A First-Principles Study of Highly Anharmonic and Dynamically Disordered Solids

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LINKÖPING STUDIES IN SCIENCE AND TECHNOLOGY. DISSERTATIONS.
NO. 2072

A First-Principles Study of Highly Anharmonic and Dynamically Disordered Solids

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Linköping 2020

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ISBN 978-91-7929-855-5
ISSN 0345-7524

Printed by LiU-tryck, Linköping 2020

This thesis is a first-principles theoretical investigation of solid materials with high degrees of anharmonicity. These are systems where the dynamics of the constituent atoms is too complex to be well-described by a set of uncoupled harmonic oscillators. While theoretical studies of such systems pose a significant challenge, they are under increasing demand due to the prevalence of these systems in next-generation technological applications. Indeed, very anharmonic systems are ubiquitous in envisioned materials for future solid-state batteries and fuel-cells, thermoelectrics and optoelectronics. In some of these cases, the anharmonicity is a “side-effect” that simply has to be dealt with in order to accurately model certain properties, while in other cases the anharmonicity is the origin of the high-performance of the material.

There are two main parts to the thesis: The first is on materials with perovskite-related structures. This is a very large class of materials, members of which are typically highly anharmonic, not least in relation to a series of complex phase transformations between different structural modifications. In the thesis, I have studied a specific class of such phase-transformations that relate to tilting of the framework of octahedra that make up the structure. The oxide CaMnO_3 and a set of inorganic halide perovskites were taken as model systems. The results shed some light on the experimentally observed differences between the local and average atomic structure in these systems. I have further studied $\text{Cs}_2\text{AgBiBr}_6$, a member of the so-called lead-free halide double perovskites. I rationalized its temperature induced phase transformation and found high degrees of anharmonicity and ultra-low thermal conductivity. Finally, I studied the influence of nuclear quantum effects, which are often ignored in computational modelling, on the structure and bonding in the hybrid organic-inorganic lead-halide perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_3$.

The second part of the thesis deals with theoretical studies of the phase stability of dynamically disordered solids. These are solids which have some sort of time-averaged long-range order, characteristic of a crystalline solid, but where the anharmonicity is so strong that the basic concept of an equilibrium atomic position cannot be statically assigned to all atoms. Examples include certain solids with very fast ionic conduction, so called superionics, and solids with rotating molecular units. This absence of equilibrium atomic positions makes many standard computational techniques to evaluate phase-stability inapplicable. I outline a method to deal with this issue, which is based on a stress-strain thermodynamic integration on a deformation path from an ordered

variant to the dynamically disordered phase itself. I apply the method to study the phase stability of the high-temperature δ -phase of Bi_2O_3 , which is the fastest known solid oxide ion conductor, and to Li_2C_2 , whose high temperature cubic phase contains rotating C_2 dimers.

The thesis exemplifies the need to go beyond many of the standard approximations used in first-principles computational materials science if accurate theoretical predictions are to be made. This is true, in particular, for many emerging material classes in the field of energy materials.

Populärvetenskaplig Sammanfattning

I den konventionella teoretiska modellen för ett (kristallint) fast material antogs varje atom kunna tillordnas en jämviktsposition. Rörelsen av atomerna runt dessa jämviktspositioner antogs sedan ofta vara harmoniskt, d.v.s. hyfsat kunna beskrivs i termer av en samling (kvantmekaniska) fjädrar. Denna avhandling behandlar teori- och beräkningsstudier av material där ett eller båda av dessa antaganden inte är giltiga, så kallade anharmoniska material. En noggrann teoretisk behandling av sådana material är ofta ordentligt utmanande.

I takt med en snabb teknologiska utveckling ställs allt mer specifika och stränga krav på de material som behövs för diverse applikationer. Inom flertalet områden dyker då denna typ av komplexa och anharmoniska material upp som potentiella kandidater. Till exempel som fastelektrolyter för batterier och bränsleceller eller som solcellsmaterial. Inom vissa applikationer är denna anharmonicitet en bieffekt som man helt enkelt måste ta hänsyn till för att kunna göra noggranna teoretiska förutsägelser om diverse materialegenskaper, i andra fall är anharmoniciteten själva ursprunget för materialets goda egenskaper.

I den första delen av avhandlingen behandlar jag material som har, eller är nära relaterade till, den så kallade perovskitstrukturen. Detta är en väldigt stor klass av material, och strukturen dyker därför upp inom en mängd olika tillämpningar, inte minst i lovande solcellsmaterial. Dessa material är ofta mycket anharmoniska, vilket tar sig uttryck bland annat i en rad komplexa fastransformationer mellan olika typer av perovskitmodifikationer. I perovskitoxiden CaMnO_3 , samt i en samling halogenperovskiter, har jag har studerat en specifik typ av fastransformationer som tillkommer på grund av rotationer av de oktaedrar som utgör en del av strukturen. Jag har fortsatt studerat den väldigt kraftiga anharmoniciteten i den så kallade blyfria halogendubbelperovskiten $\text{Cs}_2\text{AgBiBr}_6$, och slutligen har jag studerat hur en kvantmekanisk behandling av atomkärnorna, något som oftast inte görs, påverkar materialegenskaper i $\text{CH}_3\text{NH}_3\text{PbI}_3$, en så kallad hybrid organisk-inorganisk bly-halogenperovskit, som är ett extremt lovande solcellsmaterial.

I den andra delen av avhandlingen studerar jag dynamiskt oordnade fasta material. I dessa material är atomernas rörelse för komplex för att varje atom ska kunna tilldelas en statisk jämviktsposition. Material i denna klass är, till exempel, lovande som fastelektrolyter i bränsleceller och batterier. Mer specifikt studerar jag en typ av fasövergång, från en ordnad fas till en fas med dynamisk ordning, som ofta sker

när dessa material värms upp. Jag introducerar en beräkningsmetod för att utvärdera deras fasstabilitet. Metoden är baserad på en så kallad termodynamisk integration, utförd mellan en ordnad variant och den dynamiskt oordnade fasen själv. Metoden gör det möjligt att beräkna fastransformationstemperaturer i denna typ av material. Jag applicerar metoden på Bi_2O_3 , som i sin δ -fas är det fasta material med högst känd syrejonledningsförmåga, samt på Li_2C_2 vars kubiska fas innehåller roterande C_2 molekyler. Resultaten stämmer bra överens med kända experimentella mätningar.

Acknowledgements

First and foremost I must acknowledge Sergei Simak, my main supervisor. Thank you for all the help and support during the years, and for always displaying a genuine (and highly contagious!) passion for science in general and physics in particular. I appreciate the encouragement to explore my own ideas and to take the research in the direction of my own interests. I also appreciate our many hours of brainstorming about physics and other things!

I must also acknowledge my co-supervisor, Per Eklund and the head of the theoretical physics division, Igor Abrikosov. Thank you both for all your help!

Thank you to friends and colleagues at IFM, in particular the whole Theoretical Physics division, for providing a pleasant working environment. Going to work has rarely felt like a chore!

Thank you to collaborators and friends for many illuminating discussions about physics (and other things!), Björn, Davide G., Davide S., Erik, Joel, Olle, Stanislav, Viktor, and many others.

To past and present members of the lunch group: Thank you for many fun discussions over lunch and coffee! Arguing with you about the strangest of topics has been a pleasure!

To friends outside of work; Thank you for all the fun times! LiTHeB!

Finally, to the family, for support in too many things to list; Thank you for everything!

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CHAPTER 1

Introduction

The task of accurately predicting the properties of a piece of material of known constituents solely from the first-principles of quantum physics may seem, on the face of it, like a completely hopeless endeavour. Indeed, the underlying foundational equations, while possessing a certain conceptual simplicity, are computationally overwhelmingly to complex to admit even numerical solutions for anything but very small or highly idealised systems. For this reason, the field of *computational materials science* is largely about finding suitable approximate computational schemes that can be employed within the realm of reasonable simulation time, in order to extract useful information on materials of interest.

First-principles, or *ab initio*, materials modelling, which is the philosophy adopted in this thesis, aims to employ approximations to the basis laws of quantum physics which are physically well founded, and not based on fits to experimental data. As such, *ab initio* computational schemes aim to have a wider range of applicability and, in particular, to have a certain predictive power.

The foundations of *Density Functional Theory* (DFT)¹ was laid by Hohenberg and Kohn [1] and Kohn and Sham [2]. DFT is, in essence, a reformulation of quantum theory where the *electron density* takes the place of the many-body wavefunction as the fundamental variable. As it happens, the DFT formulation is susceptible to conceptually simple and well founded approximations that turn out to be surprisingly accurate. Together with the development of accurate and efficient numerical schemes, and the rapid increase in performance and availability of computational resources, DFT has ushered in a revolution in first-principles materials modelling. This is particularly true in the field of solid-state physics, where DFT provides a suitable trade-off between accuracy and computational complexity and is now being employed on a very wide scale.

Many DFT calculations on crystalline solids are performed under the assumption that the atoms of the solid do not move. This is done out of convenience and is, of course, not true, even at the absolute zero of temperature due to the quantum nature of the atoms. It does, however, provide useful, and often quantitative, information on many properties of materials. For accurate predictions of other properties, the fact

¹For which Walter Kohn (1923-2016) was jointly awarded the 1998 Nobel Prize in Chemistry.

that the atoms move has to be explicitly considered.

In the standard model of the dynamics of a crystalline solid, it is taken as a periodically repeating set of atoms, each vibrating around some well-defined, fixed, point in space. Any motion that permanently displaces an atom away from its center of vibration is typically considered rare, and can thus be accurately disregarded. Furthermore, at low or intermediate temperature, these solids are often considered to be *harmonic*, i.e., the oscillatory motion of the atoms are taken to be well modelled as a set of springs, with spring-constants determined by the curvature at the bottom of the underlying, static, potential energy surface (PES). Quantum mechanically, this corresponds to describing the dynamics by a set of non-interacting quasi-particles termed *phonons*. While this model is, virtually without exception, an idealisation, a lot of understanding and many quantitatively accurate predictions have been made and continues to be made based on it.

This thesis will be concerned with first-principles computations of solids that are not at all well-described in this harmonic model, to be referred to as *anharmonic solids*. If the anharmonicity is weak, an accurate treatment can be derived by augmenting the harmonic description by low order interactions among the phonon quasi-particles. This type of perturbative treatments have been widely applied, e.g. to calculate thermal conductivities, but breaks down once the level of anharmonicity becomes too large. This breakdown typically manifests itself as a too strongly interacting set of phonons. A remedy can often be found by constructing a set of *renormalized phonons*. These are quasi-particles which are no longer defined by the curvature of the underlying static PES, but are designed to include parts of the anharmonicity. A perturbative treatment on top of such renormalized phonons can typically remain accurate in the presence of a much higher degree of anharmonicity.

From a computational perspective, the phonon picture laid out above hinges on the existence of well-defined equilibrium positions for all atoms. There are sets of solids, which we will collectively refer to as *dynamically disordered*, which appear to possess a type of time-averaged long-range order, characteristic of crystalline solids, but where equilibrium positions cannot be statically assigned to all atoms. One example is solids with very high ionic conductivity, so called superionics [3], where one of the atomic species exhibit diffusional properties akin to that of a liquid. Another example is solids that contain rotating molecular units, referred to as "rotationally-disordered", or sometimes "plastic", crystals. Typically, these solids will have a temperature-induced phase transformation from a state where the molecules are directionally ordered to a phase where they are rotationally disordered.

From the point of view of technological application, a proper understanding of strong anharmonicity is of great interest. In the simplest case, anharmonic effects often have large impact on important materials properties, and thus have to be accurately included in the theoretical models if useful information is to be extracted. This is, for instance, true of many systems with the perovskite crystal-structure, which is a focus of this thesis. The subclass of halide perovskites, which are highly promising materials in photovoltaics and related fields, are highly anharmonic [4].

In another case, the physical phenomena on which the application is based may be a direct manifestation of extreme anharmonicity. This is particularly true of the dynamically disordered solids. For instance, the great promise of superionics as solid state electrolytes for batteries or fuel-cells is based on their "liquid-like" diffusional properties, which is a direct manifestation of the extreme anharmonicity of these sys-

tems. Another such example is the potential use of rotationally disordered solids in solid-state cooling [5], which is based on using an external stress field to drive the order to dynamical-disorder phase transformation often present in these systems, another direct manifestation of extreme anharmonicity.

In this thesis, after introducing the theoretical background involved in the first-principles materials modelling employed to perform all simulations (Chapters 1, 2 and 3), I treat two (not mutually exclusive) classes of highly anharmonic systems.

Chapter 4, which is based on Papers I - IV, investigates materials with, or closely related to, the perovskite crystal structure.

In Papers I and II I study phase transformations related to tilting of the octahedral framework that makes up the perovskite crystal structure in the perovskite oxide CaMnO_3 and the two inorganic halide perovskites CsSnI_3 and CsPbI_3 . These materials are found in a phase with tilted octahedra at low temperature, and subsequently transform into the ideal cubic perovskite at high temperature through a sequence of octahedral tilting transformations. The nature of the cubic phase that emerge at high T is, however, not clear. Experimental evidence points to differences between the local and average structures in these systems. I investigate the energetics related to this octahedral tilting and attempt to rationalize these transitions in the three mentioned material systems.

In Paper III, I investigate the highly anharmonic lattice dynamics of $\text{Cs}_2\text{AgBiBr}_6$. This is the prototypical member of the so called lead-free halide double perovskites [6]. These are systems which are envisioned to solve issues relating to long-term stability and the presence of toxic lead in the lead-halide perovskites mentioned above. I find that the system is highly anharmonic and rationalise the experimentally known phase transformation, I further find that the system possess an "ultra-low" thermal conductivity.

