{\text{HK}}[n] = T[n] + E_H[n] + E_{\text{xc}}[n] - \int V_{\text{ext}}[n]ndr.$$

(2.6)

It is divided into kinetic energy ($T$), Hartree energy ($E_H$), the external potential ($V_{\text{ext}}$) and a term containing all the many-body terms, $E_{\text{xc}}$. The exact form of the exchange-correlation is not known, but later we will see that it can be approximated. We can now define the total energy functional

$$E_i[n] = T[n] + E_H[n] + E_{\text{xc}}[n] + \int V_{\text{ext}}(r)n(r)dr.$$  

(2.7)

We want to find the density that minimises this energy functional. In order to do so we perform a constrained search for the stationary points, with the constant particle number $N$ as the constraint and Lagrange multipliers $\epsilon_i$:

$$\mathcal{L} = E_i[n] - \epsilon_i \left( \int n(r)dr - N \right),$$

(2.8)

$$\delta \mathcal{L} = \int \frac{\delta \mathcal{L}}{\delta n} \delta ndr = 0.$$  

(2.9)

At this point we take advantage of the previously mentioned Kohn-Sham ansatz. We denote the ground state many-body wavefunction for the non-interacting quasiparticles $\Psi^0$. This can always be written as a determinantal state of one-particle wavefunctions:

$$\Psi^0 = \frac{1}{\sqrt{N!}} \left\| \phi_i(r_j) \right\|, \quad \langle \phi_i | \phi_j \rangle = \delta_{ij}$$  

(2.10)
and the density expressed in these orbitals:

\[ n = \sum_i \phi_i^* \phi_i \]

\[ \delta n = \sum_i \delta \phi_i^* \phi_i + \phi_i^* \delta \phi \]  

(2.11)

and thus define the kinetic energy functional as

\[ T[n] = \frac{1}{2} \sum_i \langle \phi_i | \hat{T} | \phi_i \rangle. \]  

(2.12)

Performing a variation on \( T \) with respect to \( \phi_i^* \) gives me

\[ \delta T = T[n + \delta \phi_i^*] - T[n] = \int \hat{T} \phi_i \delta \phi_i^* \, dr = \int \frac{\delta T}{\delta \phi_i} \delta \phi_i^* \, dr, \]

which tells me

\[ \frac{\delta T}{\delta \phi_i^*} = \hat{T} \phi_i = \int \frac{\delta T}{\delta n(r')} \delta n(r') \, dr' = \frac{\delta T}{\delta n} \phi_i. \]  

(2.13)

Putting equation 2.11 into 2.9 gives

\[ \delta L = \sum_i \int \frac{\delta L}{\delta n} \phi_i \delta \phi_i^* \, dr + \sum_i \int \frac{\delta L}{\delta n} \phi_i^* \delta \phi \, dr = 0. \]  

(2.14)

This will give us constraints on the orbitals:

\[ \frac{\delta L}{\delta n} \phi_i = \left( \frac{\delta T}{\delta n} + \frac{\delta E_H}{\delta n} + \frac{\delta E_{xc}}{\delta n} + V_{ext} - \epsilon_i \right) \phi_i = 0. \]  

(2.15)

Looking at these terms we find the Hartree potential

\[ \frac{\delta E_{H}[n]}{\delta n} = \int \frac{n(r') \, dr'}{|r' - r|} = V_{H}[n] \]  

(2.16)

and

\[ \frac{\delta E_{xc}[n]}{\delta n} = V_{xc}[n] \]  

(2.17)

as the definition of the exchange-correlation potential. Combining these terms we have

\[ \left( \hat{T} + V_{H} + V_{xc} + V_{ext} - \epsilon_i \right) \phi_i = 0. \]  

(2.18)

By putting the potentials into one term, \( V_{eff} = V_{H} + V_{xc} + V_{ext} \), we have the Schrödinger-like Kohn-Sham equations for the quasiparticle orbitals \( \phi_i \) that produce the ground state density

\[ \left( \hat{T} + V_{eff}[n] \right) \phi_i = \epsilon_i \phi_i. \]  

(2.19)
One can then show that the total energy functional becomes

\[ E_t[n] = \sum_i \epsilon_i + \int n(r)V_{\text{eff}}[n]dr. \tag{2.20} \]

We can now solve equations 2.11, 2.19 and 2.20 self-consistently and find the electronic ground state density.

We have not yet mentioned spin-polarised densities. If we knew the exact \( E_{\text{xc}} \) and solved the Kohn-Sham equations an oxygen atom, for example, density functional theory would produce the correct ground state energy and density, but it could not tell us anything about the spin polarisation. In practise, when using approximate \( E_{\text{xc}} \), one has to explicitly introduce spin polarised densities and spin dependent \( E_{\text{xc}} \) to get accurate electronic structure for magnetic systems. The Kohn-Sham equations for this case can be obtained in a similar manner.

**Exchange-correlation**

So far we have applied no approximations, the theory is still exakt. To practically solve the equations the unknown \( V_{\text{xc}} \) has to be defined somehow. The local density approximation (LDA) was introduced at the same time as the Kohn-Sham equations. \(^{41}\) It takes the form

\[ E_{\text{xc}}^{\text{LDA}} = \int \epsilon(n(r))n(r)dr, \tag{2.21} \]

where \( \epsilon \) is the exchange-correlation of a uniform electron gas, something that can be calculated with the quantum Monte Carlo method. This is a very successful approximation, yielding good results for a broad range of materials. The success can be attributed to the reasonable treatment of the exchange-correlation hole and cancellation of errors.\(^{14}\) The natural extension to this is to include the gradient of the density, and obtain the exchange and correlation from a uniform electron gas with a gradient. This is the generalised gradient approximation (GGA),\(^{51}\) which has the form

\[ E_{\text{xc}}^{\text{GGA}} = \int f(n(r), \nabla n(r))n(r)dr. \tag{2.22} \]

There is no unique way to determine the gradient dependence of the uniform electron gas, that is why there are several forms of GGA optimized for different cases.

There are notable limitations to these functionals. For example: the band gap of semiconductors is underestimated (and sometimes outright missing, predicting a metallic state). In addition the LDA underestimates lattice parameters, whereas the GGA overestimates them.
Pseudopotentials and projector augmented waves

When solving the Kohn-Sham equations for a crystalline solid the resulting wavefunctions oscillate rapidly around the nuclei and vary more slowly in the interstitial regions. To solve the equations numerically one needs to use a basis set. It is a non-trivial task to find basis functions that can describe both the region around the nuclei, where atomic orbitals would work well, as well as the interstitial, where plane waves are more suitable. It would also be beneficial if one could find a way to ignore the deep core states. These states do not contribute much to bonding and are weakly affected by it. The computational complexity usually scales as $O(N^3)$, with $N$ being the number of electrons. Any electron that can be omitted would greatly increase the computational efficiency.

The pseudopotential approach was introduced by Hellmann in 1935\(^3\) but was put in the modern form by Phillips and Kleinman in 1959\(^5\). They showed that one can construct a modified valence wave function $\tilde{\varphi}_v$ using the true core $\varphi_c$ and valence wave functions $\varphi_v$:

$$\tilde{\varphi}_v = \varphi_v + \sum_c a_{cv} \varphi_c, \quad a_{cv} = \langle \varphi_v | \tilde{\varphi}_v \rangle.$$  \hfill (2.23)

This pseudo-wavefunction satisfy

$$\left( \hat{H} + \sum_c (\epsilon_v - \epsilon_c) \langle \varphi_c | \varphi_v \rangle \right) \tilde{\varphi}_v = \epsilon_v \tilde{\varphi}_v.$$  \hfill (2.24)

That is the pseudowavefunctions have the same eigenvalues as the true wavefunctions. What is added is an extra potential term in the Hamiltonian. This early attempt showed that the division between core and valence states is possible, and if choosing fixed core states the number of electrons in the problem at hand will be dramatically reduced. There are many pseudopotential approaches, suited for different tasks.\(^{45,40}\)

We have used the projector augmented wave (PAW)\(^9\) method throughout this thesis. This is a modern approach that keeps the all-electron wave function via a linear transformation

$$\mathcal{T} = 1 + \sum_c T_c,$$  \hfill (2.25)

where $T_c$ only acts within a region around nuclei $c$. This transformation can be applied to any operator

$$\tilde{\mathcal{A}} = \mathcal{T}^{-1} \hat{\mathcal{A}} \mathcal{T}$$  \hfill (2.26)

allowing it to work on the smooth pseudowaves but keeping the information from the full wavefunction. This increases the transferability of the potentials.
Strongly correlated systems

In strongly correlated systems, where the inherent many-body effects are crucial, the local density-based functionals fails to model the systems completely. The effects cannot be described well with non-interacting quasiparticles. These materials include, but are not limited to, transition metal oxides, Mott insulators and cuprates. Hubbard \textsuperscript{35,36} introduced the first attempts at solving these problems. Presently, the methods most widely used are LDA+U,\textsuperscript{5} hybrid functionals\textsuperscript{32,7} and dynamical mean-field theory (DMFT).\textsuperscript{4} In this thesis we have exclusively used LDA+U. Although it is a simple model, it is well suited for the problems in question. The main strength is the minimal added computational complexity, making it usable for large systems. The major drawback is the need for adjustable parameters as well as the fact that it is an inherently one-electron theory and can never describe strongly correlated systems where electrons simultaneously show localised and itinerant behaviour. DMFT or hybrid functionals would solve this, but for our systems of interest the added computational complexity unfortunately renders it practically impossible to use them. The principle of LDA+U is rather simple. We will motivate it in the rotationally invariant case via the variational principle, as detailed in Eshrig.\textsuperscript{21} Add an extra term to equation 2.7:

\[ E_t[n] = T[n] + E_{\text{ext}}[n] + E_{\text{xc}}[\phi, o] + \int V_{\text{ext}}(r)n(r)dr \]  

(2.27)

that depends on the Kohn-Sham orbitals and their occupation numbers $o$. When varying this expression with respect to $\phi_i^*$ to get the Kohn-Sham equations, an extra term will appear:

\[ \frac{\delta E_{U}}{\delta \phi_i^*} = \sum_{j \mu \sigma} \frac{\partial E_{U}}{\partial \bar{o}_{\mu \sigma}} \frac{\delta \bar{o}_{\mu \sigma}}{\delta \phi_i^*} \]  

(2.28)

where

\[ \frac{\partial E_{U}}{\partial \bar{o}_{\mu \sigma}} = V_U(\mu, \sigma) \]  

(2.29)

\[ \frac{\delta \bar{o}_{\mu \sigma}}{\delta \phi_i^*} = \langle \psi | \langle \psi | \phi \rangle . \]  

(2.30)

$j$ is a site, $\mu$ is an orbital quantum number and $\sigma$ is a spin quantum number. $E_U$ will depend a projection onto correlated local orbitals $|j \mu \sigma \rangle = |\psi \rangle$. This projection is given by local orbital occupation numbers, $\bar{o}_{\mu \sigma}$, that depend on the Kohn-Sham orbitals and occupation numbers. We choose to describe the angular component of the strongly correlated electrons with eigenstates to angular momentum, centered at site $i$:

\[ |\psi_i \rangle = |m_i \sigma_i \rangle \quad m_i = -l_i, \ldots, l_i \]  

\[ \sigma_i = \uparrow, \downarrow . \]  

(2.31)
We only consider interaction within the site. That gives the form of the expectation value for the screened electron-electron interaction:

\[
\langle m_1 m_2 | V_{ee} | m_3 m_4 \rangle = \sigma_1 = \sigma_3, \quad \sigma_2 = \sigma_4, \quad V_{ee} \approx V_{ee}(|r_1 - r_2|).
\]  

(2.32)

The dependence on solely \(|r_1 - r_2|\) is of course an approximation. We investigate how these matrix elements transform under a rotation. \(R(\hat{O})\) is the unitary transformation for the rotation \(\hat{O}\).

\[
\langle m_1 m_2 | V_{ee} | m_3 m_4 \rangle = \sum_{m'_1 m'_2 m'_3 m'_4} R^l_{m'_1 m'_2} (\hat{O}) R^l_{m_2 m'_2} (\hat{O}) \times
\]

\[
\langle m'_1 m'_2 | V_{ee} | m'_3 m'_4 \rangle R_{m_3 m'_3} (\hat{O}) R_{m_4 m'_4} (\hat{O})
\]

and

\[
\int R_{m_1 m_2} (\hat{O}) R^l_{m_3 m_4} (\hat{O}) d\hat{O} = \frac{1}{2l+1} \delta_{m_1 m_4} \delta_{m_2 m_4} \quad (2.33)
\]

\[
\int d\hat{O} = 1. \quad (2.34)
\]

Using these relations we integrate over all rotations and look at:

\[
\sum_{m_1} \langle m_1 m_2 | V_{ee} | m_1 m_4 \rangle
\]

\[
= \sum_{m_1} \int \langle m_1 m_2 | V_{ee} | m_1 m_4 \rangle d\hat{O} d\hat{O}'
\]

\[
= \sum_{m_1} \int \int \sum_{m'_1 m'_2 m'_3 m'_4} R^l_{m_1 m'_1} (\hat{O}') R^l_{m_2 m'_2} (\hat{O})
\]

\[
\langle m'_1 m'_2 | V_{ee} | m'_3 m'_4 \rangle R_{m'_3 m_3} (\hat{O}) R_{m'_4 m_4} (\hat{O}) d\hat{O} d\hat{O}'
\]

\[
= \int \sum_{m'_2 m'_4} \int \sum_{m_1 m'_1 m'_3 m'_4} R^l_{m'_1 m'_1} (\hat{O}) R_{m'_3 m_3} (\hat{O}) R_{m'_4 m_4} (\hat{O}) d\hat{O} d\hat{O}'
\]

\[
\times \delta_{m_1 m_1'} \delta_{m_2 m_2'}
\]

\[
\langle m'_1 m'_2 | V_{ee} | m'_3 m'_4 \rangle R_{m'_3 m_3} (\hat{O}) d\hat{O}
\]

\[
= \int \sum_{m'_1 m'_2 m'_4} R^l_{m'_2 m'_4} (\hat{O}) \langle m'_1 m'_2 | V_{ee} | m'_3 m'_4 \rangle R_{m'_3 m_3} (\hat{O}) d\hat{O}
\]

\[
= \frac{1}{2l+1} \sum_{m'_1 m'_2 m'_4} \langle m'_1 m'_2 | V_{ee} | m'_3 m'_4 \rangle \delta_{m_2 m_4} \delta_{m_2 m_4'}
\]

\[
= \frac{1}{2l+1} \sum_{m'_1 m'_2} \langle m'_1 m'_2 | V_{ee} | m'_1 m'_2 \rangle
\]

\[
= (2l + 1) \delta_{m_2 m_4}.
\]
FIRST PRINCIPLES CALCULATIONS

\[ \sum_{m_1} \langle m_1 m_2 | V_{ee} | m_3 m_1 \rangle = \delta_{m_2 m_3} (U + 2J). \] (2.35)

These sum rules gives an expression for the energy that depends only on \( U \) and \( J \). The following steps depend on the specific implementation. As it stands it follows Dudarev: \(^1\) First one has to build the density matrix on each site \( i \):

\[
\rho_{ij}^\sigma = \delta_{ij} \rho_{ii}^\sigma = \int n^\sigma(r) \psi_i^\dagger(r) \psi_i(r) \, dr
\]

where \( o_i \) is the occupation of states projected onto the density at site \( i \) using the atomic orbitals \( \psi_i \). The energy functional is then

\[
E_{\text{LDA}+U} = E_{\text{LDA}} + \frac{U - J}{2} \sum_{\sigma} \left( \sum_i \rho_i^\sigma - \sum_{ij} \rho_{ij}^\sigma \rho_{ij}^\sigma \right)
\] (2.36)

and the corresponding \( U \)-potential is

\[
V_{ij}^U = (U - J) \left( \frac{1}{2} \delta_{ij} - \rho_{ij}^0 \right).
\] (2.37)

Since only the difference between \( U \) and \( J \) enters the calculations one usually denotes \( U - J \) just \( U \). Although the method is named LDA+U it can equally well be used together with GGA.

Finally, it only remains to determine the value of \( U \). Although it can in principle be calculated from restricted LDA calculations it is usually fitted to some experimental value. \(^3\) The extra potential will shift the Kohn-Sham eigenvalues according to

\[
\epsilon_{i}^{\text{LDA}+U} = \epsilon_{i}^{\text{LDA}} + U \left( \frac{1}{2} - o_i \right),
\] (2.38)
that is occupied states will have lower energy and unoccupied will be shifted up. For example, rare earth oxides with incompletely filled 4f-shells are problematic in the LDA. By applying \( U \) one can obtain the correct semiconductor ground state. Figure 2.2 shows the density of states of Nd\(_2\)O\(_3\) for different values of \( U \).

The ideas presented in sections 2.1–2.4 are by no means a complete description of the field. They illustrate how the generality and simplicity of expressions such as equation 2.1 has to make way for long and complex formulations when it comes to actual implementation. They are classes approximations: exchange-correlation being one out of necessity since the exact form is unknown, in contrast to pseudopotentials that are introduced for practical reasons to decrease the computational complexity. The LDA+U formalism is a good example of how to increase the longevity of the density functional theory. While it is a crude and nearly phenomenological approach, it extends the reach of DFT to systems it was never imagined for.
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What most first principles ultimately come down to is the comparison of energies, be it configurational energies, surface energies, mixing enthalpies or lattice stabilities. What is usually compared are total energies. That is appropriate when the effects of temperature can be neglected, if the temperate effects are not negligible it is the Gibbs free energy that should be compared if the temperature $T$ and pressure $p$ are external conditions:

$$G = U - TS + pV.$$  \hfill (3.1)

Modern DFT technique give us a very efficient way of determining $U$, the internal energy and $S_e$, the electronic contribution to the entropy via the Mermin functional.\textsuperscript{47} The thermal properties of the lattice, the major part of $S$, are more complicated.

At the beginning of the 20th century Born and von Kármán\textsuperscript{13} introduced the dynamical theory of lattices. It revolves around determining the response of the system to a displaced atom and the resulting vibrations, in essence what happens when you heat the lattice.\textsuperscript{34,11}

The harmonic approximation

The starting point of lattice dynamics is a Taylor expansion in the atomic displacements of the potential energy.\textsuperscript{34} It is convenient to define the atomic positions as displacements $u$ from their equilibrium positions $R_i + \tau_i$:

$$r_i = R_i + \tau_i + u_i.$$  \hfill (3.2)

$R_i$ is a lattice vector and $\tau_i$ the position in the unit cell. The potential energy per unit cell of the crystal can then be expanded as

$$U(\{u\}) = U_0 + \sum_i \sum_\mu \Phi_\mu^i u_\mu^i +$$

$$\frac{1}{2I} \sum_{ij} \sum_{\mu\nu} \Phi_{ij}^{\mu\nu} u_\mu^i u_\nu^j +$$

$$\frac{1}{3I} \sum_{ijk} \sum_{\mu\nu\xi} \Phi_{ijk}^{\mu\nu\xi} u_\mu^i u_\nu^j u_\xi^k + \ldots$$  \hfill (3.3)
where $ijk$ are indices to atoms and $\mu\nu\xi$ Cartesian indices. The constants

$$
\Phi^\mu_i = \left. \frac{\partial U}{\partial u^\mu_i} \right|_{u=0} = 0 \quad (3.4)
$$

$$
\Phi^\mu_{ij} = \left. \frac{\partial^2 U}{\partial u^\mu_i \partial u^\nu_j} \right|_{u=0} \quad (3.5)
$$

$$
\Phi^\mu_{ijk} = \left. \frac{\partial^3 U}{\partial u^\mu_i \partial u^\nu_j \partial u^\xi_k} \right|_{u=0} \quad (3.6)
$$

are called the force constant matrices. The constant term is usually set to the energy of the static lattice. The first order terms have to be zero since we stated that the derivatives are taken at equilibrium positions. That leaves only second and higher order terms. If we truncate at the second derivatives we have the so-called harmonic approximation. It has the Hamiltonian

$$
\hat{H} = \sum_i \frac{\hat{p}_i^2}{2M_i} + \sum_{ij} \mathbf{u}_i \cdot \Phi_{ij} \cdot \mathbf{u}_j, \quad (3.7)
$$

noting that the second term above involves a sum over pairs. We can rearrange this sum. From each atom $i$ at position $\tau_\alpha$ in the unit cell we will have a star of vectors to every atom $j$ at position $\tau_\beta$. This set of $l$ vectors we denote $\{\mathbf{R}_{\alpha\beta}^l\}$ and only depends on the indices to the positions in the unit cell, $\alpha\beta$, and not on the global atomic indices $ij$. The Hamiltonian can then be written

$$
\hat{H} = \sum_{i\alpha} \left( \frac{\hat{p}_{i\alpha}^2}{2M_{i\alpha}} + \sum_\beta \sum_l \mathbf{u}_{i\alpha} \cdot \Phi_{i\beta}(\mathbf{R}_{\alpha\beta}^l) \cdot \mathbf{u}_{i\beta} \right). \quad (3.8)
$$