To close out Chapter 4 (Paper IV), I study methylammonium lead iodide (MAPI), $\text{CH}_3\text{NH}_3\text{PbI}_3$, which is the champion photovoltaic material in the lead-halide perovskite class of materials. This is an extremely intensively studied material system, but is also very complex, and its properties are far from fully understood. I focus on the effects of the quantum nature of the nuclei, which has, since it represents a significant increase in the complexity of the simulations, been very sparsely addressed in the literature. I show that nuclear quantum effects could potentially be of high significance in the modelling of this system.

Chapter 5, which is based on Papers V - VII, treats dynamically disordered systems. In particular, I investigate the nature and critical temperature of transitions from low temperature ordered phases to the high temperature dynamically disordered phases.

Paper V addresses the lattice dynamics and the superionic transition in fluorite-structured ceria, CeO_2 . In particular, I investigate the previously proposed connection between a soft phonon mode and the superionic transition, and find that anharmonic renormalisation of this phonon mode is of high relevance.

I finally, in Papers VI and VII, lay out and apply a computational methodology to calculate the free energy of a subset of these dynamically disordered phases. This methodology is based on a stress-strain thermodynamic integration between a dynamically disordered phase and a (meta)stable, artificial or real, variant of it. I apply the method to study the phase stability in Bi_2O_3 , whose high-temperature superionic δ -phase is the fastest known solid oxide ion conductor, and Li_2C_2 , which is a very "clean" model-system of a transformation from a state with ordered- to one with rotationally

disordered molecules.

CHAPTER 2

First-Principles Materials Modelling

In this and the following two chapters, I aim to describe the background and basics of the theoretical concepts that underlie the theoretical and computational modelling performed in this thesis. The underlying philosophy is, as mentioned in the introduction, that of *ab-initio*, or "first-principles", modelling, meaning that the computational techniques should be derived essentially directly from basic physical laws, with minimal experimental input.

I will start from the many body Schrödinger Equation, which is taken to describe the behaviour of the nuclei and electrons of a material system. I will then show how this problem can be divided into two distinct, but connected, problems, one for the electronic structure of the system, which depends parametrically on the positions of the nuclei, and one for the behaviour of the nuclei. These two problems will then be separately addressed in the following two chapters.

2.1 The Many Body Schrodinger Equation

In the theoretical model to be described in this chapter, any piece of material is taken to consist of a set of electrons and a set of nuclei, both treated as point particles. Any effect originating from the smaller constituents of the nuclei will thus be ignored. Furthermore, in order to present the concepts with more clarity, we will base our description in a non-relativistic framework, although some concepts originating from a relativistic treatment are typically taken into account in the final computations.

The starting point is the *time-dependent Schrödinger equation* (SE),

$$\hat{H}\Psi(\{\mathbf{r}, \mathbf{R}\}, t) = i\hbar \frac{\partial \Psi(\{\mathbf{r}, \mathbf{R}\}, t)}{\partial t}, \quad (2.1)$$

where $\Psi(\{\mathbf{r}, \mathbf{R}\}, t)$ is the many-body wave function of the system, which completely specifies its state and depends on the coordinates of all electron, $\{\mathbf{r}\}$, and nuclei, $\{\mathbf{R}\}$, and time t . The Hamiltonian operator, $\hat{H}$, describes all interactions in the system and

takes the form (in Hartree atomic units and in the absence of external fields):

$$\begin{aligned} \hat{H} = & - \sum_{i=1}^n \frac{1}{2} \nabla_i^2 - \sum_{I=1}^N \frac{1}{2M_I} \nabla_I^2 + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & + \sum_{I>J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|}, \end{aligned} \quad (2.2)$$

where Z_I and M_I is the charge and mass of nuclei I , respectively. The five terms in Eq. (2.2) are, in turn, the kinetic energy operator of the electrons, $\hat{T}_e$, and nuclei, $\hat{T}_N$, the electron-electron repulsion, $\hat{V}_{ee}$, the nucleus-nucleus repulsion $\hat{V}_{II}$ and the electron-nuclei attraction $\hat{V}_{Ie}$.

When $\hat{H}$ is time-independent, the time-dependence of $\Psi(\{\mathbf{r}, \mathbf{R}\}, t)$ can be separated out, leaving a wavefunction $\Psi(\{\mathbf{r}, \mathbf{R}\})$ that satisfies the time-independent Schrödinger equation, which takes the form of an eigenvalue equation:

$$\hat{H}\Psi(\{\mathbf{r}, \mathbf{R}\}) = E\Psi(\{\mathbf{r}, \mathbf{R}\}), \quad (2.3)$$

where E is the total energy of the system. This is the main equation that we will aim to approximately solve.

It is easy to convince oneself of the complete futility of attempting a direct numerical solution to Eq. (2.3) for anything but systems with just a handful of particles [7]. The strategy going forward will thus be to introduce a set of approximations that will, in the end, result in a computational framework that is able to make relatively accurate predictions on properties of materials of interest.

2.2 The Born-Oppenheimer Approximation

The first of this set of approximations is the so-called Born-Oppenheimer (BO) approximation, which is based on the fact that there is an orders-of-magnitude difference between the mass of an electron and a nucleus. This suggests that the motions of the electrons and the nuclei should be largely decoupled, which will allow us to treat the electronic and nuclear problems largely separately.

Technically, one proceeds by writing $\Psi(\{\mathbf{r}, \mathbf{R}\})$ from Eq. (2.3) (exactly) as an adiabatic expansion [8]:

$$\Psi(\{\mathbf{r}, \mathbf{R}\}) = \sum_i \Theta_i(\{\mathbf{R}\}) \Phi_i(\{\mathbf{r}\} : \{\mathbf{R}\}). \quad (2.4)$$

Here, $\Phi_i(\{\mathbf{r}\} : \{\mathbf{R}\})$ is a complete set of electron states at fixed nuclei coordinates $\{\mathbf{R}\}$, which are solutions to the electronic SE

$$[\hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne}] \Phi_i(\{\mathbf{r}\} : \{\mathbf{R}\}) = \epsilon_i(\{\mathbf{R}\}) \Phi_i(\{\mathbf{r}\} : \{\mathbf{R}\}) \quad (2.5)$$

and the notation $\{\mathbf{r}\} : \{\mathbf{R}\}$ indicates a parametrical dependence on $\{\mathbf{R}\}$. $\Theta_i(\{\mathbf{R}\})$ are expansion coefficients that will turn out to represent nuclear wavefunctions.

From Eqs. (2.4) and (2.3) and (2.5), neglecting any coupling between the different Φ_i , one can derive [8] an SE for the nuclear wavefunctions $\Theta_i(\{\mathbf{R}\})$ that takes the form:

$$[\hat{T}_{nn} + \hat{V}_{nn} + \epsilon_i(\{\mathbf{R}\})] \Theta_i(\{\mathbf{R}\}) = E \Theta_i(\{\mathbf{R}\}) \quad (2.6)$$

An implicit assumption in this derivation is that the set of electronic eigenstates are well separated. While this is mostly a good approximation for semiconductors and insulators, its suitability for metals is less obvious.

We thus see that for each i , Eq. (2.6) depends on the solution to Eq. (2.5). The energy surface $V_{nn} + \epsilon_i(\{\mathbf{R}\})$ is known as the i :th *BO energy surface*. In this thesis I am only going to be concerned with the ground-state solution $\epsilon_0(\{\mathbf{R}\})$, and correspondingly $V_{nn} + \epsilon_0(\{\mathbf{R}\})$ will be referred to simply as the BO energy surface.

The strategy for approaching the combined electron-nuclear problem defined by the many body SE of Eq. (2.3) thus becomes to separately address two connected problems:

- Solve the *electronic structure problem* defined by Eq. (2.5), strategies for this will be laid out in Chapter 3, the main player will be the Density Functional Theory (DFT).
- Solve for the behaviour of the nuclei starting from Eq. (2.6) and then use the principles of statistical mechanics to eventually calculate properties of interest. Chapter 4 briefly lays out how this can be done, the typical starting point being the approximation that the nuclei can be treated as classical particles.

We note that in many related works, properties of interest can typically be determined by solving the electronic structure problem at one, or a few, positions of the nuclei, and the main emphasis is thus put on the first of the two problems above. In this thesis, I instead largely focus on properties of materials that relate directly to the motion of the nuclei, and as such, the second problem becomes the main focus. In a sense, the electronic structure problem is solved primarily to provide the BO energy surface on which the ions move, and more detailed information on the electronic structure is of secondary interest.

Solving The Electronic Structure Problem

The aim of this chapter is to give an overview of how the *electronic structure problem* stated in Eq. (2.5) can be addressed. This is achieved in the framework of the *Density Functional Theory* (DFT), where the central idea is to recast the problem in a form where the electron density, $n(\mathbf{r})$, acts as the fundamental variable in place of the many-body wavefunction. The main benefit of such a reformulation is that it will be susceptible to relatively simple and transparent approximations, that turn out to be surprisingly accurate. DFT-based computational methodology thus achieves a very effective trade-off between accuracy and computational complexity and has therefore become extremely popular in the last few decades.

3.1 Density Functional Theory

We start by restating the electronic structure problem of Eq. (2.5) in the form from which DFT is typically derived,

$$[\hat{T}_e + \hat{V}_{ee} + \hat{V}_{ext}]\Phi(\{\mathbf{r}\}) = E\Phi(\{\mathbf{r}\}), \quad (3.1)$$

where the parametrical dependence on some fixed nuclear coordinates is understood. The electron-nuclear interaction has also been replaced with an external potential, which could represent, for instance, the electron-nuclear interaction at fixed nuclei.

The probability of electron 1 being at $\mathbf{r}$, while the other electrons can be anywhere, is

$$P(\mathbf{r}_1 = \mathbf{r}) = \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{N_e})|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (3.2)$$

The electron density, $n(\mathbf{r})$ is the probability of finding any electron at $\mathbf{r}$. Since the electrons are indistinguishable we have,

$$n(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{N_e})|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (3.3)$$

The central statement of DFT was formulated through two theorems due to Hohenberg and Kohn (HK) [1]:

1. For systems described by Eq. (3.1), the ground state electron density $n_0(\mathbf{r})$ uniquely determines the external potential V_{ext} , up to an additive constant.
2. For each and any external potential, there exists a functional of the electron density $E[n]$, whose global minimum is the ground state energy E_0 and the density at this minimum is the ground state density, n_0 .

It follows that the ground state wavefunction is a functional of $n(\mathbf{r})$, and we can thus construct the energy functional,

$$\begin{aligned}
 E[n] &= \langle \Phi[n] | \hat{T}_e | \Phi[n] \rangle + \langle \Phi[n] | \hat{V}_{ee} | \Phi[n] \rangle + \langle \Phi[n] | \hat{V}_{ext} | \Phi[n] \rangle \\
 &= T[n] + V_{ee}[n] + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \\
 &= F[n] + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r},
 \end{aligned} \tag{3.4}$$

where we have defined kinetic energy, $T[n]$, and electron-electron interaction, $V_{ee}[n]$, functionals, as well as the so-called universal functional $F[n] = T[n] + V_{ee}[n]$. Note that since we are treating the nuclei at fixed positions, the nucleus-nucleus energy E_{II} is simply a constant and can be added to Eq. (3.4) at will.

Finding the ground state energy of a system thus entails finding the global minimum of Eq. (3.4), the density at this minimum is the ground-state density $n_0(\mathbf{r})$. It should be noted that the energy functional Eq. (3.4) is defined only for "V-representable" densities, i.e. those that can be generated by some external potential. A functional valid instead for all "N-representable" densities, those that correspond to some anti-symmetric N-body wavefunction, is the Levy-Lieb functional, $F_{LL}[n]$ [9, 10]. $F_{LL}[n]$ is the universal energy functional $F[n]$, defined in Eq. (3.4), minimized over all N-body antisymmetric wavefunctions corresponding to the density $n(\mathbf{r})$. At the variational minimum, in a given external potential, the two functionals coincide.

While a direct minimization of Eq. (3.4) using some approximate form of $F[n]$ is possible, the known approximations are typically not accurate or universal enough to be of wide practical use. In particular, one severe issue is the difficulty in finding an accurate approximate form for the kinetic energy functional $T[n]$. This branch of DFT is known as *orbital-free* DFT.

3.1.1 Kohn-Sham DFT

The overwhelmingly most popular branch of DFT is the Kohn-Sham (KS) form [2]. The basic idea in KS-DFT is to construct an auxiliary system of non-interacting "KS particles", with single-particle orbitals, $\{\psi_i\}$, moving in an effective potential, V_{KS} . This potential is constructed so that this auxiliary system has the same ground-state density as the fully interacting system, i.e. that obtained at the minimum of Eq. (3.4). Note that this construction relies on the *assumption* that the ground-state density of any reasonable system can, in fact, be expressed as the density of a non-interacting system.