Given a sufficiently large crystal, large enough that the surface effects can be ignored, this expression is independent of the atomic index $i$. That gives us an equation of motion for each atom in the unit cell:

$$
\ddot{\mathbf{u}}_{i\alpha} M_{i\alpha} = -\sum_\beta \sum_l \Phi_{i\beta}(\mathbf{R}_{\alpha\beta}^l) \cdot \mathbf{u}_{i\beta}. \quad (3.9)
$$

This is a drastic reduction in the number of coupled equations that have to be solved. It is possible to find a coordinate transformation that simultaneously diagonalises the momentum and positions since the Hamiltonian is a sum of two positive definite quadratic forms. This canonical transformation is an expansion of $u$ and $p$ in plane waves

$$
u^\mu_i = \sum_{q_j} \sqrt{\frac{\hbar}{2NM_{\alpha\beta}(\mathbf{q})}} \epsilon^{\alpha\mu\nu\xi}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_\alpha} \left( a_{qj} + a_{-qj}^\dagger \right) \quad (3.10)
$$

$$
p^\mu_i = \sum_{q,\beta} \frac{1}{\sqrt{2N}} \sqrt{\frac{\hbar}{M_{\alpha\beta}(\mathbf{q})}} \epsilon^{\alpha\mu\nu\xi}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_\alpha} \left( a_{qj} - a_{-qj}^\dagger \right) \quad (3.11)
$$
and their inverse

\begin{align}
    a_{qj} &= \sum_{l,\alpha,\mu} c_{j}^{\alpha\mu}(q) \frac{e^{-iq\cdot r_l}}{2Nh} \left( \alpha_{\alpha}^{\mu} \sqrt{M_{\alpha} \omega_{j}(q)} + i \frac{p_{\alpha}^{\mu}}{\sqrt{M_{\alpha} \omega_{j}(q)}} \right) \tag{3.12} \\
    a_{qj}^{\dagger} &= \sum_{l,\alpha,\mu} c_{j}^{\alpha\mu}(q) \frac{e^{-iq\cdot r_l}}{2Nh} \left( \alpha_{\alpha}^{\mu} \sqrt{M_{\alpha} \omega_{j}(q)} - i \frac{p_{\alpha}^{\mu}}{\sqrt{M_{\alpha} \omega_{j}(q)}} \right). \tag{3.13}
\end{align}

\(N\) is the number of atoms in the unit cell. \(q\) is a wave vector in the first Brillouin zone. \(\omega^2\) and \(\epsilon\) are the eigenvalues and eigenvectors of the dynamical matrix

\[\omega^{2}(q)\epsilon(q) = \bar{\Phi}(q)\epsilon(q)\]  
\[\bar{\Phi}(q) = \begin{pmatrix} \bar{\Phi}_{11}(q) & \cdots & \bar{\Phi}_{N1}(q) \\ \vdots & \ddots & \vdots \\ \bar{\Phi}_{N1}(q) & \cdots & \bar{\Phi}_{NN}(q) \end{pmatrix} \]  

with

\[\bar{\Phi}_{\alpha\beta}(q) = \sum_{l} e^{iq \cdot R_{l}} \sqrt{\frac{M_{\alpha} M_{\beta}}{2}} \bar{\Phi}_{\alpha\beta}(R_{l}).\]  

The vibrational frequency \(\omega\) is a multivalued function of \(q\). It will have \(3N\) values for each wavevector (some of them can be degenerate). These are the dispersion relations. Using the orthonormality relations of \(u\) and \(p\), and switching to quantum operators one realises that we have defined annihilation and creation operators for a quantum mechanical harmonic oscillator. The bosonic quasiparticles that are created are called phonons. The Hamiltonian takes the remarkably simple form

\[\hat{H} = \sum_{q_j} \hbar \omega_{j}(q) \left( a_{qj}^{\dagger} a_{qj} \right) + \frac{1}{2}, \]  

a sum of uncoupled harmonic oscillators. Each have the partition function

\[Z_{j} = \sum_{n=0}^{\infty} e^{-\beta \left( n + \frac{1}{2} \right) \hbar \omega_{j}} = \frac{e^{-\beta \hbar \omega_{j}}}{1 - e^{-\beta \hbar \omega_{j}}}, \]  

that yields the total partition function

\[Z = \prod_{jq} e^{-\beta \hbar \omega_{jq}} \left( 1 - e^{-\beta \hbar \omega_{jq}} \right). \]  

(3.19)
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FIGURE 3.2: Illustration of how to go from Helmholtz to Gibbs free energy. Helmholtz free energy in the right panel is determined on a regular grid of volumes and temperatures. The pressure in the left panel is given by

\[
p = -\left. \frac{\partial F}{\partial V} \right|_T.
\]

The pressure at each point yields a one-to-one mapping between the free energies. Note how the pressure-temperature grid is no longer evenly spaced. This particular example is for Al in the face centered cubic (fcc) phase.

From this we can get, for instance, the Helmholtz free energy

\[
F = -k_B T \ln Z
= \sum_j \frac{\hbar \omega_{jq}}{2} + k_B T \ln \left(1 - \exp \left(-\frac{\hbar \omega_{jq}}{k_B T}\right)\right)
= \int_0^{\infty} g(\omega) \left(\frac{\hbar \omega}{2} + g(\omega) k_B T \ln \left(1 - \exp \left(-\frac{\hbar \omega}{k_B T}\right)\right)\right) d\omega.
\]

The transition from a sum over wave vectors and branches to an integral over the phonon density of states is out of convenience. The phonon density of states is given by

\[
g(\omega) = \sum_j \int_{BZ} \frac{\delta (\omega - \omega_j (q))}{2\pi^3} dq.
\]

Explicit knowledge of the partition function is very useful. In addition to the Helmholtz free energy we can, among other things, determine the vibrational entropy and constant volume heat capacity.

There are several limitations in the harmonic approximation. Thermal expansion, for example, is absent. This can be remedied by using the harmonic approximation for several volumes and temperatures. This is called the quasi-harmonic approximation, and can provide a mapping from the Helmholtz to the Gibbs free energy, as illustrated in figure 3.2.

The omission of anharmonic terms can have serious consequences. If any of the second derivatives in equation 3.5 are negative they will carry through to the dynamical matrix and
the eigenvalues $\omega^2$ will become negative. This indicates that the crystal is dynamically unstable. In reality the crystal can be stabilised by the anharmonic contribution. To compare the free energies of two competing crystal structures is impossible if one of them is dynamically unstable at zero temperature, since the free energy is not defined for imaginary frequencies.

Dealing with anharmonism

Traditionally the problem of dynamical instability was addressed either by a self-consistent approach or including more terms in the expansion.\(^{39,10,11}\) Born and Hooton made the realisation that even though the second derivatives at the equilibrium position are negative, the atoms rarely occupy these positions. They move in the effective potential of their non-stationary neighbours. By sampling the potential energy surface not at the equilibrium positions but at the probable positions for a given temperature we get a harmonic approximation that describes the system at elevated temperatures.

The self-consistent formalism uses an iterative procedure.\(^{26}\) By creating a harmonic potential that is used to create thermal excitations that give a new harmonic potential. This is repeated until self-consistency.

The double-time Greens functions, developed by Choquard,\(^{17}\) use a cumulant expansion in the higher order terms. Although formally exact, it requires knowledge of the higher order force constants. Obtaining these accurately from from first principles calculations for something other than the simplest of systems is computationally very demanding.\(^{16}\)

A recent approach by Souvatzis\(^{56}\) uses ab initio supercell calculations and a self-consistent formalism. A problem with this approach is that the excitations can only be done in the harmonic sense which means probing phase space with a limited basis set. Where the harmonic approximation works well this is not a problem. For strongly anharmonic systems a harmonic basis set is by definition a bad way of describing the dynamics of the system. A harmonic Hamiltonian will probe the wrong part of phase space.

I have developed a new method that is similar in spirit to Born and Hootons\(^{32}\) original idea, but with a foundation in ab initio molecular dynamics that overcomes the limitations of earlier techniques, described in chapter 5.
Molecular Dynamics

The phonon formalism, detailed in the previous chapter, is well suited to describe averaged thermal quantities. It provides a model how the thermal excitations behave but is limited in describing the actual dynamics of the system. Diffusion, for example, cannot be described with phonon formalism.

Molecular dynamics (MD) gives explicit knowledge about the movement of atoms at finite temperature. This technique solves the equations of motion for the atoms and produces the trajectories over time. The simulation is an idealised version of an experiment with few constraints on the information that can be accessed.

Born-Oppenheimer molecular dynamics

To perform an MD simulation one needs a way to determine interatomic forces. Historically this has been done using empirical potentials. These have yielded good results in the past but are severely limited in terms of transferability, and the fact that electrons are completely abstracted. They have the advantage of being computationally very efficient, which is why I have used them throughout this thesis for illustration purposes.

When investigating properties of materials at finite temperature we have exclusively used Born-Oppenheimer molecular dynamics (BOMD), where the interatomic forces are calculated using quantum mechanics. When discussing DFT in the previous chapters the first approximation was to separate the nuclei and electronic degrees of freedom. In the same way that the nuclei can be considered stationary from the electronic point of view the nuclei can be seen as classical particles moving in a potential created by the electrons. This is provided the relaxation time for the electrons is sufficiently small, which is usually the case. With the Hellmann-Feynmann theorem

$$\frac{dE}{d\lambda} = \langle \Psi | \frac{d\hat{H}}{d\lambda} | \Psi \rangle$$  (4.1)

one can obtain the forces $f_i$ acting on each atom. The classical equations of motion

$$\dot{r}_i = \frac{p_i}{M_i}$$

$$\dot{p}_i = f_i$$  (4.2)

are $6N$ coupled differential equations. Since we calculate forces at instantaneous positions these have to be solved iteratively. We
use the velocity Verlet algorithm:\(^\text{62}\)

\[
\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \dot{\mathbf{r}}_i(t)\Delta t + \frac{1}{2}\ddot{\mathbf{r}}_i(t)\Delta t^2 \quad (4.3)
\]

\[
\dot{\mathbf{r}}_i(t + \Delta t) = \dot{\mathbf{r}}_i(t) + \frac{\ddot{\mathbf{r}}_i(t + \Delta t) + \ddot{\mathbf{r}}_i(t)}{2}. \quad (4.4)
\]

Here \(\Delta t\) is the step discretising time. Given initial positions and velocities, the forces are given by DFT calculations and the system is propagated from time \(t\) to time \(t + \Delta t\). After an appropriate number of steps, statistics and other properties of interest are gathered.

While this essentially describes the technique there is still a wealth of things to consider. The classical molecular dynamics, that govern the motion of our nuclei, are well reviewed in Allen and Tildesley\(^\text{1}\), Hansen and McDonald\(^\text{28}\) and Frenkel and Smit\(^\text{25}\) among others. The intricacies of ab initio molecular dynamics is thoroughly described in Marx and Hutter.\(^\text{46}\) In the rest of this chapter will touch upon some key points that are often overlooked in the literature.

**Ergodicity and phase space sampling**

The apparent straightforwardness of molecular dynamics can be misleading. The formalism for the classical trajectories were originally developed for classical systems of massive sizes (as compared to the sizes accessible with ab initio calculations). The finite size effects can, if one is not careful, have unpredictable consequences. The finite size applies not only to the number of atoms but also to the limited simulation time. A limited simulation time severely affects the quality of averaged quantities.

The average value of property \(a\) in thermal equilibrium is given by the ensemble average:

\[
\langle a \rangle = \int \frac{a(\{p\}, \{q\}) \exp (-\beta H(\{p\}, \{q\})) d\{p\}d\{q\}}{\int \exp (-\beta H(\{p\}, \{q\})) d\{p\}d\{q\}}. \quad (4.5)
\]

This is not possible to solve. The ergodic principle tells us we can replace this by a time average

\[
\langle a \rangle = \lim_{N\to\infty} \frac{1}{N} \sum_{t=1}^{N} a(t) \quad (4.6)
\]

if the system is ergodic. That means the system should forget its initial state and travel through all parts of phase space. If we were to solve the equations of motion analytically for our molecular dynamics simulation the time evolution would be perfectly deterministic. Molecular dynamics exhibits a sensitivity to initial conditions. In figure 4.1 we see the exponential divergence between two simulations that differ initially only by one part in
Figure 4.1: Illustrations regarding the Lyapunov instability in a Lennard-Jones system. The left panel shows the mean separation per atom vs time,
\[
\langle \Delta r(t) \rangle = \frac{1}{N} \sum_i |r_i(t) - \bar{r}_i(t)|
\]
between two systems. The systems differ only in the addition of a random noise of one part in 10^6 to the initial coordinates. It has a clear exponential behaviour, and this exponent is called the Lyapunov exponent. The right panel shows the magnitude of this exponent as a function of system size. It is clear that the ergodicity imposed by this exponent decreases drastically with system size.

10^{-6}. This, together with other factors, ensures that the simulation forgets its initial condition and can therefore be considered ergodic.

In classical molecular dynamics, often using millions or billions of particles, ergodicity can be considered intrinsic. In BOMD, with particle numbers typically ranging from the tens to the hundreds, one can end up in situations where the system is not ergodic. If it happens the properties derived from the simulations are void of meaning. While it is difficult to explicitly measure ergodicity, we have developed some ideas to test the prerequisites of ergodicity.

From a simulation with \(N_t\) timesteps and \(N_a\) atoms we can construct the matrix

\[
\Psi = \begin{pmatrix}
    r_x^1(1) & r_x^1(2) & \cdots & r_x^1(N_t) \\
    r_y^1(1) & r_y^1(2) & \cdots & r_y^1(N_t) \\
    \vdots & \vdots & \ddots & \vdots \\
    r_x^{N_a}(1) & r_x^{N_a}(2) & \cdots & r_x^{N_a}(N_t) \\
    r_y^{N_a}(1) & r_y^{N_a}(2) & \cdots & r_y^{N_a}(N_t) \\
    \vdots & \vdots & \ddots & \vdots \\
    p_x^1(1) & p_x^1(2) & \cdots & p_x^1(N_t) \\
    p_y^1(2) & \cdots & \cdots & \cdots \\
    p_x^{N_a}(1) & p_x^{N_a}(2) & \cdots & p_x^{N_a}(N_t)
\end{pmatrix}
\]

(4.7)

from the positions and momentums. The \(N_t\) row vectors describe the points in phase space we have visited. We then do a singular value decomposition

\[
\Psi = P\Sigma U.
\]

(4.8)

The diagonal matrix \(\Sigma\) holds the singular values. The effective rank of \(\Psi\) is the number of nonzero entries in \(\Sigma\). The effective rank is the number of dimensions of the phase space of the simulation. If this number is not \(6(N_a - 1)\) we do not span phase space.
Spanning and sampling phase space is not the same thing. But if one does not span phase space one cannot sample it. This singular value decomposition is a routine check after a simulation has finished. If the spanning is not appropriate no thermal parameter extracted holds any actual information.

If we have a harmonic potential for the system in question the phase space trajectories can be probed in a more direct way. By using the canonical transformation of equation 3.10 we can access the normal mode coordinates over time. In figure 4.2 the normal mode intensities are plotted over time. It is initialised to only occupy a single mode. One can clearly see the decay of this mode into a steady state of thermally appropriate occupation. This is a good indication that the system is ergodic. Initiating the system in a single mode is not particularly useful in general. The coordinate transformation still provides insight: the presence of fluctuations in the intensities indicate finite phonon lifetimes, which is a requirement for ergodicity.
Ensembles and thermostats

Often the reason one turns to molecular dynamics is to see what effect the added thermal entropy has on some property at temperature $T$. Integrating the equations of motion as they stand yields the microcanonical ensemble, with constant number of particles, volume and energy. Averaging over states to find a thermal average is cumbersome, as is controlling the temperature.

One would rather have the simulations in the canonical ensemble, constant number of particles, volume and temperature. In the macroscopic sense a constant temperature is easily imagined, one puts the system in contact with a large heat bath. In that case, the temperature is related to the time averaged kinetic energy as

$$T = \frac{3}{2k_B N_a} - 1 \sum_i^{N_a} \left( \frac{M_i v_i^2}{2} \right).$$

(4.9)

With a finite number of particles in a microcanonical ensemble the instantaneous temperature will fluctuate. We would like these fluctuations to be around the desired temperature $T$. To transform the microcanonical to the canonical ensemble with temperature $T$ a thermostat is introduced.

It could be as simple as velocity scaling. Velocity scaling adjusts the velocities every $n$ timestep to match the kinetic energy to the desired temperature. This is not a particularly efficient technique. It does reproduce a canonical ensemble if the scaling is done at every timestep and in the limit of a large number of particles, something that can not be satisfied in ab initio molecular dynamics. The trajectories will also be discontinuous at every rescaling step.\(^{30}\)

Temperature of a system is defined through contact with a heat bath. The Andersen\(^2\) thermostat introduces a probability at every timestep that an atom will collide with the heat reservoir, gaining a new momentum drawn from the appropriate Maxwell-Boltzmann distribution. This series of microcanonical ensembles will over time represent a canonical ensemble. For small systems the perturbation introduced by the atom with the new velocity can have undesirable effects. If the system consist of $\sim$100 atoms

---

**FIGURE 4.3**: Trajectories for a classical two-dimensional harmonic oscillator using different ensembles and thermostats. We see how the Nosé-Hoover thermostat slightly disturbs the trajectories and how the Andersen thermostat is a series of microcanonical trajectories. The phase space sampling of the Langevin dynamics is superior, and the trajectories are for the most part smooth with the occasional kink.
it will take some time to recover to an equilibrium state. To remed-edy this the collision has to be set low, but rare collisions will make the time to reach a canonical ensemble very long.

The Nosé-Hoover\textsuperscript{49,33} thermostat couples the equations of motion to an external system with fictitious mass and an extra degree of freedom that controls the temperature. Compared to the stochastic schemes it only weakly disrupts the trajectories. It does not break the mode-locking\textsuperscript{I} of near harmonic systems,\textsuperscript{33} which must be taken into account when, for example, performing a thermodynamic integration. The accurate trajectories are well suited for small systems since only a smooth disturbance is introduced.

Another stochastic way of controlling temperature is to solve Langevin’s equations of motion instead of Newton’s:

\begin{equation}
\dot{r}_i = \frac{p_i}{M_i}, \quad \dot{p}_i = f_i + \gamma p_i + \xi_i.
\end{equation}

These equations were originally intended to describe Brownian motion, with a friction parameter $\gamma$ and a random contribution $\xi$ to the forces from collisions. These equations can be integrated in a Verlet-like scheme\textsuperscript{1} with the random collisions controlling the temperature and speeding up the phase space sampling.

In figure 4.3 we ran simulations using the different schemes for a two-dimensional harmonic oscillator. The mode-locking of the non-stochastic schemes is clearly illustrated.

\textit{Free energy and thermodynamic integration}

Many parameters derived from molecular dynamics are mere indicators of what happens when the system is minimizing the free instead of the internal energy. High temperature elastic constants, averaged electronic densities of state or radial distribution functions are used to show that the system wants to go one way or another. If the full Gibbs free energy surface would be accessible most of these indicators would become redundant.

Unfortunately, the free energy is a thermal parameter and not directly accessible from the phase space trajectories. One can, however, extract it from a series of calculations coupling a harmonic and the ab initio potential energy surfaces.\textsuperscript{25}

The partition function for a system with a given potential energy function $U(r)$ is

\begin{equation}
Z = \frac{1}{\Lambda^{3N} N!} \int \exp \left( -\beta U(\{r\}) \right) d\{r\}
\end{equation}

and we remember that Helmholz free energy is given by

\begin{equation}
F = -k_B T \ln Z.
\end{equation}
The Kirkwood coupling technique\textsuperscript{38} starts by writing $U$ as a linear combination of two potential energy functions

$$U(\{r\}, \lambda) = (1 - \lambda)U_i(\{r\}) + \lambda U_f(\{r\}).$$ (4.13)

Inserting this into the equations above and differentiating with respect to $\lambda$ gives us

$$\frac{\partial F}{\partial \lambda} = -k_B T \frac{\partial}{\partial \lambda} \ln Z(\lambda)$$

$$= k_B T \frac{\partial Z(\lambda)}{Z(\lambda)} \frac{\partial \lambda}{\partial \lambda}$$

$$= \int \frac{\partial U}{\partial \lambda} \exp (-\beta U(\{r, \lambda\})) d\{r\}$$

$$= \langle \frac{\partial U}{\partial \lambda} \rangle_{\lambda}$$

$$= (U_f - U_i)_t$$

and the opportunity to integrate it

$$F_f - F_i = \int_0^1 (U_f - U_i) d\lambda.$$ (4.15)

If we choose $U_i$ to be a harmonic potential energy we know exactly the free energy of that system. We can then integrate to the free energy of any system, $F_f$. This is practically done by performing molecular dynamics with the mixed Hamiltonian for several values of $\lambda$ and integrating numerically.
TEMPERATURE DEPENDENT EFFECTIVE POTENTIAL

Born–von Karman-theory describes the potential energy surface of the atoms as a Taylor expansion from the ideal positions at zero temperature. At finite temperature the potential energy surface can be significantly different. Molecular dynamics provides accurate trajectories along this finite temperature surface, but thermodynamic properties are significantly harder to determine.