The KS orbitals satisfy single-particle Schrödinger like equations:

$$\left(-\frac{1}{2} \nabla_i^2 + V_{KS}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \tag{3.5}$$

for $i = 1, \dots, N$, and the density is trivially,

$$n(\mathbf{r}) = \sum_i^{occ.} |\psi_i|^2. \quad (3.6)$$

The energy functional of the KS non-interacting system is then simply

$$\tilde{E}[n] = T_S[n] + \int V_{KS}(\mathbf{r})n(\mathbf{r})d\mathbf{r}, \quad (3.7)$$

where $T_S[n]$ is the non-interacting kinetic energy functional. At this point, one rewrites the energy functional Eq. (3.4) in the form

$$E[n] = T_s[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_H[n] + E_{XC}[n], \quad (3.8)$$

where $E_H[n]$ is the Hartree energy, i.e. the interaction energy of a classical system with density $n(\mathbf{r})$,

$$E_H[n] = \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \quad (3.9)$$

and $E_{XC}[n]$ is the *exchange-correlation energy*, which is a complicated object, defined to make Eq. (3.8) exact.

Requiring the variations of the energy functionals Eqs. (3.7) and (3.8) to coincide at the minimum yields an expression for the KS potential,

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}), \quad (3.10)$$

where we have defined the Hartree potential,

$$V_H(\mathbf{r}) = \frac{\delta E_H[n]}{\delta n} = \int \frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad (3.11)$$

and the XC-correlation potential,

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n]}{\delta n}. \quad (3.12)$$

The many-body electronic structure problem posed by the SE of Eq. (2.5) has now been transformed into solving a set of single particle SE equations (Eq. 3.5), with all the many-body complexity "hidden away" into the XC-potential, V_{XC} . Since the effective KS potential depends on the density, the equations (3.5), (3.6) and (3.10) are solved self-consistently.

Such a self-consistent solution requires an explicit form for the XC-potential, which is unfortunately not readily available. Indeed, since this object has to contain information about the full many-body complexity of the problem, it is obviously extremely complicated. As it turns out, however, conceptually simple approximations are surprisingly accurate.

3.1.2 Exchange-Correlation Functionals

In order to see what should formally be included in the exact XC energy, we can equate Eqs. (3.8) and (3.4) and solve for $E_{XC}[n]$:

$$E_{XC}[n] = (T[n] - T_S[n]) + (V_{ee}[n] - E_H[n]). \quad (3.13)$$

The exact XC energy can thus be thought of as containing two parts, the first being the correction to the kinetic energy from that of the non-interacting KS particles, and the second is the correction to the electron-electron repulsion from that of the Hartree energy.

It is common practice to define the exchange part of the XC energy by its expression from Hartree-Fock theory, using KS orbitals:

$$E_X = -\frac{1}{2} \sum_{i,j} \int \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \quad (3.14)$$

and the correlation is thus $E_C = E_{XC} - E_X$.

The simplest useful approximations to the XC energy is the local density approximation (LDA), where the XC energy takes the form

$$E_{XC}^{LDA}[n] = \int n(\mathbf{r})\epsilon_{XC}^{hom}(n(\mathbf{r}))d\mathbf{r}. \quad (3.15)$$

Here $\epsilon_{XC}^{hom}(n(\mathbf{r}))$ is the XC energy per-particle of a homogeneous electron gas. The approximation is thus that we take the energy associated with each volume element $d\mathbf{r}'$ at $\mathbf{r}'$ to be that of the homogeneous electron gas with the density of the system at this point, $n(\mathbf{r}')$. The exchange contribution can be calculated exactly, while the correlation is parameterized from quantum Monte-Carlo (QMC) solutions to the full SE of the homogeneous electron gas [11]. Somewhat unintuitively, the LDA is quite accurate for solids. This is in large part due to a cancellation of errors between the exchange and correlation parts and since it fulfills the sum rule for the so-called XC-hole [12]. The LDA tends, however, to over-bind solids resulting in somewhat underestimated lattice constants and overestimated bulk moduli [13].

The second rung on the ladder of approximations consists of the generalized gradient approximations (GGA), where the XC energy per particle is made to be a function of both the density, $n(\mathbf{r})$ and its gradient $\nabla n(\mathbf{r})$,

$$E_{XC}^{GGA}[n] = \int n(\mathbf{r})\epsilon_{XC}^{GGA}(n(\mathbf{r}), \nabla n(\mathbf{r}))d\mathbf{r}. \quad (3.16)$$

Many GGA forms have been devised following different philosophies. One route is to take a semi-empirical approach and fit some parameters of a (cleverly devised) functional form, in order to accurately reproduce target properties of a large data set, as for example in the original Becke88 functional [14]. A different approach is to design functional forms to make $\epsilon_{XC}^{GGA}(n(\mathbf{r}), \nabla n(\mathbf{r}))$ satisfy a set of properties (typically certain constraints and limiting behaviours) known to be obeyed by the exact XC functional. Well-known examples along this route are the Perdew-Wang91 [15], the Perdew-Burke-Ernzerhof (PBE) [16] and the PBEsol [17]

The PBE form is the overwhelmingly most widely used GGA¹. PBE tends to, oppositely to LDA, overestimate lattice constants [13]. Functionals such as PBEsol

¹The paper introducing PBE, "Generalized Gradient Approximation Made Simple" [16], currently has $\sim 112\,000$ Google Scholar citations, making it one of the most cited research papers of all time.

and AM05 [18] tend to provide lattice constants somewhere in-between LDA and PBE, thus providing on average better agreement with experiment.

The LDA and GGA will often fail to accurately describe electron states that are strongly localized, typically d- or f-like states. This is largely a manifestation of the self-interaction of the KS particles in the LDA/GGA description, i.e., that the KS particles feel a repulsion from their own presence. There are many approaches in use to attempt to resolve this issue. Taking inspiration from the well-studied Hubbard model, one common way is by augmenting the DFT description with an on-site, Hubbard-like term. The total energy is then modified to read

$$E_{DFT+U}[n] = E_{DFT}[n] + E_{Hubbard}[\{n_{m,m'}^{I,\sigma}\}] - E_{DC}[\{n^{I,\sigma}\}], \quad (3.17)$$

where $E_{Hubbard}[\{n_{m,m'}^{I,\sigma}\}]$ is the Hubbard-like on-site term and $E_{DC}[\{n^{I,\sigma}\}]$ is a "double-counting" term, which is needed since $E_{DFT}[n]$ already describes part of the energy that is added in $E_{Hubbard}[\{n_{m,m'}^{I,\sigma}\}]$. $n_{m,m'}^{I,\sigma}$ is the on-site occupation matrix,

$$n_{m,m'}^{I,\sigma} = \sum_i^{occ.} \langle \psi_i^\sigma | \phi_m^{I,\sigma} \rangle \langle \psi_i^\sigma | \phi_{m'}^{I,\sigma} \rangle, \quad (3.18)$$

with ψ_i^σ the KS-orbitals, $\phi_m^{I,\sigma}$ localized (typically d- or f-)orbitals at atomic site I and σ the spin-index. Several different forms exist for both $E_{Hubbard}$ and E_{DC} . A popular variant is that of Dudarev *et al.* [19] where the energy takes the form

$$E_{DFT+U}[n] = E_{DFT}[n] + \frac{U - J}{2} \sum_{I,\sigma} \left(\sum_m n_{m,m}^{I,\sigma} - \sum_{m,m'} n_{m,m'}^{I,\sigma} n_{m',m}^{I,\sigma} \right). \quad (3.19)$$

Note that U and J do not enter separately, only the value of $U_{eff} = U - J$ is significant. In the end, values of U and J or U_{eff} must be chosen, and some results may depend sensitively on the value of U . In principle methods exist to determine them from first-principle [20], but in practice they are often chosen to match results from higher-order theory or from experiment.

Another very popular set of approximations for the XC-energy is provided by the so-called *hybrid* functionals, first introduced by Becke [21]. These functionals mix part of the exact exchange from Hartree-Fock theory (Eq. (3.14)) with that of a regular LDA/GGA functional,

$$E_X^{Hybrid} = \alpha E_X^{HF} + (1 - \alpha) E_X^{DFT}, \quad (3.20)$$

while the correlation part is typically kept at the LDA/GGA level. These functionals are often significantly more accurate than regular semi-local DFT functionals, in particular in regards to bandgaps and treatment of localized orbitals, albeit at a significantly (in practice often ~ 1 -2 orders-of-magnitude) higher computational cost. An additional drawback is that the results are often strongly dependent on the mixing parameter α .

3.2 Practicalities of DFT Calculations of Solids

The material systems treated in this thesis are all such that their structures may be approximated as being spatially periodic. The KS potential is thus periodic, $V_{KS}(\mathbf{r}) =$

$V_{KS}(\mathbf{r} + \mathbf{R})$ where $\mathbf{R}$, is any direct lattice vector. The *Bloch theorem* then allows us to represent the KS orbitals as

$$\psi_i(\mathbf{r}) \rightarrow \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (3.21)$$

where $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})$ is periodic in the direct lattice. The KS orbitals are now labeled by a band index, n , and a wave vector, $\mathbf{k}$. The set of unique such states are found in one unit cell of the reciprocal lattice, conventionally taken to be the first Brillouin zone (BZ).

The problem of treating a large piece of a crystalline material, containing an enormous amount of electrons, is thus replaced by treating a set of bands, indexed by n , which is of the order of the number of electrons in the unit cell, at each $\mathbf{k}$ in the BZ. Formally the number of $\mathbf{k}$ -vectors in the BZ is the same as the number of unit cells in the full crystal, which for large crystals becomes a continuum of values. Many properties of interest are expressed as integrals over the BZ,

$$\bar{f} = \frac{V}{(2\pi)^3} \int f(\mathbf{k}) d\mathbf{k}, \quad (3.22)$$

where V is the volume of the unit cell. In practical calculations the BZ is sampled over a discrete grid of $\mathbf{k}$ -points. This sampling space can be reduced to the irreducible BZ (IBZ), i.e., the symmetry unique part of the BZ. Quantities of interest are then evaluated as

$$\bar{f} = \sum_{\mathbf{k}}^{IBZ} w_{\mathbf{k}} f(\mathbf{k}), \quad (3.23)$$

where $w_{\mathbf{k}}$ is a weight-factor related to the number of $\mathbf{k}$ -points in the full BZ that are symmetry-related to the corresponding one in the IBZ.

3.2.1 Plane-Wave Representation of KS orbitals

In practical KS-DFT calculations, the equations either have to be solved on a real-space grid, or the orbitals have to be expanded in terms of a set of basis functions. Common classes of such basis functions are atomic-like orbitals and plane waves. "Atomic-sphere" methods, where an atomic-like representation is taken in the core region and (typically) a plane-wave expansion is used in the interstitial region, are also common. All these approaches have their own benefits and drawbacks.

Likely the most common basis set at this point in time are plane waves (PW), which have been used for all calculations in this thesis. The cell periodic part of the KS orbitals are then expanded as

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}, \quad (3.24)$$

and the KS-orbitals are hence expanded as

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}. \quad (3.25)$$

Other relevant cell periodic quantities, such as the KS potential and the density, are expanded similarly. In practice, the number of plane waves included in the expansion

has to be truncated. The cutoff point is typically specified as an energy, E_{cut} , which corresponds to the quantum mechanical kinetic energy of the plane waves, i.e., only $\mathbf{G}$ -vectors that satisfy,

$$\frac{1}{2}|\mathbf{G} + \mathbf{k}|^2 < E_{cut}, \quad (3.26)$$

are included in the expansion, at a particular $\mathbf{k}$ -point.

The main advantage of PW-DFT is that efficient Fast Fourier Transform (FFT) algorithms allows passing between real and reciprocal space and relevant steps in the computational scheme can thus be evaluated in the most appropriate of these spaces.

3.2.2 Pseudo- and Projector-Augmented Wave Potentials

The major drawback of the PW expansion of the KS orbitals is that features that are localized in real space will require large wavevectors, and hence a large cutoff energy, for the wavefunction representation. In particular, valence electron wavefunctions will be strongly oscillating close to the ionic cores. A remedy of this problem is the *pseudopotential* approach. This approach is based on the observation that, in a typical solid or molecule, only a subset of the constituent atom's electrons participate in the bonding and are significantly altered from their state in an isolated atom. Treating only these *valence electrons* explicitly in the calculation while keeping the *core electrons* fixed in their atomic state corresponds to the *frozen core* approximation. The basic idea of the pseudopotential approach is to replace the nuclear potential with a modified potential which produces smooth wavefunctions close to the nuclear core, while matching the true wavefunctions outside some pre-prescribed radius. The theory of pseudopotentials is highly specialized and involved, and many different flavours exists [8, 22].

A popular, closely related, alternative to the pseudopotential approach is the *projector-augmented wave* (PAW) method [23], which has been used in all DFT calculations in this thesis. In the PAW approach, a linear operator $\hat{\mathcal{T}}$ is constructed, which relates the pseudo-wavefunction $|\tilde{\psi}\rangle$ to the all-electron wavefunction $|\psi\rangle$:

$$|\psi\rangle = \hat{\mathcal{T}}|\tilde{\psi}\rangle. \quad (3.27)$$

The operator $\hat{\mathcal{T}}$ is

$$\hat{\mathcal{T}} = 1 + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle p_i|, \quad (3.28)$$

where $\{|\phi_i\rangle\}$ and $\{|\tilde{\phi}_i\rangle\}$ are sets of partial waves in which $|\psi\rangle$ and $|\tilde{\psi}\rangle$, respectively, can be expanded inside the pseudization radius and $\langle p_i|$ are a set of projector operators that are duals to $\{|\phi_i\rangle\}$ and define the expansion coefficients.

Explicitly, the PAW all-electron wavefunction is

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle p_i|\tilde{\psi}\rangle. \quad (3.29)$$

This essentially amounts to expressing the all-electron wavefunction, which is typically smooth only in the interstitial region, as a pseudo wavefunction, which is smooth everywhere, plus the difference between a wavefunction which is atom-like in the core region and one that is smooth in the core region.

Expectation values of an operator A over the all-electron wavefunction $\langle A \rangle = \langle \psi|A|\psi \rangle$ can now be written as the expectation value of a "pseudo-operator" $\tilde{A} = \hat{\mathcal{T}}^\dagger A \hat{\mathcal{T}}$ over the pseudo-wavefunction, i.e. $\langle A \rangle = \langle \tilde{\psi}|\tilde{A}|\tilde{\psi} \rangle$.

CHAPTER 4

Dynamics and Thermodynamics of the Nuclei

The last chapter discussed how to solve for the electronic structure of a system at fixed positions, $\{\mathbf{R}\}$, of the nuclei. This gives us access to the BO energy surface,

$$E_0(\{\mathbf{R}\}) = \frac{1}{2} \sum_{I,J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \epsilon_0(\{\mathbf{R}\}), \quad (4.1)$$

where the first term is the classical electrostatic repulsion of the nuclei, and $\epsilon_0(\{\mathbf{R}\})$ is the ground state energy solution of the electronic structure problem at fixed nuclear coordinates. In this chapter we discuss how to solve for the evolution of the nuclei on the BO surface, and how to use this to eventually derive dynamical and thermodynamic properties. Primarily this will be done under the approximation that the nuclei move as classical particles on the BO energy surface, but I will sketch how the full quantum nature of the nuclei can be included in computations.

The governing equation for the nuclei on the BO energy surface is the nuclear SE, Eq. (2.6), (now in SI units),

$$\left[- \sum_I \frac{\hbar^2}{2M_I} \nabla^2 + E_0(\{\mathbf{R}\}) \right] \Theta(\{\mathbf{R}\}) = \tilde{E} \Theta(\{\mathbf{R}\}), \quad (4.2)$$

If the nuclei are heavy enough, the wave function, $\Theta(\{\mathbf{R}\})$, will be a set of spatially well-localized wave-packets and we can make the *classical nuclei approximation*. This leads to a set of classical equations of motion for the nuclei [22]:

$$M_I \dot{\mathbf{R}}_I = \mathbf{P}_I, \quad (4.3a)$$

$$\dot{\mathbf{P}}_I = \mathbf{F}_I, \quad (4.3b)$$

where the force on atom I is, through application of the Hellman-Feynman theorem [24], $\mathbf{F}_I = -\nabla_I E_0(\{\mathbf{R}\})$. In this approximation the nuclei move as classical objects on the (quantum mechanical) BO energy surface.

4.1 Molecular Dynamics

The computational methodology of numerically integrating Eqs. (4.3) receives the name of *Born-Oppenheimer molecular dynamics* (BOMD), which is probably the most common way of treating nuclear dynamics from first-principles. The force $\mathbf{F}_I$, of course, does not have to be calculated from first-principles, although for reasons of accuracy and transferability this is certainly preferable. It is instead often obtained through pre-determined functional forms of varying complexity, usually at an orders-of-magnitude reduced computational cost, this is referred to as "classical MD".

Typically, the external conditions that one wants to recreate in an MD simulation have constant temperature. Propagating the ions according to Eqs. (4.3) results in constant energy trajectories, that is, typical implementations will sample the *micro-canonical* ensemble, with constant number of particles, N , volume, V , and energy, E , (NVE). In the thermodynamic limit, there will be a corresponding, well-defined, temperature, but its value may be difficult to control. Furthermore, numerical inaccuracies will cause the systems energy to drift. This is due to the finite timestep used in the numerical integration, but also due to inaccuracies in determining full BO ground state at each timestep. It is therefore significantly more convenient to alter Eqs. (4.3) in order to sample the *canonical* (NVT) ensemble.

Many scheme have been devised to accommodate the goal of constant temperature MD. I will review a few common ones of relevance to the thesis work.

Likely the most common way of controlling temperature in MD simulations is the *Nosé-Hoover thermostat*. The basic idea of Nosé [25] was to augment the physical system with an additional artificial degree of freedom in such a way that constant energy evolution in this extended phase-space corresponds to canonical evolution in the physical phase-space. In the reformulation due to Hoover [26], the EOM takes the form

$$M_I \dot{\mathbf{R}}_I = \mathbf{P}_I, \quad (4.4a)$$

$$\dot{\mathbf{P}}_I = \mathbf{F}_I - \gamma \mathbf{P}_I. \quad (4.4b)$$

Where a friction-like term γ has been introduced, which is not constant, but has a time-evolution driven by the difference between the target- and instantaneous temperatures:

$$\dot{\gamma} = \frac{1}{Q} \left(\sum_I \frac{\mathbf{P}_I^2}{M_I} - g k_B T \right), \quad (4.5)$$

where g is related to the number of degrees-of-freedom and Q is the so-called Nosé-mass, which effectively determines the strength of the coupling between the physical system and the external system (the "heat bath"). Nosé-Hoover dynamics has advantages in that it is fully deterministic and the atomic trajectories (for reasonable values of Q) are only lightly disturbed with respect to the microcanonical ones, and dynamical properties are thus typically accurate. It has problems, however, for weakly anharmonic systems, and in particular is non-ergodic for a single harmonic oscillator. This can be a sever problem, for example when performing thermodynamic integration from a harmonic reference (see Section 4.3.2).

Another canonical sampling method is the *Langevin thermostat* [27], whose EOM

can be written:

$$M_I \dot{\mathbf{R}}_I = \mathbf{P}_I, \quad (4.6a)$$

$$\dot{\mathbf{P}}_I = \mathbf{F}_I - \gamma \mathbf{P}_I + \sqrt{2M_I k_B T} \gamma \boldsymbol{\xi}_I. \quad (4.6b)$$

where γ is now a constant friction term and the last term is a white noise, uncorrelated random force with a Gaussian distribution. Langevin dynamics is typically quite efficient for canonical sampling, but unless γ is small, the microcanonical trajectories are typically quite severely disturbed, and dynamical properties may therefore not be accurate. Note that Eqs. (4.3) are recovered in the limit $\gamma \rightarrow 0$.

4.2 Lattice Dynamics

Another way of introducing the dynamics of the nuclei into the problem starts by Taylor expanding the Born-Oppenheimer potential energy surface of the system with respect to displacements, $\{\mathbf{u}\}$, from a set of reference equilibrium atomic positions,

$$E = E_{ref} + \sum_{i\alpha} \frac{\partial E}{\partial u_i^\alpha} u_i^\alpha + \frac{1}{2} \sum_{ij\alpha\beta} \frac{\partial^2 E}{\partial u_i^\alpha \partial u_j^\beta} u_i^\alpha u_j^\beta + \frac{1}{3!} \sum_{ijk\alpha\beta\gamma} \frac{\partial^3 E}{\partial u_i^\alpha \partial u_j^\beta \partial u_k^\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \dots, \quad (4.7)$$

where all derivatives are taken at the equilibrium positions. Indices $i, j, \dots$ now label atoms while $\alpha, \beta, \dots$ label cartesian directions. The first order derivatives vanish as they correspond to the forces on the atom which are zero by definition at the equilibrium positions. Disregarding all terms above second order corresponds to the *harmonic approximation*, i.e.,

$$E^{harm} = E_{ref} + \frac{1}{2} \sum_{ij\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta, \quad (4.8)$$

where we have defined the 2nd order *interatomic force constants* (IFCs) with elements $\Phi_{ij}^{\alpha\beta}$ and higher order IFCs are defined analogously.

As is conventional, I will first treat the harmonic approximation classically. The EOM for atom i are then simply

$$M_i \ddot{u}_i^\alpha = - \sum_{j\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta. \quad (4.9)$$

As we are to treat periodic solids, we temporarily switch to label an atom i with a unit cell index l and an index μ for the equilibrium position of the atom in the unit cell, the position of an atom is thus $\mathbf{R}_i = \mathbf{r}_l + \mathbf{r}_\mu + \mathbf{u}_{l\mu} = \mathbf{r}_{l\mu} + \mathbf{u}_{l\mu}$. The EOMs can be solved by a plane-wave expansion:

$$\mathbf{u}_{l\mu} = \frac{1}{\sqrt{M_\mu}} \sum_{\mathbf{q}s} A_{\mathbf{q}s} \boldsymbol{\epsilon}_{\mathbf{q}s,\mu} e^{i(\mathbf{q}\cdot\mathbf{r}_{l\mu} - \omega_{\mathbf{q}s}t)}. \quad (4.10)$$

The atomic positions are thus specified (from each component in the expansion) by a *polarization vector* $\boldsymbol{\epsilon}_{\mathbf{q}s,\mu}$, which determines displacements of all atoms within the unit cell, and the long-range, periodic, modulation given by the factor $e^{i\mathbf{q}\cdot\mathbf{r}_{l\mu}}$. $A_{\mathbf{q}s}$ are the normal-mode coordinates. We have thus associated each component of the plane-wave expansion with a wavevector $\mathbf{q}$ and a branch index s . Insertion of Eq. (4.10) in Eq.

(4.9) along with some straightforward manipulation results in the eigenvalue problem, given in a compact notation,

$$\mathbf{D}(\mathbf{q})\boldsymbol{\epsilon}_{\mathbf{q}s} = \omega_{\mathbf{q}s}^2 \boldsymbol{\epsilon}_{\mathbf{q}s}, \quad (4.11)$$

where the *dynamical matrix* $\mathbf{D}(\mathbf{q})$ is the $3N \times 3N$ matrix of mass-scaled Fourier transforms of the IFCs, each 3×3 submatrix is given by:

$$\mathbf{D}_{\mu\nu}(\mathbf{q}) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_k \Phi_{0\mu,k\nu} e^{i\mathbf{q} \cdot (\mathbf{r}_{k\nu} - \mathbf{r}_{0\mu})}. \quad (4.12)$$

At each $\mathbf{q}$ vector we thus get $3N$ *phonon branches*, indexed by s , where N is the number of atoms in the considered unit cell and unique $\mathbf{q}$ -vectors are limited to the first BZ. It is often convenient to use the contracted notation $\lambda = (\mathbf{q}, s)$ and $-\lambda = (-\mathbf{q}, s)$. The full spectrum of eigenvalues of dynamical matrix is thus given as $\omega_{\mathbf{q}s}^2$. And the function $\omega = \omega(\mathbf{q}s)$ is called the *phonon dispersion relation*. Three of the phonon branches necessarily have $\omega_{\mathbf{q}s} \rightarrow 0$ as $\mathbf{q} \rightarrow 0$, and are called *acoustic*. The remaining $3N - 3$ branches are the *optical* branches.

The dynamical matrix is Hermitian and its eigenvalues $\omega_{\mathbf{q}s}^2$ are thus real. The requirement that any displacement of any atom away from its reference position should have a restoring force, i.e. that the crystal has *dynamical stability*, is equivalent to the requirement that the IFC matrix is positive definite, which in turn may be translated into the requirement that the eigenvalues of the dynamical matrix, $\omega_{\mathbf{q}s}^2$, are positive. A dynamically unstable crystal can thus be identified by the appearance of *imaginary frequencies* in the phonon dispersion-relations.

In order to proceed to a quantum mechanical treatment, we introduce phonon creation and annihilation operators $\hat{a}^\dagger$ and $\hat{a}$. The atomic displacements are then promoted to operators which are written in terms of $\hat{a}^\dagger$ and $\hat{a}$ as:

$$\hat{u}_{l\mu}^\alpha = \sqrt{\frac{\hbar}{2N_0 M_\mu}} \sum_\lambda \frac{\epsilon_{\lambda,\mu}^\alpha}{\sqrt{\omega_\lambda}} e^{i\mathbf{q} \cdot \mathbf{r}_{l\mu}} \left(\hat{a}_\lambda + \hat{a}_\lambda^\dagger \right). \quad (4.13)$$

In terms of $\hat{a}^\dagger$ and $\hat{a}$ the harmonic Hamiltonian becomes simply

$$\hat{H} = \sum_\lambda \hbar \omega_\lambda \left(\hat{a}_\lambda^\dagger \hat{a}_\lambda + \frac{1}{2} \right). \quad (4.14)$$

This essentially amounts to considering the vibrations of the solids as a non-interacting gas of quasi-particles, which are termed phonons.