As mentioned in chapter 3 the idea of sampling the potential energy surface at a thermally excited state is not new. It came to be when treating solid He, where the Taylor expansion fails to predict a stable state even at arbitrary order. In his 1955 paper Hooton introduced the idea of an effective potential energy surface that changes with temperature, and to predict thermal behaviour the surface should be sampled in its relevant states. Modern tools such as BOMD were not available at the time, and the work was focused on developing thorough formalisms. With modern DFT-based techniques the problem is significantly easier. We can directly probe the potential energy surface and invert the problem using basic algebra.

I will first describe my approach, the temperature dependent effective potential method (TDEP), using a single anharmonic oscillator in one dimension, to make it clear how straightforward the method is. I will then generalise it to the three dimensional periodic lattice, to follow up with examples and some details on the numerics.

A one-dimensional anharmonic oscillator

Consider the following one-dimensional potential:

$$U(x) = \frac{k(x - x_0)^2}{2} + \alpha e^{-\beta(x - x_0)^2}.$$  \hspace{1cm} (5.1)

It is a harmonic potential with an extra term to make it anharmonic. The equilibrium position can depend on temperature and is shifted an unknown amount $x_0$ from 0, the assumed equilibrium position at $T = 0$. The aim is to find the second degree polynomial that best describes the system. If this polynomial only consist of a quadratic and a constant term it will describe a harmonic oscillator with well defined energy levels, making the extraction of thermodynamic properties trivial (see chapter 3). If one were to apply the harmonic approximation to potential 5.1 it would not work well. The second derivative

$$\frac{d^2U}{dx^2} = k - 2\alpha \beta e^{-\beta(x - x_0)^2} + (4\alpha \beta (x - x_0))^2 e^{-\beta(x - x_0)^2}$$  \hspace{1cm} (5.2)
FIGURE 5.1: Comparison of performance of TDEP and the harmonic Taylor expansion for the potential described by equation 5.1. Three examples when the harmonic approximation fails to describe the potential and TDEP succeeds. The left hand panels show the potentials and the right hand show the forces. $\alpha$ and $x_0$ are the parameters in equation 5.1.

In panel (a) the harmonic approximation is dynamically unstable, whereas TDEP provides an appropriate description. In panel (b) the harmonic approximation provides an inaccurate potential. Panel (c) shows how TDEP finds the high temperature equilibrium position.

will determine the force constant $\Phi$. Since we are unaware of the shift of the equilibrium from the ideal position at $x = 0$ we will end up with

$$\Phi = \frac{d^2U}{dx^2} |_{x=0} = k + 2\alpha\beta(2\alpha\beta x_0 - 1)e^{-\beta x_0^2}. \quad (5.3)$$

This, as seen in figure 5.1, will not be a particularly good model for the true potential. These issues arise from the fact that the potential energy surface is only probed at the equilibrium positions. To work around this problem, let us put a particle in the potential given by equation 5.1 and perform a MD simulation. When controlled by an appropriate thermostat, the particle will yield a set of $N_t$ forces, positions and energies, $\{F_t, x_t, E_t\}$, one for each timestep. This data can now be used to fit a potential of the form

$$U(x) = \Phi^{(0)} + \frac{1}{2} \Phi^{(2)} (x - x')^2, \quad (5.4)$$

a harmonic potential centered at $x'$. Let us begin by determining the second order term. To do that we guess a value for $x'$, use the forces from molecular dynamics $\{F_t\}$ and minimize

$$\min_{\Phi^{(2)}} \Delta F = \min_{\Phi^{(2)}} \frac{1}{N_t} \sum_{t=1}^{N_t} |F_t - \Phi^{(2)} (x_t - x')|. \quad (5.5)$$

This is easiest realized as a least squares fit of a straight line in forces, as demonstrated in the right panel of figure 5.1. Equation 5.5 determines the second order term. The residual force at $x'$,
\( \Delta F \), can be used to find the equilibrium position \( x' \). It is done in the following manner: a guess for \( x' \) gives us \( \Phi^{(2)} \) and \( \Delta F \). This residual force is used to move \( x' \) to a new position, and the process is repeated. When the equilibrium position is determined we can safely assume that any first order term in our polynomial can be set to zero. The constant energy term, \( \Phi^{(0)} \), can be determined from the energies \( \{ E_t \} \):

\[
\Phi^{(0)} = \left\langle E_t - \frac{1}{2} \Phi^{(2)} (x_t - x')^2 \right\rangle_t. \tag{5.6}
\]

This is the best possible potential of the harmonic form at a given temperature. In figure 5.1 the true potential and the fit is illustrated for different \( \alpha, \beta \) and \( x' \). The anharmonism of the potential is implicitly described by the polynomial fit. In figure 5.2 the expansion has been extended to higher orders for an anharmonic potential. TDEP, probing the effective potential at finite temperature, converges to the true potential rapidly whereas including more terms in the Taylor expansion does by no means guarantee numerical stability at finite temperature.
Extending the method to the periodic lattice

In order to describe a periodic lattice in a crystal potential the framework has to be generalized. The model potential in the one-dimensional case is replaced by DFT and the phase space is sampled using BOMD. This will provide positions, forces and energies at finite temperature. Application of TDEP is just as straightforward as the polynomial fit for the one dimensional case, but since the simulations can only be performed with limited accuracy some effort must be put into handling the numerical errors.

The starting point is to introduce a model Hamiltonian on the harmonic form for $N_a$ atoms:

$$
\hat{H} = U_0 + \sum_{i=1}^{N_a} \frac{p_i^2}{2M_i} + \sum_{i=1}^{N_a} \sum_{j=1}^{N_a} u_{ij} \tilde{\Phi}_{ij} u_j
$$

(5.7)

where the interatomic force constants $\Phi$ and the ground state energy $U_0$ are yet to be determined. In this model system the forces are given by

$$
\begin{pmatrix}
 f_1 \\
 f_2 \\
 \vdots \\
 f_{N_a}
\end{pmatrix}
= \begin{pmatrix}
 \tilde{\Phi}_{11} & \tilde{\Phi}_{12} & \cdots & \tilde{\Phi}_{1N_a} \\
 \tilde{\Phi}_{21} & \tilde{\Phi}_{22} & \cdots & \tilde{\Phi}_{2N_a} \\
 \vdots & \vdots & \ddots & \vdots \\
 \tilde{\Phi}_{N_a1} & \tilde{\Phi}_{N_a2} & \cdots & \tilde{\Phi}_{N_aN_a}
\end{pmatrix}
\begin{pmatrix}
 u_1 \\
 u_2 \\
 \vdots \\
 u_{N_a}
\end{pmatrix}
.$$

(5.8)

This is a reformulation of equation 3.9 to matrix form. The mapping between this form and the one used in chapter 3 is determined by the BOMD simulation cell. What we seek is the effective second order force constant matrix $\tilde{\Phi}$. A BOMD simulation will provide a set of displacements $\{U_{MD}^t\}$, forces $\{F_{MD}^t\}$ and potential energies $\{E_{MD}^t\}$. We seek to minimize the difference in forces from BOMD ($F_{MD}^t$) and our harmonic form ($F_{H}^t$):

$$
\min \Delta F = \min_{\tilde{\Phi}} \frac{1}{N_t} \sum_{t=1}^{N_t} \left| F_{MD}^t - F_{H}^t \right|^2 = \min_{\tilde{\Phi}} \frac{1}{N_t} \sum_{t=1}^{N_t} \left| F_{MD}^t - \tilde{\Phi} U_{MD}^t \right|^2 = \min_{\tilde{\Phi}} \frac{1}{N_t} \left\| \left(F_{MD}^1 \ldots F_{MD}^{N_t}\right) - \tilde{\Phi} \left(U_{MD}^1 \ldots U_{MD}^{N_t}\right) \right\|.
$$

(5.9)

This is realized with a Moore-Penrose pseudoinverse

$$
\tilde{\Phi} = \left(F_{MD}^1 \ldots F_{MD}^{N_t}\right) \left(U_{MD}^1 \ldots U_{MD}^{N_t}\right)^+.
$$

(5.10)

to obtain the linear least squares solution for $\tilde{\Phi}$. This is then mapped to the form

$$
\tilde{\Phi} \rightarrow \Phi_{\alpha\beta}^{\mu\nu}(R_t).
$$

(5.11)
where $\alpha\beta$ are indices to a unit cell with $N_{uc} \leq N_a$ atoms and $\mu\nu$ are Cartesian indices. The pair vectors in the supercell $R_{ij}$ are mapped to stars of vectors $R_l$ connecting atoms of type $\alpha$ and $\beta$. From this form the phonon dispersion relations, free energy and all other quantities are extracted. This direct implementation of TDEP works well, but the numerical efficiency can be improved.

In figure 5.3 we have a diatomic system where we consider interactions up to the second nearest neighbour. The straightforward implementation described above would solve for $\Phi$ with all the $(3N_a)^2$ components of $\Phi$ as unknown quantities, but judging from the figure there should be several interactions that are equivalent. Each arrow in the figure represent a force constant, and there are due to symmetry only three inequivalent interactions. The following section describes how to constrain the extraction of the interactions making them obey the proper symmetry.
Symmetry constrained force constant extraction

The form of the force constant matrices depends only on the supercell used in the BOMD and the crystal lattice. We begin by populating the force constant matrices $\Phi_{\alpha\beta}^{\mu\nu}(R_l)$ with unknown variables $\theta_k$

$$\Phi^{11}(R_1) = \begin{pmatrix} \theta_1 & \theta_2 & \theta_3 \\ \theta_4 & \theta_5 & \theta_6 \\ \theta_7 & \theta_8 & \theta_9 \end{pmatrix}$$

$$\Phi^{11}(R_2) = \begin{pmatrix} \theta_{10} & \theta_{11} & \theta_{12} \\ \theta_{13} & \theta_{14} & \theta_{15} \\ \theta_{16} & \theta_{17} & \theta_{18} \end{pmatrix}$$

and so on, including vectors $R_l$ up to a cutoff determined by the size of the supercell. Many of these $\theta_k$ are equivalent. To find out which, we study the symmetry relations the force constant matrices have to obey. We have

$$\sum_{l\alpha} \Phi_{\alpha\beta}^{\mu\nu}(R_l) = 0 \text{ for each } \beta$$

$$\Phi_{\alpha\beta}^{\mu\nu}(R_l) = \Phi_{\beta\alpha}^{\mu\nu}(\text{S} R_l)$$

$$\Phi_{\alpha\beta}^{\mu\nu}(R_l) = \Phi_{\mu\nu}^{\alpha\beta}(R_l)$$

that stem, in order, from the facts that there is no net translation of the crystal, all Bravais lattices have inversion symmetry, and that the order of the second derivatives does not matter. Each relation will give a few equations for the unknowns $\theta_k$, reducing the number of independent variables. In addition to these fundamental properties of the force constant matrices we can benefit from the symmetry of the lattice. If symmetry operation $S$, belonging to the point group of the lattice, relates two vectors $R_l = SR_k$ we have the following relation:

$$\Phi_{\alpha\beta}^{\mu\nu}(R_l) = S \Phi_{\alpha\beta}^{\mu\nu}(R_k) S^T. \quad (5.16)$$