4.2.1 Including Higher Order Terms

A strength of the quasi-particle description of lattice vibrations is that going back and reintroducing higher order terms in the Taylor expansion (Eq. 4.7) corresponds, in this picture, to introducing interactions in the phonon-gas. In terms of the creation and annihilation operators $\hat{a}^\dagger$ and $\hat{a}$, the Hamiltonian up to fourth order is

$$\hat{H} = \Phi_0 + \hat{H}_2 + \hat{H}_3 + \hat{H}_4, \quad (4.15)$$

where Φ_0 is a constant energy term and

$$\begin{aligned}\hat{H}_2 &= \sum_{\lambda} \hbar \omega_{\lambda} \left(\hat{a}_{\lambda}^{\dagger} \hat{a}_{\lambda} + \frac{1}{2} \right), \\ \hat{H}_3 &= C_3 \sum_{\lambda\lambda'\lambda''} \Phi_{\lambda\lambda'\lambda''} \left(\hat{a}_{\lambda} + \hat{a}_{-\lambda}^{\dagger} \right) \left(\hat{a}_{\lambda'} + \hat{a}_{-\lambda'}^{\dagger} \right) \left(\hat{a}_{\lambda''} + \hat{a}_{-\lambda''}^{\dagger} \right), \\ \hat{H}_4 &= C_4 \sum_{\lambda\lambda'\lambda''\lambda'''} \Phi_{\lambda\lambda'\lambda''\lambda'''} \left(\hat{a}_{\lambda} + \hat{a}_{-\lambda}^{\dagger} \right) \left(\hat{a}_{\lambda'} + \hat{a}_{-\lambda'}^{\dagger} \right) \left(\hat{a}_{\lambda''} + \hat{a}_{-\lambda''}^{\dagger} \right) \left(\hat{a}_{\lambda'''} + \hat{a}_{-\lambda'''}^{\dagger} \right).\end{aligned}\tag{4.16}$$

where C_3 and C_4 are constants and $\Phi_{\lambda\lambda'\lambda''}$ and $\Phi_{\lambda\lambda'\lambda''\lambda'''}$ are the three- and four-phonon matrix elements, respectively, corresponding essentially to the reciprocal-space representation of the third- and fourth-order IFCs

$$\Phi_{\lambda\lambda'\lambda''} = \sum_{ijk} \sum_{\alpha\beta\gamma} \frac{\epsilon_{\lambda,i}^{\alpha} \epsilon_{\lambda',j}^{\beta} \epsilon_{\lambda'',k}^{\gamma}}{\sqrt{M_i M_j M_k} \sqrt{\omega_{\lambda} \omega_{\lambda'} \omega_{\lambda''}}} \Phi_{ijk}^{\alpha\beta\gamma} e^{i\mathbf{q}\cdot\mathbf{r}_i + i\mathbf{q}'\cdot\mathbf{r}_j + i\mathbf{q}''\cdot\mathbf{r}_k}, \tag{4.17}$$

$$\Phi_{\lambda\lambda'\lambda''\lambda'''} = \sum_{ijkl} \sum_{\alpha\beta\gamma\delta} \frac{\epsilon_{\lambda,i}^{\alpha} \epsilon_{\lambda',j}^{\beta} \epsilon_{\lambda'',k}^{\gamma} \epsilon_{\lambda''',l}^{\delta}}{\sqrt{M_i M_j M_k M_l} \sqrt{\omega_{\lambda} \omega_{\lambda'} \omega_{\lambda''} \omega_{\lambda'''}}} \Phi_{ijkl}^{\alpha\beta\gamma\delta} e^{i\mathbf{q}\cdot\mathbf{r}_i + i\mathbf{q}'\cdot\mathbf{r}_j + i\mathbf{q}''\cdot\mathbf{r}_k + i\mathbf{q}'''\cdot\mathbf{r}_l}. \tag{4.18}$$

For notational convenience we have passed back to label atoms with a single index.

With $\hat{H}_3$ and $\hat{H}_4$ written in terms of creation and annihilation operators, Eq. (4.16), it becomes clear that $\hat{H}_3$ represents interactions corresponding to three phonons, while $\hat{H}_4$ represents 4-phonon interactions.

One can now proceed by treating the effect of $\hat{H}_3$ and $\hat{H}_4$ perturbatively, using many-body perturbation theory. The lowest order contribution to the *phonon self-energy* contains terms originating from both third and fourth order [28]. Explicitly, this phonon self-energy is $\Sigma_{\mathbf{q}s}(\Omega) = \Sigma_{\mathbf{q}s}^{(3)}(\Omega) + \Sigma_{\mathbf{q}s}^{(4)}$, where $\Sigma_{\mathbf{q}s}^{(3)}(\Omega) = \Delta_{\mathbf{q}s}^{(3)}(\Omega) + i\Gamma_{\mathbf{q}s}^{(3)}(\Omega)$ is complex and frequency dependent while $\Sigma_{\mathbf{q}s}^{(4)} = \Delta_{\mathbf{q}s}^{(4)}$ is real and static.

The imaginary part of $\Sigma_{\mathbf{q}s}^{(3)}(\Omega)$ is given by,

$$\begin{aligned}\Gamma_{\lambda}^{(3)}(\Omega) &= \frac{\hbar\pi}{16} \sum_{\lambda'\lambda''} |\Phi_{\lambda\lambda'\lambda''}|^2 \left\{ (n_{\lambda'} + n_{\lambda''} + 1) \delta(\Omega - \omega_{\lambda'} - \omega_{\lambda''}) + \right. \\ &\quad \left. (n_{\lambda'} - n_{\lambda''}) [\delta(\Omega - \omega_{\lambda'} + \omega_{\lambda''}) - \delta(\Omega + \omega_{\lambda'} - \omega_{\lambda''})] \right\},\end{aligned}\tag{4.19}$$

where n_{λ} is the (Bose-Einstein) phonon occupation number, or phonon population,

$$n_{\lambda} = \frac{1}{e^{\beta\hbar\omega_{\lambda}} - 1}, \tag{4.20}$$

the δ -functions ensure energy conservation and only three-phonon processes that conserve crystal momentum contributes to the sum, i.e. those where

$$\mathbf{q} + \mathbf{q}' + \mathbf{q}'' = \mathbf{G} \tag{4.21}$$

where $\mathbf{G}$ is a reciprocal lattice vector. Processes where $\mathbf{G} = 0$ are called *Normal* processes, while the others are termed *Umklapp* processes.

The corresponding real part can be calculated in a similar fashion, i.e. as an explicit expression of the third-order reciprocal space IFCs [28], but is more conveniently obtained as a Kramers-Kronig transformation of the imaginary part [29]:

$$\Delta_{\lambda}^{(3)}(\Omega) = \frac{1}{\pi} \int \frac{\Gamma_{\lambda}^{(3)}(\omega)}{\omega - \Omega} d\omega. \tag{4.22}$$

The lowest order contribution from the fourth-order IFCs, $\Delta_\lambda^{(4)}$, is given by,

$$\Delta_\lambda^{(4)} = \frac{\hbar}{8} \sum_{\lambda'} \Phi_{\lambda-\lambda\lambda'-\lambda'} (2n_{\lambda'} + 1). \quad (4.23)$$

Practically, the self-energy should be thought of as providing a frequency shift from the real part and a broadening, i.e. a finite lifetime, from the imaginary part. This intuitive picture formally holds in the case $\omega \gg \Gamma, \Delta$, which tends to be true for weakly anharmonic systems, but breaks down in cases of extreme anharmonicity. If such a breakdown is observed, the suitability of the employed phonon picture to describe the dynamics of the studied system should be questioned. In order to gauge whether this might be so, and to connect with inelastic scattering experiments, an approximation for the one-phonon spectral function [28] can be derived. One will typically calculate a function $S(\mathbf{q}, \Omega)$ of the form

$$S(\mathbf{q}, \Omega) = \sum_s \frac{2\omega_{\mathbf{q}s}\Gamma_{\mathbf{q}s}(\Omega)}{(\Omega^2 - \omega_{\mathbf{q}s}^2 - 2\omega_{\mathbf{q}s}\Delta_{\mathbf{q}s})^2 + 4\omega_{\mathbf{q}s}^2\Gamma_{\mathbf{q}s}(\Omega)^2}. \quad (4.24)$$

In the limit $\omega \gg \Gamma, \Delta$, this spectral function reduces to a sum of Lorentzian functions centered at $\omega_{\mathbf{q}s} + \Delta_{\mathbf{q}s}$ with widths determined by $\Gamma_{\mathbf{q}s}$. Large deviations of $S(\mathbf{q}, \Omega)$ from a sum of Lorentzians is thus a sign of strong anharmonicity.

4.2.2 Renormalized Phonons

The harmonic frequencies ω_λ (and polarization vectors) of the phonon quasi-particles introduced above do not depend on temperature, while the interactions among them depend on temperature through their population numbers (cf. eg. Eqs. (4.19)). It is often desirable to have access to a set of temperature dependent phonons, referred to as *renormalized phonons*. I will sketch a few ways in which such phonons can be obtained.

The conceptually, and computationally, simplest way of introducing a temperature dependence into the problem is through a temperature dependent volume. This is known as the *quasi-harmonic approximation* (QHA), which corresponds, essentially, to the approximation $\omega(V, T) \approx \omega(V(T))$. Practically, this entails calculating the derivatives of the BO energy surface (cf. Eq. (4.7)) at thermally expanded crystal configurations. The temperature dependence of the crystal configuration is conventionally obtained by a minimization of the harmonic free energy (see Sec. 4.3.1 below), but one can in principle obtain it using AIMD simulations or from experimental measurements. An advantage of this approach is that it avoids the need to calculate higher order IFCs.

While the QHA often provides a significant improvement compared to the pure harmonic case, it will typically fail for highly anharmonic systems, and for moderately anharmonic systems once the temperature becomes too high.

In principle, a set of temperature dependent phonon frequencies can be obtained through the real part of the self-energy obtained in the last section, $\tilde{\omega}_\lambda(T) = \omega_\lambda + \Delta_\lambda(T)$, this requires, as opposed to the QHA, the calculation of higher order IFCs. Note that one could, of course, add a shift also on top of the QHA frequencies, i.e. $\tilde{\omega}_\lambda(T) = \omega_\lambda(V(T)) + \Delta_\lambda(T, V(T))$.

For highly anharmonic systems, however, using only perturbation results from the first few higher order terms in the Taylor expansion on top of the "bare" harmonic phonons, will typically not work. Indeed, the bare phonons will often end up being too strongly interacting for perturbation theory to be accurate [30].

A popular framework to obtain temperature renormalized phonons is the *self-consistent phonon* (SCP) approximation. There are many flavors to this approach. In one variant [31], one introduces a trial free energy $F_H + \langle U - U_H \rangle_H$ which satisfies a *Gibbs-Bogoliubov inequality*

$$F \leq F_H + \langle U - U_H \rangle_H, \quad (4.25)$$

where F is the true free-energy of the system. A minimization of a trial free energy with respect to the renormalized phonon frequencies $\{\Omega_\lambda\}$ leads to the pair of equations

$$\begin{cases} \Omega_\lambda^2 = \omega_\lambda^2 + 2\Omega_\lambda I_\lambda, \\ I_\lambda = \frac{\hbar}{8} \sum_{\lambda'} \Phi_{\lambda-\lambda\lambda'-\lambda'}^\Omega (2n_{\lambda'} + 1), \end{cases} \quad (4.26)$$

which are solved self-consistently. The $\Phi_{\lambda-\lambda\lambda'-\lambda'}^\Omega$ notation is to indicate that the renormalized phonon frequencies $\{\Omega_\lambda\}$ should be used in Eq. (4.18). Note that exchanging $\Omega_\lambda = \omega_\lambda$ corresponds approximately to correcting the harmonic frequencies by the real-part self energy $\Delta^{(4)}$, Eq. (4.23). Note further that the correction from $\Delta^{(3)}$ (Eq. 4.22) is absent in this formulation.

Eqs. (4.26) capture the general idea, but a potential problem is that they treat the polarization vectors as constants, which is formally not correct. There are several more complete SCP variant, including the *stochastic self-consistent harmonic approximation* (SSCHA) [32], or a recently developed operator-renormalization [33] based method [30].

The Temperature Dependent Effective Potential (TDEP) Method

The phonon renormalization method that I use in this thesis is the *temperature dependent effective potential* (TDEP) method [34–36]. The original idea was to fit a model Hamiltonian to best reproduce the forces obtained by AIMD. In the simplest case, one takes an effective harmonic potential,

$$U_{eff}^H = U_0 + \frac{1}{2} \sum_{ij\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta, \quad (4.27)$$

where $\Phi_{ij}^{\alpha\beta}$ are now elements of some effective IFCs, not derivatives of the BO energy surface as Eq. (4.8). The associated force is

$$f_{i\alpha}^H = - \sum_{j\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta. \quad (4.28)$$

One can now determine the effective IFCs by a least-squares minimization of the true AIMD forces, $\{f_{i\alpha}^{BO}\}$, and $\{f_{i\alpha}^H\}$. Given sets of displacements $\{\mathbf{U}_c\}$ and forces $\{\mathbf{F}_c^{BO}\}$ from a series of AIMD configurations, $c = 1, \dots, N_c$, we can symbolically write the effective TDEP IFCs as

$$\Phi = \arg \min_{\Phi} \frac{1}{N_c} \sum_c |\mathbf{F}_c^{BO} - \tilde{\Phi} \mathbf{U}_c|^2. \quad (4.29)$$

This can be straightforwardly cast into an appropriate matrix form, so that the minimization can be solved as a standard least-squares problem [35].

Higher order terms can in principle be included directly into the minimization, Eq. (4.29). Writing a higher order effective potential,

$$U_{eff}^M = U_0 + \frac{1}{2} \sum_{ij\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{3!} \sum_{ijk\alpha\beta\gamma} \Phi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \frac{1}{4!} \sum_{ijkl\alpha\beta\gamma\delta} \Phi_{ijkl}^{\alpha\beta\gamma\delta} u_i^\alpha u_j^\beta u_k^\gamma u_l^\delta, \quad (4.30)$$

there is a corresponding force

$$\begin{aligned} f_{i\alpha}^M &= - \sum_{j\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta - \sum_{jk\beta\gamma} \Phi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma - \sum_{jkl\beta\gamma\delta} \Phi_{ijkl}^{\alpha\beta\gamma\delta} u_j^\beta u_k^\gamma u_l^\delta. \\ &= f_{i\alpha}^H + f_{i\alpha}^{(3)} + f_{i\alpha}^{(4)}. \end{aligned} \quad (4.31)$$

One can now in principle minimize the difference between the true BO forces and $\{f_{i\alpha}^M\}$. However, doing so one has, in principle, no explicit control over the relative sizes of the contributions from the different terms in Eq. (4.31). This is a problem since it may invalidate the use of the perturbation theory results of Section 4.2.1 if the phonon system becomes too strongly interacting. A more physically sound approach is to first fit effective 2nd order IFCs to best reproduce the true force (i.e. according to Eq. (4.29)), then fit effective 3rd order IFCs to the residual of the BO force, i.e. to $\{f_{i\alpha}^{BO} - f_{i\alpha}^H\}$, and finally fit effective 4th order IFCs to $\{f_{i\alpha}^{BO} - f_{i\alpha}^H - f_{i\alpha}^{(3)}\}$. This procedure ensures that the 2nd order term in Eq. (4.30) will be the dominant contribution, while higher order terms become progressively smaller, justifying the use of perturbation theory. The set of phonon quasi-particles thus defined becomes, in a sense, the most weakly interacting such set available at the specified external conditions (e.g. temperature, volume), and should thus be the best possible starting point for a perturbative treatment.