By applying equations 5.13–5.16 the number of inequivalent $\theta_k$ are massively reduced. For example, a body centered cubic (bcc) lattice modelled as a $4 \times 4 \times 4$ supercell (128 atoms) has 147456 unknowns in $\Phi$ not considering symmetry. The symmetry reduced problem has 11 unknown variables $\theta_k$. Having found the reduced problem with $N_{\theta}$ unknown variables, it can be substituted back into $\Phi$. The expression for the forces at timestep $t$ will
schematically look like:

\[
\begin{pmatrix}
  f_1 \\
  f_2 \\
  \vdots \\
  f_\gamma \\
  \vdots \\
  f_{3N_a}
\end{pmatrix}
= 
\begin{pmatrix}
  \theta_1 & 0 & 0 & \ldots \\
  0 & \theta_1 & 0 & \ldots \\
  0 & 0 & \theta_1 & \ldots \\
  \theta_2 & \theta_3 & -\theta_4 & \ldots \\
  \theta_3 & -\theta_2 & 0 & \ldots \\
  -\theta_4 & 0 & 0 & \ldots \\
  \vdots & \vdots & \vdots & \ddots
\end{pmatrix}
\begin{pmatrix}
  u_1 \\
  u_2 \\
  \vdots \\
  u_\gamma \\
  \vdots \\
  u_{3N_a}
\end{pmatrix}.
\]

(5.17)

The actual distribution of the \( \theta_k \) will depend on the problem at hand. Carrying out the matrix product produces a new set of equations for the forces

\[
f_\gamma = \sum_k \theta_k \sum_\delta c_{\gamma \delta} u_\delta.
\]

(5.18)

where second sum describes the coefficients for each \( \theta_k \) contained in the expression for force component \( f_\gamma \). These coefficients are linear combinations of the displacement components \( u_\delta \). The explicit form is determined by the lattice. In matrix form this is written

\[
F = \tilde{C}(U)\Theta, \quad C(U)_{\gamma \delta} = \sum_k \theta_k \delta_{\gamma \delta} u_\delta.
\]

(5.19)

This equation is equivalent to equation 5.8, it is just rewritten in the terms of the symmetry inequivalent interactions. Our implementation of TDEP symbolically reduces the number of unknowns, generates the function that gives the matrix \( \tilde{C} \) from a set of displacements \( U \) and the mapping from the set of \( \theta_k \) back to the force constant matrix \( \Phi^{\mu\nu}_{\alpha\beta}(R_i) \).

To find \( \Theta \) we repeat the process used to find \( \Phi \): minimize the difference in forces between BOMD and the model Hamiltonian

\[
\min_\Theta \Delta F = \min_\Theta \frac{1}{N_t} \sum_{t=1}^{N_t} \left| F_{MD}^t - F_{H}^t \right|^2 = \\
\min_\Theta \frac{1}{N_t} \sum_{t=1}^{N_t} \left| F_{MD}^t - \tilde{C}(U)_{MD}^t \Theta \right|^2 = \\
\min_\Theta \frac{1}{N_t} \left| \begin{pmatrix}
  F_{MD}^1 \\
  \vdots \\
  F_{MD}^{N_t}
\end{pmatrix} - \begin{pmatrix}
  \tilde{C}(U)^{MD}_1 \\
  \vdots \\
  \tilde{C}(U)^{MD}_{N_t}
\end{pmatrix} \Theta \right|^2.
\]

(5.20)

This is again realised with the least squares solution for \( \Theta^{\text{II}} \)

\[
\Theta = \begin{pmatrix}
  \tilde{C}(U)^{MD}_1 \\
  \vdots \\
  \tilde{C}(U)^{MD}_{N_t}
\end{pmatrix} + \begin{pmatrix}
  F_{MD}^1 \\
  \vdots \\
  F_{MD}^{N_t}
\end{pmatrix}
\]

(5.21)

\[ \text{II} \text{ Once again a note on the dimensions: the force vector will have } 3N_aN_t \text{ rows. Each submatrix } \tilde{C} \text{ will have } 3N_a \text{ rows and } N_\theta \text{ columns. The full coefficient matrix has } 3N_aN_t \text{ rows and } N_\theta \text{ columns. } \Theta \text{ is a row vector with } N_\theta \text{ rows.} \]
Having determined $\Theta$ we can substitute the components into the force constant matrix and proceed to calculate phonon dispersion relations and thermodynamic properties.

This is a numerically superior way of using symmetry to improve the numerical accuracy. Most schemes involving symmetry revolve around determining the interaction in one direction and then using the symmetry relations to translate and rotate that interaction. The unavoidable numerical errors will propagate to all interactions, whereas in my method the errors will be averaged and should cancel each other out.
**Internal degrees of freedom**

Just as in the one-dimensional case we have started with determining the second order force constants. If the system has internal degrees of freedom, such as a system with defects, an interface or a random alloy, the atoms ideal positions and equilibrium positions do not coincide. While one could find the relaxed positions from 0K calculations, the equilibrium positions are by no means constant with respect to temperature. TDEP handles this in an elegant fashion. Just as for the one-dimensional oscillator we find the second order terms with a least squares fit of the slope of force versus displacement. Even though the displacements are calculated with respect to the wrong equilibrium position the slope will be the same. That allows for the following procedure:

- Guess equilibrium positions, usually the ideal lattice positions.
- Use these to calculate the displacements $u$ from the BOMD simulations.
- Determine $\Theta$ and from that the residual force

$$F_r = \sum_{t=1}^{N_t} \frac{1}{N_t} F_{t}^{MD} - F_{t}^{H},$$

(5.22)

where $F_{t}^{MD}$ are the BOMD forces and $F_{t}^{H}$ are given by equation 5.19.
- Use forces are then used to move the atoms towards the equilibrium positions.
- Repeat until convergence.

Tests shows that this procedure is remarkably stable. The second order force constants $\Phi$ are weakly affected by the choice of equilibrium position. The vibrational entropy and phonon dispersion relations are largely unaffected as well. Eliminating the first order term, however, is formally important and crucial when extracting higher order terms. In figure 5.4 the difference between the ideal positions, the 0 K relaxed positions and the finite temperature positions of reduced ceria is illustrated.
TEMPERATURE DEPENDENT EFFECTIVE POTENTIAL

- A, high temperature
- A, 0K relaxed
- A, ideal
- B, high temperature
- B, 0K relaxed
- B, ideal

FIGURE 5.4: Finite temperature equilibrium positions for a low-symmetry diatomic system. For clarity, the displacements from ideal positions are greatly exaggerated, both for the 0K and high temperature case. In general, the equilibrium positions move towards the ideal positions with increased temperature. If this is a general trend is too early to tell, but has turned out to be true for all systems investigated. This specific case is for ceria with an oxygen vacancy.

**Determining the free energy**

We will begin by reiterating the traditional way of how free energy is determined in the quasiharmonic approximation. Divided into parts it will be

\[
F = U - TS
= U_{\text{tot}} - TS_{\text{el}} + \langle E_k \rangle + \langle U_{\text{vib}} \rangle + U_{\text{zp}} - TS_{\text{vib}},
\]

(5.23)

a clear distinction between the electronic contribution \( F_{\text{el}} \) and the vibrational contribution \( F_{\text{vib}} \). The electronic contribution is divided into the total energy of the lattice, \( U_{\text{tot}} \), and the electronic entropy \( S_{\text{el}} \). The vibrational contribution is divided into average kinetic \( E_k \) and potential energy \( U_{\text{vib}} \) of the ions, vibrational entropy \( S_{\text{vib}} \) and zero point energy \( U_{\text{zp}} \). The lattice contribution is obtained from DFT calculations with the Mermin functional and the vibrational part from the harmonic approximation via equation 3.20. In this approach, all the vibrational contributions are within the harmonic approximation.

Turning to BOMD, the free energy (in the canonical ensemble) is divided as

\[
F = (U_{\text{MD}}) + \langle E_k \rangle - TS_{\text{vib}} + U_{\text{zp}}.
\]

(5.24)

Where the potential energy \( U_{\text{MD}} \) fully contains the temperature dependence. There is unfortunately no information about the entropy, but through the force constant matrices obtained using TDEP, the vibrational entropy and zero point energy can be estimated. For TDEP to have an accurate free energy the potential
DETERMINING THE FREE ENERGY

![Figure 5.5](image)

**Figure 5.5**: Illustration of the different terms included in free energy calculations using different approaches. The filled boxes denote the terms that are included, and the striped areas what is omitted. The main message is to point out that the internal energy has a non-trivial temperature dependence, something that is omitted in the quasiharmonic approximation. The missing part of the free energy for TDEP is denoted higher order terms (HOT), and can in principle be calculated using thermodynamic integration.

<table>
<thead>
<tr>
<th>Method</th>
<th>U correct at 0K</th>
<th>Harmonic F</th>
<th>No vibrational contribution</th>
<th>No anharmonic contributions</th>
<th>Correct temperature dependent U</th>
<th>No explicit entropy</th>
<th>Model Hamiltonian entropy contribution</th>
<th>HOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static DFT calculations</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Harmonic approximation</td>
<td>U correct at 0K</td>
<td>Harmonic F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOMD</td>
<td>Correct temperature dependent U</td>
<td>No explicit entropy</td>
<td></td>
<td>Model Hamiltonian entropy contribution</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HTEP</td>
<td>U extracted from BOMD, correct temperature dependence</td>
<td>Model Hamiltonian entropy contribution</td>
<td></td>
<td>Model Hamiltonian entropy contribution</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Energy should, on average, be equal to that of BOMD. This would ensure that the full anharmonic $\langle U_{\text{vib}} \rangle$ is included. The problem is that $U_{\text{MD}}$ is rapidly oscillating over time, requiring a long simulation time to converge. If we look at the TDEP potential energy

$$U(t) = U_0 + \frac{1}{2} \sum_{ij\alpha\beta} \Phi_{ij} \alpha_i(t) \alpha_j(t)$$

and recognise that it should model the thermal fluctuations we can overcome the numerical issues. Setting the average potential energies equal, $\langle U_{\text{MD}} \rangle = \langle U_{\text{HTEP}} \rangle$, gives us

$$U_0 = \left\langle U_{\text{MD}}(t) - \sum_{ij\alpha\beta} \frac{1}{2} \Phi_{ij} \alpha_i(t) \alpha_j(t) \right\rangle$$

By removing the thermal excitations on the harmonic form the fluctuations have been decreased by roughly an order of magnitude and we have thus increased the accuracy by the same amount. Including higher order terms in the energy expansion would further serve to minimize these fluctuations.

The potential energy that was removed will be added again when the Helmholtz free energy is calculated:

$$F_{\text{TDEP}} = U_0 + F_{\text{vib}},$$

where $F_{\text{vib}}$ is the phonon contribution given by equation 3.20. It includes the kinetic and potential energy of the ions. In figure 5.5 we further illustrate the difference in methods of obtaining the free energy.

As described in section 4.4, the formally exact method of thermodynamic integration can be used to determine the free energy. This method will determine the anharmonic correction to the free energy.
energy. If the TDEP model Hamiltonian is used as the reference point the full free energy will be

\[ F = U_0 + F_{\text{vib}} + \int_0^1 \left( U_{\text{MD}|\lambda} - U_{\text{HTEP}|\lambda} \right) \, d\lambda. \]  

(5.28)

The mixing of the Hamiltonians enter in implementations as the mixing of forces. At \( \lambda = 0 \) the ions propagate according to the model Hamiltonian and at \( \lambda = 1 \) they move as in a regular BOMD simulation. By definition, at \( \lambda = 1 \) the average difference is 0. The model Hamiltonian is constructed to describe the system as accurately as possible while retaining the harmonic form. It is then easy to argue that the anharmonic correction term \( \Delta F_{\text{AH}} \) should be small. While it is difficult to make general statements regarding this, the trend in every system tested is that this correction is very small.

Unfortunately, the thermodynamic integration technique is numerically inefficient. While one can accurately control the numerics,\(^27\) the finite size effects are important. In figure 5.6 we show that the error due to the limited size is of the same order as the correction to the free energy in reasonable simulation sizes. It makes little use to add a correction where the uncertainty is of the same order of magnitude as the correction itself. TDEP on the other hand, behaves better with respect to limited simulations size. In figure 5.7 we see that the reasonable system size of 100 atoms the free energy is converged within 1 meV/atom. This makes, as far as I know, TDEP the most accurate method to determine anharmonic free energies given the present limitations on computational resources.

FIGURE 5.6: Convergence of the free energy correction with respect to system size. The correction is the last term in equation 5.28, obtained through thermodynamic integration. At system sizes smaller than \( \sim 700 \) atoms the uncertainty is of about the same size as the correction. This particular case is for fcc Cu modelled with an embedded atom potential.\(^9\)

FIGURE 5.7: Convergence of the free energy from TDEP with respect to simulation size. The energy is calculated from equation 5.27 and is presented as the difference to the converged value. The system in question is fcc Cu with a classical embedded atom potential.\(^9\) At sizes about 100 atoms it is converged within 1 meV/atom.
Upsampling and error analysis

When performing BOMD the numerical accuracy of the DFT calculations are usually at a level far below that of static calculations. In many cases one needs higher accuracy, but it is computationally demanding.

When performing a thermodynamic integration the energies from BOMD have to be well converged, when calculating elastic constants the stress tensor needs to be accurate. TDEP needs accurate energies and forces. Well converged DFT calculations are far too costly to achieve a sufficient phase space sampling. If one instead performs the calculations with low accuracy we can sample phase space well. From these low accuracy calculations we choose a set of $n$ uncorrelated samples and correct scalar parameter $a$ as

$$a = \left\langle a^L \right\rangle + \frac{1}{n} \sum_{i=1}^{n} a^H_i - a^L_i$$  \hspace{1cm} (5.29)

where $a^L$ are the low accuracy calculations and $a^H$ are calculations done with high accuracy. This exploits the fact that most omissions of numerical accuracy, such as basis set and k-point selection, lead to additive errors. This technique is well suited to accurately determine $U_0$ in the TDEP model Hamiltonian via equation 5.26.

When it comes to quantities that are not scalar the method is just as useful. In systems that are nearly harmonic the number of uncorrelated configurations needed for convergence of the extracted force constants (and by extension the free energy) is rather low. In these cases the force constant matrices can be extracted from the upsampled configurations alone.

In systems that are strongly anharmonic one needs a much denser sampling of phase space to converge, sometimes so dense that it is impractical to upsample. The procedure still gives us some important insights: the errors in forces due to low accuracy are normally distributed around the converged values, and the standard deviation depends only weakly on the magnitude of the force. In figure 5.8 we show the distribution of the errors, and in figure 5.9 the weak dependence on the magnitude of the forces.

Because the errors are normally distributed around the fully converged values one can compensate for low accuracy with large numbers of less accurate calculations. The extracted force constants will converge to the same value. Tests have confirmed this, phonon dispersion relations agree within line thickness. Convergence with respect to the number of uncorrelated configurations is slower in the low accuracy case, but sometimes it is the only option.
Small displacements
Molecular dynamics
Relative error in forces

FIGURE 5.10: Histograms of magnitudes of forces, comparing molecular dynamics and the small displacement method for FeV. The relative error in forces (due to insufficient accuracy) is not constant with respect to the magnitude of the force. The line shows that by sampling the forces at thermally relevant excitations we decrease the numerical error by two orders of magnitude.

We also see that sampling forces at a thermally excited state is numerically beneficial. With the absolute error in forces weakly depending on the magnitude the relative error in forces behaves as $\sim |F|^{-1}$. In figure 5.10 histograms of the force magnitudes in FeV are illustrated, together with the relative error in forces. We compare forces obtained from BOMD to the small displacement method. The small displacement method samples forces at magnitudes where the relative errors is about two orders of magnitude larger than at a thermally relevant state. So not only do we better describe the physics at high temperature, we do it in a numerically superior manner.
Computational efficiency

Born-Oppenheimer molecular dynamics is computationally demanding. With a method based on it, some care should be taken to make the use of our computers as efficient as possible. The implementations of BOMD that scale weakly with added computational resources we need an alternative to waiting for the simulations to dynamically decorrelate, and transform the problem to a strongly scaling one.

The standard procedure in BOMD is to initialize the velocities according to a Maxwell-Boltzmann distribution with no initial displacements. The system then spends considerable time equilibrating itself. This period is then omitted in the final analysis. West et al.\textsuperscript{64} proposed a method to prepare the initial state of the supercell to minimize or completely remove this equilibration time.

Given a harmonic potential, we can write the equations of motion for the atoms in the supercell:

$$
\begin{pmatrix}
M_1 \ddot{u}_1 \\
M_2 \ddot{u}_2 \\
\vdots \\
M_{Na} \ddot{u}_{Na}
\end{pmatrix}
= 
\begin{pmatrix}
\Phi_{11} & \Phi_{12} & \cdots & \Phi_{1Na} \\
\Phi_{21} & \Phi_{22} & \cdots & \Phi_{2Na} \\
\vdots & \vdots & \ddots & \vdots \\
\Phi_{Na,1} & \Phi_{Na,2} & \cdots & \Phi_{Na,Na}
\end{pmatrix}
\begin{pmatrix}
u_1 \\
u_2 \\
\vdots \\
u_{Na}
\end{pmatrix}
$$

(5.30)

These equations are solved by diagonalizing the problem with a normal mode transformation. The $3Na$ eigenvalues $\omega_k^2$ and eigenvectors $\epsilon_k$ from equation 3.14 provides the details of this transformation:

$$
u_j = \sum_{h=1}^{3Na} \epsilon_{jh} c_k e^{i(\omega_k t + \delta_k)}$$

(5.31)

$$
\dot{u}_j = \sum_{h=1}^{3Na} i \epsilon_{jh} c_k \omega_k e^{i(\omega_k t + \delta_k)}.
$$

(5.32)

The amplitudes of the modes are defined up to the constant $c_k$ and the random phase $\delta_k$. We know that the velocity components should be normally distributed with a standard deviation of $\sigma = \sqrt{k_B T/M}$ and that each mode $k$ should contribute, on average, $k_B T/2$ to the internal energy. If we choose the coefficients

$$
c_k = \frac{1}{\omega_k} \sqrt{\frac{2k_B T}{M}} \sqrt{-\ln \chi}
$$

(5.33)

with $\chi$ as a uniformly distributed random number $0 < \chi < 1$ we fulfill these criteria. The $\delta_k$ are introduced to give each mode a random phase to ensure an even distribution of potential and kinetic energy, they are uniformly distributed as $0 < \delta_k < 2\pi$.

This means, that for a given temperature I can estimate the appropriate excitation and eliminate the equilibration time. With
FIGURE 5.11: Illustration of the improvement of the phase space spanning when using several starting configurations. This particular case is fcc Cu with an embedded atom potential. With 125 atoms the momentum space should have 372 dimensions. A single simulation spans 70 of these dimensions, whereas the combined set of 10 configurations spans all of phase space.

no equilibration time there is no disadvantage to run several calculations in parallel, in fact it makes sampling the phase space embarrassingly parallel. It is not just efficient, it also makes phase space sampling faster. In figure 5.11 I have plotted the singular value decompositions of the momentums from an increasing number of included configurations. The phase space spanning increases rapidly when performing calculations in parallel from different starting configurations.
Practical procedure

To summarize this chapter I present the scheme used to calculate accurate Gibbs free energy surfaces in the TDEP formalism.

- Obtain static DFT total energy calculations. These provide an equation of state that allows us to choose an approximate pressure regime.

- If feasible, obtain approximate harmonic potentials for the systems at hand in this pressure regime. These potentials are used to speed up the calculations as described in section 5.7.

- On a grid of volumes and temperatures, perform BOMD simulations in the canonical ensemble.

- Extract internal energy and interatomic force constants and ensure the convergence of the free energy with respect to simulation length.

- If possible, select a subset of uncorrelated samples from the BOMD simulations and upsample these to high accuracy, as per section 5.6. Adjust the model Hamiltonian and the free energy accordingly.

- The equation of state is interpolated over the grid of temperatures and volumes providing the Gibbs free energy surface. This is then repeated for each structure, compound or composition of interest.

This is a thorough and time-consuming method, but the results are excellent. The phonon dispersion relations of dynamically unstable materials is a good example.
In figure 5.12 I present the dispersion relations for bcc Li. The bcc phase is unstable at 0K. It is stabilized by the anharmonic contributions at around 70K and is the phase at ambient conditions. The standard methods of determining phonon dispersion relations show imaginary frequencies, whereas my method have excellent agreement with experimental values.
Phonon dispersion relations for bcc Zr. Solid lines correspond to calculations at 1300 K, dashed lines to the quasiharmonic results and symbols to experimental values from Heiming et al. 29 (circles) and Stassis et al. 57 (filled circles).