4.2.3 Thermal Transport

Setting up a temperature gradient, ∇T , across a sample will, assuming linear response, result in a heat flux, $\mathbf{J}$, according to *Fourier's law*,

$$\mathbf{J} = -\boldsymbol{\kappa} \nabla T, \quad (4.32)$$

which defines the *thermal conductivity tensor*, $\boldsymbol{\kappa}$.

In semiconducting and insulating crystals, the heat is primarily carried by the (interacting) phonons, for which the heat flux can be written

$$\mathbf{J} = \frac{1}{V} \sum_{\lambda} \hbar \omega_{\lambda} \mathbf{v}_{\lambda} \bar{n}_{\lambda} \quad (4.33)$$

where ω_{λ} and $\mathbf{v}_{\lambda}$ are the frequency and group velocity of phonon mode λ , respectively, and $\bar{n}_{\lambda}$ is the non-equilibrium phonon distribution function. $\bar{n}_{\lambda}$ is solved for in the steady-state using the phonon *Boltzmann transport equation* (BTE) [37]:

$$-\nabla T \cdot \mathbf{v}_{\lambda} \frac{\partial \bar{n}_{\lambda}}{\partial T} + \left[\frac{\partial \bar{n}_{\lambda}}{\partial t} \right]_{\text{collision}} = 0. \quad (4.34)$$

In practice, this is solved by linearizing $\bar{n}_{\lambda}$ around the equilibrium phonon distribution $n_{\lambda} = n_{\lambda}^{(0)}$, i.e. writing $\bar{n}_{\lambda} = n_{\lambda}^{(0)} + n_{\lambda}^{(1)}$, where $n_{\lambda}^{(1)}$ is linear in ∇T . The collision term in Eq. (4.34) should, in principle, involve all relevant mechanisms that can scatter the

heat-carrying phonons, including impurity scattering, scattering with boundaries of the sample and electron-phonon and phonon-phonon scattering to all relevant orders. Most commonly, only three-phonon and isotope scattering is included in computations.

In the so called (single mode) relaxation time approximation (RTA) the linearized BTE results in a closed form solution for the thermal conductivity,

$$\kappa_{\alpha\beta} = \frac{1}{V} \sum_{\lambda} C_{\lambda} v_{\alpha,\lambda} v_{\beta,\lambda} \tau_{\lambda}, \quad (4.35)$$

where $C_{\lambda} = \hbar \omega_{\lambda} \frac{dn_{\lambda}}{dT}$ is the phonon heat capacity and τ_{λ} the phonon lifetime of mode λ . τ_{λ} is related to the imaginary part of the phonon self-energy as $\frac{1}{\tau_{\lambda}} = 2\Gamma_{\lambda}$.

The RTA solution is often quite accurate, in particular when the thermal conductivity is low. It fails, however, to account for the difference between Umklapp and Normal phonon scattering processes (cf. Eq. 4.21); in reality only Umklapp processes should be resistive. This can be addressed through a full iterative solution to the linearized BTE [38].

The contribution to Γ_{λ} from three-phonon scattering was given in Eq. (4.19) and the isotope scattering contribution can also be added [39]. Recently, the contribution from four-phonon scattering has also begun to be included in *ab initio* calculations of thermal conductivities [30, 40, 41]. It is also worth noting that the thermal conductivity can be evaluated from MD simulations either in a non-equilibrium framework, or using the Green-Kubo framework. These types of simulations are typically difficult to converge in the time- and length-scales available to AIMD, although progress in this regard is being made [42].

4.2.4 Practical DFT calculations of phonons

In practice, harmonic phonons are typically calculated either by linear response in reciprocal space, using density functional perturbation theory (DFPT) [43], or by the so called small-displacement method [44].

In the small displacement method the IFCs are typically estimated by finite differences as follows [45]

$$\Phi_{ij}^{\alpha\beta} = \frac{\partial^2 E}{\partial u_i^{\alpha} \partial u_j^{\beta}} = \frac{\partial f_{j\beta}}{\partial u_i^{\alpha}} \approx \frac{f_{j\beta}(R_{eq} + \Delta r_{i\alpha}) - f_{j\beta}(R_{eq})}{\Delta r_{i\alpha}}, \quad (4.36)$$

where $f_{j\beta}(R_{eq})$ is the β -component of the force on atom j with all atoms in their equilibrium positions, which should in principle be zero if the equilibrium positions are proper, and $\Delta r_{i\alpha}$ is the α -component of a small displacement (usually on the order of ~ 0.01 Å) of atom i .

Not all elements of the IFCs have to be determined, as many are related by symmetry. Firstly, translational, rotational and the so-called Huang invariance has to be satisfied. Secondly, the IFCs should satisfy the symmetry relations of the underlying lattice. In combination, this typically dramatically reduces the number of IFC elements that have to be explicitly calculated.

4.3 Statistical Mechanics and Thermodynamics

The central quantity in statistical mechanics is the partition function,

$$Z = \text{Tr}(e^{-\beta \hat{H}}). \quad (4.37)$$

which is most commonly evaluated in a basis of eigenstates of the Hamiltonian, with eigenvalues E_s , where it takes the form

$$Z = \sum_s e^{-\beta E_s}. \quad (4.38)$$

In classical statistical mechanics, Z is given as an integral over phase space, $\{\mathbf{q}, \mathbf{p}\}$,

$$Z_{cl} = C \int e^{-\beta H(\{\mathbf{q}, \mathbf{p}\})} d\mathbf{q} d\mathbf{p}. \quad (4.39)$$

Essentially all other statistical mechanical and thermodynamic properties can be evaluated in terms of the partition function. In particular, the internal energy, U ,

$$U = -\frac{\partial \log Z}{\partial \beta}, \quad (4.40)$$

and Helmholtz free energy, F ,

$$F = U - TS = -\beta^{-1} \log Z, \quad (4.41)$$

where S is the entropy. F is the thermodynamic potential in the canonical ensemble, meaning that at external conditions corresponding to constant N , V and T , thermodynamic stability is determined by minimizing F . It is then clear to see that, for example, the thermodynamically stable crystal structure is determined through a competition between low energy and high entropy.

Often, the relevant external conditions are those of constant pressure instead of volume, in which case the relevant thermodynamic potential is the Gibbs free energy,

$$G = U - TS + pV = F + pV. \quad (4.42)$$

The differential of F is (ignoring here terms related to changes in the number of particles N)

$$dF = -SdT - pdV \quad (4.43)$$

which defines relations of partial derivatives of F to the entropy, S , and pressure, p . It is interesting to note that the pressure,

$$p = -\frac{\partial F(V, T)}{\partial V} = -\frac{\partial U(V, T)}{\partial V} + T \frac{\partial S(V, T)}{\partial V}, \quad (4.44)$$

can be written (second equality) as the sum of an energy pressure and an entropy pressure.

4.3.1 Phonon Thermodynamics

As laid out in Section 4.2, in the harmonic approximation the state of a solid is given as a superposition of uncoupled normal mode vibrations. The partition function can thus be expressed analytically as a collection of harmonic oscillators:

$$Z_{ph} = \prod_{\lambda} Z_{\lambda} = \prod_{\lambda} \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega_{\lambda}} = \prod_{\lambda} \frac{e^{-\beta\hbar\omega_{\lambda}/2}}{1 - e^{-\beta\hbar\omega_{\lambda}}}. \quad (4.45)$$

The harmonic phonon free energy can then be simply calculated:

$$F_{ph} = -\beta^{-1} \log Z_{ph} = \sum_{\lambda} \left(\frac{\hbar\omega_{\lambda}}{2} + \beta^{-1} \ln(1 - e^{-\beta\hbar\omega_{\lambda}}) \right). \quad (4.46)$$

Another quantity of interest, not least for computational convenience, is the phonon density of states (DOS),

$$g(\omega) = \frac{V_{uc}}{(2\pi)^3} \sum_s \int_{\text{BZ}} \delta(\omega - \omega_{\mathbf{q}s}) d\mathbf{q}. \quad (4.47)$$

For example F_{ph} can now be written,

$$F_{ph} = \int g(\omega) \left(\frac{\hbar\omega}{2} + \beta^{-1} \ln(1 - e^{-\beta\hbar\omega}) \right) d\omega. \quad (4.48)$$

The reference energy, Φ_0 , of the atoms in their equilibrium positions should then be added to obtain the harmonic free energy of the crystal:

$$F_{harm} = \Phi_0 + F_{ph}. \quad (4.49)$$

Φ_0 is also typically taken to include relevant non-vibrational entropy contributions, eg. electronic, magnetic or possibly configurational entropies.

Harmonic estimates for several relevant thermodynamic quantities, eg. heat capacities and entropies, can now be simply obtained by appropriate differentiation of F_{harm} . The internal energy of the phonon system is

$$U_{ph} = -\frac{\partial \log Z_{ph}}{\partial \beta} = \sum_{\lambda} \hbar\omega \left(n_{\lambda} + \frac{1}{2} \right). \quad (4.50)$$

In the TDEP formalism, once an effective Hamiltonian and the corresponding renormalized phonons have been determined, F_{ph} is evaluated as in Eq. (4.46). When it comes to choosing the reference energy Φ_0^{TDEP} the most natural choice is no longer the static energy of the atoms in their static equilibrium positions. This is due to the fact that the TDEP IFCs are not derivatives of the BO energy surface at these equilibrium positions. A more natural choice is instead to ensure that the internal energies of the TDEP and the full BO Hamiltonian, that governs the dynamics in the AIMD simulation, are the same. That is, to choose Φ_0^{TDEP} such that

$$\langle H_{TDEP} \rangle = \langle H_{BO} \rangle, \quad (4.51)$$

where the averages are taken over the AIMD simulation, i.e. w.r.t. H_{BO} . Practically this implies choosing

$$\Phi_0^{TDEP} = \left\langle E_0(\{\mathbf{R}\}(t)) - \frac{1}{2} \sum_{ij\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^{\alpha}(t) u_j^{\beta}(t) \right\rangle_t. \quad (4.52)$$

This is also a powerful choice because Eq. (4.51) allows connecting to a Gibbs-Bogoliubov type inequality, similar to Eq. (4.25).

4.3.2 Thermodynamic Integration

A formally exact set of methods to extract free energies from MD simulations is provided by *thermodynamic integration*. These methods are based on the fact that while it is difficult to directly extract free energies, or more precisely entropies, from MD simulations, certain free energy derivatives are more readily accessible. This is a direct result of the fact that derivatives of the free energy equal averages over *energy* derivatives, i.e. it holds that

$$\left(\frac{\partial F(V, T, \lambda)}{\partial \lambda} \right) = \overline{\frac{\partial H(\{\mathbf{q}, \mathbf{p}\}; \lambda)}{\partial \lambda}}. \quad (4.53)$$

λ is now some external control-parameter added to the system¹. In practice, the phase-space ensemble average on the right is, as usual, evaluated as a time average under the ergodic assumption.

The free energy change on switching λ from 0 to 1 is then

$$\begin{aligned} F(V, T, \lambda = 1) &= F(V, T, \lambda = 0) + \int_0^1 \frac{\partial F(V, T, \lambda)}{\partial \lambda} d\lambda \\ &= F(V, T, \lambda = 0) + \int_0^1 \left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda \end{aligned} \quad (4.54)$$

In practice, one will chose $\lambda = 0$ to correspond to a system with a known, preferably analytical, free energy, and $\lambda = 1$ to the "true" simulated system whose free energy one wishes to compute. Values in between are typically taken as a linear interpolation so that $\left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle_\lambda = \langle H_1 - H_0 \rangle_\lambda$.

The same result, Eq. (4.53) also holds when the external parameter is the volume. From Eq. (4.44) it thus holds that

$$p = -\frac{\partial F(V, T)}{\partial V} = -\frac{\partial U(V, T)}{\partial V} + T \frac{\partial S(V, T)}{\partial V} = -\left\langle \frac{\partial H}{\partial V} \right\rangle. \quad (4.55)$$

It is thus possible to obtain the change in free energy over a change in volume, V_1 to V_2 , by

$$F(V_2, T) = F(V_1, T) + \int_{V_1}^{V_2} \left\langle \frac{\partial H}{\partial V} \right\rangle dV. \quad (4.56)$$

This is a very useful result since energy derivatives w.r.t. volume can typically be evaluated analytically in DFT based simulations, the average in Eq. (4.56) can thus be evaluated over an AIMD simulations and the free energy change can subsequently be obtained by running a series of simulations at different volumes.

When it comes to analysing crystalline materials, the restriction of the free energy to depend solely on volume (and temperature) is often overly restrictive. In principle we want to be able to consider arbitrary homogeneous deformations of a crystal, not only isotropic volume changes. Towards this end we introduce the notation $\mathbf{h}$ for the 3×3 matrix with the supercell lattice vectors $\mathbf{a}, \mathbf{b}$ and $\mathbf{c}$ as columns:

$$\mathbf{h} = \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix}. \quad (4.57)$$

¹ λ here should not be confused with the label for a phonon-mode $\lambda = (\mathbf{q}s)$, used in previous sections

Further introduce $\mathbf{X}$ and $\mathbf{x}$ as (an arbitrary) reference and deformed configuration of the crystal, respectively. The deformation gradient $\boldsymbol{\alpha}^2$ is then the derivative of each component of a material point in the configuration $\mathbf{x}$ with respect to each component of the material point in the reference configuration $\mathbf{X}$,

$$\alpha_{ij} = \frac{\partial x_i}{\partial X_j}. \quad (4.58)$$

For homogeneous deformations $\boldsymbol{\alpha}$ relates $\mathbf{h}$ in the configurations $\mathbf{X}$ and $\mathbf{x}$:

$$\mathbf{h}(\mathbf{x}) = \boldsymbol{\alpha} \mathbf{h}(\mathbf{X}). \quad (4.59)$$

The *Lagrangian*, or thermodynamic, strain, $\boldsymbol{\eta}$, can then be defined,

$$\boldsymbol{\eta} = \frac{1}{2} (\boldsymbol{\alpha}^T \boldsymbol{\alpha} - \mathbf{I}), \quad (4.60)$$

where $\mathbf{I}$ is the identity matrix.

With these definitions, the differential of the free energy can now be generalized from pressure-volume variables (Eq. 4.43) to stress-strain variables. For a rotationally invariant crystal, the configuration $\mathbf{x}$ is completely specified by $\{\mathbf{X}, \boldsymbol{\eta}\}$, i.e. a reference configuration and the strain defined w.r.t. this reference. The differential then reads [46]:

$$dF(\{\mathbf{X}, \boldsymbol{\eta}\}, T) = -SdT + V(\mathbf{X}) \boldsymbol{\tau} : d\boldsymbol{\eta}, \quad (4.61)$$

where $\boldsymbol{\tau}$ is the second Piola-Kirchoff stress. The notation ':' signifies a contraction over both indices, i.e. $\boldsymbol{\tau} : d\boldsymbol{\eta} = \sum_{i,j} \tau_{ij} d\eta_{ij}$. From DFT-based calculations we have access to a different stress measure, the so called Cauchy stress, $\boldsymbol{\sigma}$ (typically refereed to as just the stress), which is related to $\boldsymbol{\tau}$ as $\boldsymbol{\tau} = J \boldsymbol{\alpha}^{-1} \boldsymbol{\sigma} \boldsymbol{\alpha}^{-T}$, where $J = \det(\boldsymbol{\alpha})$. The stress is practically evaluated in an AIMD simulation in the spirit of Eq. (4.53), i.e. as a time-average over energy derivatives w.r.t. strain.

The differential Eq. (4.43) can then be integrated over strain at constant temperature to yield free energy changes. As we shall see in Chapter 6, this will allow us to derive computationally convenient expressions for the free energy change under homogeneous deformations, corresponding essentially to a generalization of Eq. (4.56). This approach is used in Papers VI and VII.

4.4 Nuclear Quantum Effects using Path Integral Molecular Dynamics

The basic equations of molecular dynamics are arrived at by making the classical nuclei approximation on the nuclear SE, Eq. (2.6). While this approximation is excellent for treating heavy nuclei, it is typically not accurate when the nuclei are light, in particular when hydrogen atoms are present. A computationally tractable way to treat the quantum nature of the nuclei is provided by *path integral molecular dynamics* (PIMD). This technique is based on the existence of a mapping of the quantum mechanical partition function of a system onto a classical ring-polymer with an infinite number of beads, i.e.

²It is worth to note that the deformation gradient is more conventionally denoted $\mathbf{F}$, but as the letter F is already used for both the free energy and the force, two other central quantities, I choose to follow Wallace [33] and use $\boldsymbol{\alpha}$.

an infinite set of classical systems with the same chemical interactions as the quantum mechanical system, connected by harmonic springs.

Starting with the expression for the quantum mechanical partition function,

$$Z = \text{Tr} \left(e^{-\beta \hat{H}} \right) = \text{Tr} \left(e^{-\beta(\hat{T} + \hat{V})} \right), \quad (4.62)$$

where $\hat{T}$ and $\hat{V}$ are the kinetic and potential energy operators of the system. Note now that, since $\hat{T}$ and $\hat{V}$ do not commute, we cannot rewrite this as $\text{Tr} \left(e^{-\beta \hat{T}} e^{-\beta \hat{V}} \right)$. This would, as it turns out, correspond precisely to the classical approximation. One may instead proceed by a Trotter decomposition

$$e^{-\beta \hat{H}} = \lim_{P \rightarrow \infty} \left(e^{-\frac{\beta}{P} \hat{V}/2} e^{\frac{\beta}{P} \hat{T}} e^{-\frac{\beta}{P} \hat{V}/2} \right)^P. \quad (4.63)$$

Evaluating the partition function in the coordinate representation, and using Eq. (4.63), it follows, after neglecting exchange effects and some relatively straightforward manipulations, that

$$Z \approx Z_P = C \int e^{-\beta H_P} d\mathbf{R}^{(s)} d\mathbf{P}^{(s)}, \quad (4.64)$$

where C is a constant, H_P is the Hamiltonian of a classical ring polymer,

$$H_P = \sum_s \left(- \sum_I \left(\frac{(\mathbf{P}_I^{(s)})^2}{2M_I} + \frac{1}{2} M_I \omega_P^2 (\mathbf{R}_I^{(s)} - \mathbf{R}_I^{(s+1)})^2 \right) + \frac{1}{P} E_0(\{\mathbf{R}_I^{(s)}\}) \right), \quad (4.65)$$

$\omega_P^2 = P/(\hbar^2 \beta^2)$, s is introduced to index the beads and cyclic boundary conditions are implied, i.e., $s + P \equiv s$. The integral in Eq. (4.64) should be taken over the extended phase-space of the whole ring-polymer, i.e. over all P copies of the system. This expression becomes exact in the limit $P \rightarrow \infty$, but P will, of course, always be finite in practice.

This provides us with a computational framework to include nuclear quantum effects in the simulations by performing AIMD with the Hamiltonian H_P . This entails running AIMD³ on P copies, or "beads" of the system, with each atom in one bead coupled to the same atom in neighbouring beads by harmonic springs. While this is conceptually straightforward, there are technicalities that severely complicate the implementation. Not least is the fact that the number of beads P will have to be rather large in order to get accurate results, but also the fact that the ring polymer frequency ω_P will typically be much larger than the physical frequencies of the system, which leads to integration and sampling issues. A lot of work has been done to attempt to resolve these issues.

One path forward, is found through how the ring-polymer is thermostated. The basic underlying idea is that a classical harmonic oscillator at a temperature $T^*(\omega) = \frac{\hbar\omega}{2k_B} \coth \frac{\hbar\omega}{2k_B T}$ has precisely the same position and momentum distribution functions as a quantum mechanical one at temperature T . Thus one could trivially simulate a single quantum mechanical harmonic oscillator in a classical simulation by simply changing the temperature. The fact that effective temperature $T^*(\omega)$ is frequency dependent makes the application of this to real systems somewhat tricky.

This can be addressed by using so called *colored noise* thermostats, which are based on the Generalized Langevin Equation (GLE). The GLE is an alteration of the standard Langevin thermostat Eqs. (4.6), which replaces the friction coefficient with a

³or "classical" MD

time-dependent friction kernel and replaces the white-noise force by one with colored noise, whose autocorrelation function should equal the friction kernel. Although more complicated, the GLE framework provides significantly more flexibility in the thermostating, in particular one can use it to enforce the frequency dependent temperature $T^*(\omega)$ over a pre-determined range of frequencies. This results in the so-called quantum thermostat (QT) [47], which enables the estimation of NQEs on a system at no increased cost relative to a standard MD simulation with classical nuclei. The main issue with the QT is that anharmonic coupling between vibrational modes will act towards equilibrating the temperature of modes thermostated at different temperatures. This will cause energy to flow from high frequency modes that are thermostated at high temperatures, toward low frequency modes, so called "zero-point leakage" [48].

Combining the path integral and GLE frameworks (PI+GLE) [49] entails designing PIMD simulations with a GLE thermostat that enforces the correct configurational fluctuations in the harmonic limit, independently of the number of beads used in the PIMD simulation, and further converge to the PIMD result in the limit of a large number of beads. The latest major development in this direction is the so called PIGLET thermostat [50], which I have used in Paper IV. The PIGLET framework drastically reduces the number of beads P that is required to converge PIMD simulations.

The PIMD simulations in Paper IV are performed using the i-PI program [51].

CHAPTER 5

Structural Complexity and Dynamics in Perovskite Structured Materials

This chapter will be concerned with perovskite-structured materials. These are systems with structures related to that of the mineral 'Perovskite', or calcium-titanate, CaTiO_3 . The original discovery of Perovskite was likely made by Rose in 1839 [52], who appears to have named it after Lev Perovski [53], and the perovskite crystal-structure was later described by Goldschmidt [54]. The generic, ideal, ABX_3 , perovskite structure is shown in Fig. 5.1. The most useful visual representation of the structure is as a network of corner-connected BX_6 octahedra with the A site ions located at the center of cubo-octahedral voids. The A-site can either be occupied by a single atom or a molecule.

There exists a remarkably large collection of materials with the perovskite, or closely related, structures, with the two most common sub-classes being the oxides, ABO_3 , and halides, ABX_3 , $\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I . As the perovskite structure hosts such a broad range of material chemistries, it finds applications in a diverse range of applications, from fuel-cells [55] and catalysis [56] to thermoelectrics [57] and solar cells [58]. In particular, the last decade has seen an absolute explosion of researcher effort devoted to the halide perovskites, mainly in relation to their photovoltaic properties [58]. This is a direct consequence of the very promising power-conversion efficiency of solar cells based on the hybrid organic-inorganic halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, now reaching above 25 % [59].

Perovskite materials have also long been of great interest from the point of view of fundamental condensed matter physics, as they have been clear-cut realizations of a range of interesting physical phenomena, including displacive- and order-disorder phase transformations [60, 61], ferroelectricity [62], piezoelectricity [63], magnetism, and multiferroicity [64].

The perovskite crystal structure displays a very rich polymorphism. There is a whole host of lower symmetry hettotypes, with close relation to the aristotype cubic perovskite. As a result, perovskite-structured materials often have very rich and complex temperature-pressure-composition phase diagrams. Quite often, these lower symmetry variants are so closely related that they are difficult to distinguish from each other and from the aristotype perovskite itself.

Figure 5.1: (Left) Illustration of the ABX₃ cubic perovskite structure. (Right) 2×2×2 expansion of the perovskite unit cell, to illustrate the corner connected BX₆ octahedra.

A whole range of "perovskite-related" material systems also exist. In fact, so many different systems are being referred to with descriptions involving the word "perovskite", many of which are only very loosely related to the aristotype, that calls from the community have recently been made toward more strict guidelines on what can be reasonably referred to as a perovskite [65, 66]. Such "perovskite-relatives" include the double-perovskites, Ruddlesden-Popper phases, vacancy-ordered perovskites, and vacant perovskites.

5.1 Perovskite Polymorphism

Many, if not most, materials typically referred to as perovskite structured, do not, in fact, have structures that correspond to the high symmetry aristotype cubic perovskite at low temperatures. They are instead found in one of many possible distorted variants, as mentioned above. Upon heating, the ideal perovskite phase is often recovered at high temperature through a sequence of phase transformations.

The majority of the atomic displacements that drive these distortions can be usefully grouped into three separate classes [67]. The first corresponds to polar displacements of the A or B site cations. These are typically related to a zone-center (Γ -point) instability of the cubic structure and are intimately related to the ferroelectricity of many perovskites. The second class are cooperative ("Jahn-Teller"-type) distortions of the BX₆ octahedra. The third class, which will be the main focus of this chapter, are the so called anti-ferrodistortive (AFD), or octahedral tilting, distortions. These correspond to collective tilts of the BX₆ octahedra, around one or several axes, in an in-phase or out-of-phase fashion (Fig. 5.2) and are typically related to imaginary phonon modes at the M- and R-point of the BZ of the cubic perovskite structure. As an example, Fig. 5.3 shows the harmonic phonon dispersion-relations of the perovskite oxide CaMnO₃¹.

¹With G-type antiferromagnetic (AFM) ordering of the Mn magnetic moments

Figure 5.2: Illustration of the in-phase (a) and out-of-phase (b) octahedral tilting modes in perovskites. Image adapted from Paper II.

The unstable octahedral tilting instabilities are clearly seen as imaginary (negative numbers in the plot) frequencies.

Naturally, these separate types of atomic displacements cannot in reality be considered to be independent of each other, but will couple through anharmonic interactions. It is indeed not uncommon that the cubic structure of some perovskite is unstable towards two of these types of distortions, but the structure arrived at by introducing one of them is stable towards the second type of distortion.

Beyond this, once one of these distortions, corresponding to a set of atomic displacements, have been frozen into the cubic structure, this will lower the symmetry and there will be symmetry allowed homogeneous deformations of the structure, that will further work to lower the energy. In the cases I will consider in this thesis, the AFD octahedral tilting modes are typically considered to be the primary mode of distortion, and I will often treat other distortions, including in particular strain related deformations and A site displacements, as secondary modes that follow the main AFD one. That is, given a certain tilt configuration, these secondary distortions will be optimized to their lowest energy state commensurate with this symmetry.