Calculated bcc-hexagonal close packed (hcp) phase diagram for Zr. The stable region for bcc is the yellow field and for hcp the teal. The black lines show the experimental phase diagram, 65 which also includes solid ω and liquid phases, not considered in simulations.

Zr in the bcc phase is a similar story. Also here we have excellent agreement with experiment as illustrated in figure 5.13. We have also determined the theoretical bcc-hcp phase diagram. Without the use of TDEP this has previously been impossible to reproduce with this level of accuracy. It is presented in figure 5.14.
A slightly more complex system is FeV. Experimentally, it is shown that the vibrational entropy pushes the system towards ordering in the B2 structure.\(^\text{48}\) In figure 5.15 we show the Gibbs free energy difference between the ordered and disordered phases. If the configurational contribution to the entropy is excluded the vibrational free energy pushes the system towards ordering at high temperatures, as predicted experimentally. This trend is overcome by the configurational contribution, and there is no disorder-order phase transition with temperature, something that agrees with the experimental picture.

\(^{48}\)
MONTE CARLO METHOD

Born-Oppenheimer molecular dynamics is a powerful and accurate tool, but it is severely limited in terms of simulation size (a few hundred atoms) and time (typically picoseconds). To model phenomena outside this window we have used the Monte Carlo method in combination with model hamiltonians.

The Metropolis algorithm

Suppose we want to calculate a thermal average of property $A$

$$
\langle A \rangle = \frac{\int A(\{r\}) \exp(-\beta U(\{r\})) d\{r\}}{\int \exp(-\beta U(\{r\})) d\{r\}} \quad (6.1)
$$

through sampling of phase space. A brute force sampling is numerically impossible. In the Metropolis scheme we identify

$$
n_i = \frac{\exp(-\beta U(\{r_i\}))}{Z} \quad (6.2)
$$

as the probability density of configuration $\{r_i\}$. The thermal average can be estimated

$$
\langle A \rangle \approx \frac{1}{N} \sum_{i=1}^{N} n_i A(\{r_i\}) \quad (6.3)
$$

where $N$ is the number of configurations considered. A majority of the points in phase space will be associated with a very low probability (high energy), and will thus have negligible impact on the average. The Metropolis scheme exploits this to only select configurations that will have a meaningful impact on the average, reducing the number of configurations considerably. The algorithm used to calculate this average looks as follows:

- From an initial state $s_i$, introduce a perturbation nudging it to state $s_j$.

- Determine the probability of state $s_i$ and $s_j$ through its energy as per equation 6.2.

- State $s_j$ is then accepted with probability

$$
p = \begin{cases} 
\frac{n_j}{n_i}, & n_j \leq 1 \\
1, & n_j > 1 
\end{cases}
$$

- Repeat until equilibrium is reached.
Model Hamiltonian

I have used the Metropolis Monte-Carlo scheme to study equilibrium configurational entropy in low-dimensional alloys. While one could in principle determine the configurational energy from DFT directly, the need for large systems usually makes it too expensive. For example, in a binary random alloy with components $A$ and $B$ the configurational energy is expressed as

$$\hat{H} = \sum_{ij} V_{ij}^{(2)} \sigma_i \sigma_j + \sum_{ijk} V_{ijk}^{(3)} \sigma_i \sigma_j \sigma_k + \sum_{ijkl} V_{ijkl}^{(4)} \sigma_i \sigma_j \sigma_k \sigma_l + \ldots$$

(6.4)

where the $\sigma_i$ are spin-like variables, taking the value +1 or -1 if site $i$ is occupied by component $A$ or $B$. The interaction parameters $V$ are derived from DFT calculations. In the Metropolis scheme, the perturbations to the system is in this case introduced as the exchange of two atoms. The steady state will then represent the finite temperature equilibrium distribution of atoms. I have used this method in Paper II to study the segregation effects in AgPd thin films.
THERMAL DEFECTS

So far we have only considered perfect lattices, real materials are riddled with defects. In fast oxygen conductors, such as ceria, the oxygen vacancy is the dominant defect. Understanding the physics behind the creation and mobility of these vacancies is crucial to improving the performance of fast ionic conductors.

Energetics of defect formation

The creation of a defect will increase the entropy of the crystal. An increasing temperature will, in general, facilitate the creation of point defects. To gain more insight into this process we have to study the energetics of defect creation. Starting with \( N \) atoms in state \( A \) (e.g. a perfect crystal) and ending up with \( N-n \) atoms in state \( B \) and \( n \) atoms in state \( C \) (here \( B \) could be the crystal with a defect and \( C \) a gas molecule) we end up with the reaction

\[
NA \rightarrow (N-n)B + nC.
\] (7.1)

The energy to create \( n \) defects in a crystal with \( N \) atoms is given by

\[
G_f^v = -NG_A + (N-n)G_B + nG_C,
\] (7.2)

where \( G \) is the Gibbs free energy per atom for the different states. At a certain pressure and temperature the equilibrium concentration of vacancies is determined by the condition

\[
\frac{\partial G_f^v(n,T,P)}{\partial n} = 0.
\] (7.3)

In general, all the components of \( G_f^v \) depend on \( n \) in a non-trivial fashion. What approximations are introduced is usually determined by the problem at hand, as such the remainder of this section will be discussed in the context of oxygen vacancies in ceria.

Oxygen vacancies in ceria

The functional properties of ceria is largely based on its ability to easily absorb and release oxygen depending on external conditions. This ability stems from a low vacancy formation energy and a high mobility of the vacancies.\(^6\) To optimise the performance a solid understanding of the vacancy creation process is crucial. We model it as the process

\[
\text{CeO}_2 \rightarrow \text{CeO}_{2-x} + \frac{x}{2}\text{O}_2.
\] (7.4)

That is we let the perfect crystal release an oxygen atom into oxygen gas, leaving a crystal with a vacancy behind. That the oxygen
atom ends up as gas is of course an approximation, in reality it could get caught at any step of the process, such as an adatom on the ceria surface, at a grain boundary or react with something in the surrounding atmosphere. In essence, the final resting place of the oxygen atom is a free parameter, but as long as it is kept constant meaningful comparisons can be made for compositions and conditions for the ceria matrix.

The second major approximation is to discuss the creation of defects only in the dilute limit, \( n \ll N \). Under these conditions the interaction between different vacancies can be ignored and the calculations are significantly simplified. The vacancy formation energy is given by

\[
G'_f = \frac{1}{x} G_{\text{CeO}_2} - \frac{1}{x} \mu_{O_2} - \frac{1}{x} G_{\text{CeO}_2}, \tag{7.5}
\]

where \( \mu_{O_2} \) is the chemical potential for oxygen in gas form. Leaving this as a parameter for the moment and dividing the Gibbs free energies into its constituent parts we have

\[
G'_f = \frac{1}{x} \left( H_{\text{CeO}_2} - T S^{\text{vib}}_{\text{CeO}_2} - T S^{\text{conf}}_{\text{CeO}_2} - x \right) + \mu_{O_2} - \frac{1}{x} \left( H_{\text{CeO}_2} - T S^{\text{vib}}_{\text{CeO}_2} \right), \tag{7.6}
\]

where \( H \) is the enthalpy and \( S \) the entropy. The configurational entropy \( S^{\text{conf}}_{\text{CeO}_2 - x} \) is easily determined and enters as

\[
S^{\text{conf}}_{\text{CeO}_2 - x} = k_B \ln \frac{N!}{(N-n)!n!}. \tag{7.7}
\]

The enthalpies and entropies can, in principle, be determined for each state using DFT. However, since the introduction of a defect destroys the periodicity of the lattice a new, larger cell, has to be introduced. The largest simulation cells possible are around 1000 atoms, nowhere near the dilute limit \( n \ll N \).

The enthalpies are directly accessible by DFT calculations. The limited size of the simulation cell can be adjusted for with a set of approximations and corrections. In Paper III I adjust this formalism to better handle ceria, whose complicated electronic structure requires special treatment.
Upon the creation of an oxygen vacancy there is a merging of the low frequency peaks as well as a rearrangement and smearing of the high frequency peaks.

Usually the change in vibrational entropy upon vacancy formation is ignored, mostly because of the complexity involved in determining the vibrational spectra of the system with defects. With the TDEP I have been able to determine the phonon density of states for both CeO$_2$ and CeO$_{2-x}$. They are presented in figure 7.2. This shows that TDEP can indeed be used for systems of low symmetry and that the change in vibrational entropy upon defect creation can have a significant impact on the vacancy formation energy.

**Vacancy migration**

At the operational temperatures of ceria, there is significant diffusion of oxygen ions. A theoretical description of the thermodynamics of vacancies has to treat this in some way. A full microscopic description is almost impossible. The interplay between defects and long timescales makes direct probing with BOMD difficult.

In the fast ionic conductor $\delta$-Bi$_2$O$_3$, the oxygen diffusion is observable in BOMD. The ionic conductivity is proportional to the diffusion constant. This constant is calculated from the mean square displacement

$$\langle r^2(t) \rangle = \frac{1}{N_a} \sum_i (r_i(t) - r_i(0))^2 \quad (7.8)$$

as

$$6D = \frac{d \langle r^2(t) \rangle}{dt} \quad (7.9)$$
In figure 7.3 an example is illustrated. Phenomenologically, the diffusion constant behaves as

$$D \sim \exp \left( -\frac{E_{a}}{k_{B}T} \right) \quad (7.10)$$

where $E_{a}$ is the activation energy of diffusion. The exponential behaviour on both activation energy and temperature indicates that it is unlikely that diffusion happens at a rate observable with BOMD.

In Paper IV I have approached diffusion via activation energies extracted from static calculations. The probability of diffusion from site $i$ to $j$ is determined as

$$\Gamma_{ij} = \exp \left( -\frac{E_{ij}}{k_{B}T} \right). \quad (7.11)$$

The matrix $\Gamma$ is the used to create a kinetic model of diffusion. This model is then used to quantitatively investigate the behaviour of vacancy migration under different external conditions. The model captures the general trends, but diffusion from a microscopic perspective in remains an open issue, especially the interplay between local electronic structure and vacancy migration.
CONCLUSIONS

As mentioned in the introduction, the aim of this thesis was to provide insight into the physics of fast ion conductors, and if possible improve upon their performance. On a personal level I can consider these goals achieved. Paper III and Paper IV are examples of just this. In the grand scheme of developing a source for clean and renewable energy I have barely made a dent. However, with proper methodological development, theoretical materials science can help gain further insights.

The temperature dependent effective potential method presented in this thesis can give a qualitatively new way of studying finite temperature properties of materials. The formal definitions of thermal parameters from statistical physics differ substantially from how these are numerically determined in existing methods. The direct access to the finite temperature free energy can help bridge that gap. Other than being aesthetically pleasing, the predictive abilities of first principles calculations will be greatly enhanced.
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