The phase transformations between different distorted variants, and to the aristotype cubic structure itself, has long been a subject of intense study. Some of these transitions fit nicely into the standard "soft-mode" picture of displacive phase transformation, i.e. there is a particular phonon mode whose frequency drops towards zero as the phase transformation temperature is approached from above, and the structure of the low temperature phase is essentially obtained by freezing in the atomic displacement of the soft mode into the high temperature phase. Not all transformations behave like this. Another transformation mechanism is the order-disorder type, where the high-symmetry phase instead emerges as a dynamical and/or spatial average over lower symmetry local distortions. One can also often expect the transformation to show a behaviour somewhere in between these two extremes [61].

Naturally, due to the features described above, many materials in the perovskite structure are highly anharmonic. This anharmonicity can be of a few distinct types. As was mentioned above, the perovskite structure is susceptible to transform into a set of different hettotypes. Naturally then, phonon modes corresponding to these atomic displacements will rarely be well-described as harmonic. In the case of a displacive transition, these phonon modes will be stabilized by phonon-phonon interaction at

Figure 5.3: Harmonic phonon dispersion-relations of CaMnO_3 . Note the imaginary modes at the M- and R-points, which corresponds to unstable in-phase and out-of-phase octahedral tilting modes, respectively. Imaginary frequencies are represented by negative numbers.

high temperature and the dynamics in the high-symmetry phase will thus be highly anharmonic. In the case of an order-disorder type situation, the anharmonicity will typically manifesting itself as dynamical hops between distinct minima on the underlying PES.

5.1.1 Octahedral Tilting

The tendency of perovskite structured materials to distort through octahedral tilting can be partly understood in terms of the size of the ion or molecule occupying the A-site. If this ion or molecule is too small, the surrounding octahedral network will have a tendency to tilt in order to achieve a better coordination of the A-site. This can be usefully quantified by the *Goldschmidt tolerance factor* [54],

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}, \quad (5.1)$$

where, r_A , r_B and r_X are the ionic radius of the constituent elements of the perovskite. Typically, perovskites with a ground-state cubic structure satisfy $0.9 < t < 1$, while for $0.8 < t < 0.9$ the structure is strongly susceptible to tilting of the octahedra. Systems with $t < 0.8$ will rarely crystallise as perovskites. t is useful metric, but certainly not universally applicable, and alternatives have been suggested [68].

These octahedral tilts most commonly appear either in-phase, where sequential octahedral around the tilting axes are tilted in the same direction, or out-of-phase, where they are instead tilted in the opposite direction, this was illustrated in Fig. 5.2. The structures can be tilted around one or around several of the pseudocubic axes and the resulting tilt configurations are conveniently analysed using Glazer notation [69]. The tilt configuration around a particular axis is then associated with a letter and a superscript. In-phase, out-of-phase, or the absence of a tilt, are denoted with superscripts +, -, and 0, respectively. The letters a , b and c are used for tilts around the three axes, unless the magnitude of the tilt around two axes are the same, in which case the same letter is used. As an example, the very common orthorhombic perovskite, with equal out-of-phase tilts around the a and b axes and an in-phase tilt around the

Figure 5.4: Potential energy change in CaMnO_3 as a function of the unstable in-phase and out-of-phase octahedral tilting modes. The mode displacement amplitude is the displacement of an O ion in fractions of the perovskite lattice constant. Image from Paper I.

c axis, is denoted $a^-a^-c^+$. The ideal cubic ("tiltless") perovskite is denoted $a^0a^0a^0$. Through a group-theoretical analysis, Howard and Stokes [70] found that in this space of in-phase and out-of-phase tilts there exists 14 (other than the ideal perovskite) distinct configurations.

It should be noted that there is, of course, no fundamental reason why the octahedral tilts should appear only in the in-phase or out-of-phase forms. Indeed, tilt patterns with longer periodicity have been predicted and likely observed [71, 72]. Although the majority of octahedrally-tilted perovskites seem to fit well into one of the "simple" tilt-patterns described above, it does not seem unlikely that there could be systems that have been mistakenly assigned to a simple tilt-pattern, when it, in fact, possesses a longer-periodicity tilt pattern.

Once any octahedral tilt breaks the cubic symmetry of the aristotype perovskite, there will be symmetry allowed homogeneous deformations available to the system, i.e. deformations that do not further reduce the symmetry. Depending on the type of octahedral tilt pattern, these deformations can be of varying form. Bechtel and van der Ven [73] have characterised the symmetry allowed deformations for all 14 tilt systems.

Clearly, most of the tilt-patterns will have several distinct but symmetry equivalent variants. For instance, the simple $a^0a^0c^+$ tilt pattern is equivalent to $a^0b^+a^0$, and to $a^0a^0(-c)^+$ where the $(-c)$ notation is to indicate that the rotation is taken in the opposite sense, i.e. anti-clockwise instead of clockwise. These can be conveniently grouped into translational and rotational variants [73]. Translational variants exist in a common strain state, while rotational variants instead belong to different strain states.

5.2 Energetics and Low-Energy Paths for Octahedral Tilting in CaMnO_3 and Inorganic Halide Perovskites

In this section I will discuss the energetics related to octahedral tilting in the perovskite oxide CaMnO_3 and the two inorganic halide perovskites CsSnI_3 and CsPbI_3 , this relates to work in Papers I and II. These three systems have in common that their lowest energy perovskite polymorph is the $a^-a^-c^+$ structure. For CaMnO_3 , this is the ground-state

Figure 5.5: Potential energy change in CsPbI_3 and CsSnI_3 as functions of the unstable in-phase and out-of-phase octahedral tilt amplitudes. Circles and squares in all four panels represent fixed and tetragonally relaxed unit cells, respectively. The tilt amplitude corresponds to the displacement of an I ion in fractions of the perovskite lattice constant. Image from Paper II.

structure [74], while for the two halides, this structure is actually metastable with respect to a non-perovskite structure, although can be temporarily stabilized [75, 76].

As was seen from the static harmonic phonon dispersion in Fig. 5.3, CaMnO_3 is unstable towards both in-phase and out-of-phase octahedral tilting modes. In Fig. 5.4 I show the potential energy change of cubic CaMnO_3 upon freezing in the in-phase and out-of-phase tilting modes with varying amplitudes. As expected large energy lowerings are seen for both the in-phase and out-of-phase modes.

A mostly analogous situation is found for the two inorganic halide perovskites where similar PESs are shown in Fig. 5.5. Here I also show the correspond PESs when the symmetry allowed tetragonal lattice distortion is included, which is seen to provide a significant additional energy lowering in both CsSnI_3 and CsPbI_3 . An additional feature of note is that the in-phase and out-of-phase PESs in both CsSnI_3 and CsPbI_3 are very similar, as opposed to the CaMnO_3 case, where the depth of the out-of-phase PES is significantly lower.

Conventionally, issues relating to changes in octahedral tilting configurations are often analysed in terms of these type of one dimensional(1D) "double-well" (DW) potentials [67, 77, 78]. However, since the ground state perovskite variant of the systems we consider have tilts around all three axes, it is unclear how descriptive these 1D DWs are.

In particular for the halide perovskite, an emerging interpretation of the nature of the high-temperature phase, that is cubic on average, is that it is actually locally symmetry broken, i.e. the local atomic environment is not well described by that of the ideal cubic perovskite, but corresponds more closely to a lower symmetry, tilted, variant [79, 80]. This indicates that the atomic positions corresponding to the high-energy cubic structure may not be a very relevant part of phase-space in these systems.

Fig. 5.6 shows the 2D $a^-a^-c^+$ PES of the two halide perovskites. Note that there

Figure 5.6: $a^-a^-c^+$ PES of (a) CsPbI_3 and (b) CsSnI_3 . The x coordinate axis gives the magnitude of the in-phase tilt around the pseudocubic c axis, while the y coordinate axis gives the magnitude of the out-of-phase tilts around the a and b pseudocubic axes. The tilt amplitude is given as the offset of one I ion in units of the lattice constant of the ideal cubic perovskite. Relaxation of Cs ions and lattice parameters are allowed in the symmetry given by the tilt pattern. The energy reference is the cubic phase (origin). The energy contours are spaced by 10 and 5 meV/f.u. in (a) and (b), respectively. Note that the energy scales differ in (a) and (b). Image from Paper II.

are two (tilt) degrees-of-freedom within this tilt system: the magnitude of the out-of-phase tilts around the a and b axes and the magnitude of the in-phase tilt around the c axis. Symmetry allowed displacements of the Cs cations and lattice deformations are included by fully relaxing these degrees-of-freedom for each individual point on the PES.

The four minima corresponds, essentially, to different but symmetry equivalent variants of the $a^-a^-c^+$ structure. The PES immediately reveals that there are low energy paths between different $a^-a^-c^+$ variants that do not pass over the cubic perovskite (which is at the origin of the PESs). Going vertically and horizontally between the two minima corresponds to paths of the type $a^-a^-c^+ \rightarrow (-a)^-(-a)^-c^+$ and $a^-a^-c^+ \rightarrow a^-a^-(-c)^+$, respectively.

At finite temperature, anharmonic thermal excitations may cause the system to hop between different $a^-a^-c^+$ minima along these types of low-energy paths. Relative frequent such "octahedral fluctuations" would produce time averaged structures of higher symmetry. One can also imagine a spatial disorder resulting from this type of PESs, with different domains occupying different minima. Further discussion of these points will follow in Section 5.2.1.

Since there are 24 distinct but symmetry equivalent $a^-a^-c^+$ variants, there will be many possible paths between them. Furthermore, it is not clear *a priori* that the 2D $a^-a^-c^+$ PESs include all relevant degrees-of-freedom to reveal the lowest energy paths. To address these issues I have performed solid-state nudged-elastic-band calculations (SS-NEB) [81] for several possible low-energy paths.

The obtained SS-NEB energy barriers on 5 paths between distinct $a^-a^-c^+$ variants in CsPbI_3 are shown in Fig. 5.7. Out of these 5, the $a^-a^-c^+ \rightarrow (-a)^-a^-c^+$ path has a barrier significantly lower than the others, while the remaining four paths have

Figure 5.7: (SS-)NEB energy landscapes on a set of paths between distinct $a^-a^-c^+$ structures in CsPbI_3 . The upper panel shows the energies while lower panel displays the octahedral distortion, Δ (see text). Blue and red markers correspond to NEB calculations with varied and fixed lattice vectors, respectively. Image from Paper II.

similar energy barriers. If this, and the equivalent $a^-a^-c^+ \rightarrow a^-(-a)^-c^+$ path, are the only active paths of octahedral fluctuation, the time averaged octahedral tilting configuration would be $a^0a^0c^+$, since the two out-of-phase tilts would average out to zero. This corresponds to the experimentally observed $a^0a^0c^+$ phase as an intermediate between $a^-a^-c^+$ and $a^0a^0a^0$ [75, 76].

The end-points of the $a^-a^-c^+ \rightarrow a^-a^-(-c)^+$ and $a^-a^-c^+ \rightarrow (-a)^-(-a)^-c^+$ paths belong to the same strain states which implies the barrier between them can also be calculated with fixed lattice vectors. The corresponding energy barriers are shown with red symbols in Fig. 5.7, where it is seen that they are much larger than the corresponding barriers when allowing the lattice vectors to vary. This shows clearly that the lattice relaxation is crucial in producing the low energy paths. The lower row in Fig. 5.7 shows the deformation of the octahedra over the path, measured as $\Delta = \frac{1}{6} \sum_{i=1}^6 \left(\frac{d_i - \bar{d}}{\bar{d}} \right)^2$, where d_i and $\bar{d}$ are the individual and average Pb-I bond length of the octahedron, respectively. Evidently, the octahedra are forced to distort to a significantly higher degree at the saddle points in this case.

An interesting observation that can be made directly from the $a^-a^-c^+$ PESs is that, given a fixed energy difference between $a^0a^0a^0$ and $a^-a^-c^+$, the energy barrier on the $a^-a^-c^+ \rightarrow (-a)^-(-a)^-c^+$ path will be *inversely related* to the depth of the in-phase double well potential of Fig. 5.5. This is clear from the fact that the saddle-point on this path is $a^0a^0c^+$, i.e., the bottom of the in-phase double well. This observation generalizes to several of the other low-energy paths identified above. Indeed, 4 out of the 5 investigated paths have saddle-points that correspond to one of the 14 simple tilt patterns, with tilts around one or two axes.

The conclusion of this observation thus becomes the following: In a framework where one is considering dynamic fluctuations of octahedra between distinct minima,

Figure 5.8: Tilt angles ϕ_a , ϕ_b and ϕ_c around the three pseudo cubic axes for one selected octahedron in CaMnO_3 as functions of simulation time at temperatures 600, 900 and 1100 K. Black lines correspond to the running average. Image from Paper I.

and the local structure of these minima can be roughly approximated as $a^-a^-c^+$, the relevant energy barriers for calculating, for example, the rate of these fluctuations, are *not*, in general, the barriers obtained from single 1D double well PESs, such as those in Fig. 5.5. Indeed, these PESs have saddle points at the cubic perovskite, while the low-energy paths instead explicitly avoid the cubic structure and have saddle points corresponding to structures where tilts are present. A more correct descriptor would instead be the energy lowering obtained on adding the additional one or two tilts that takes the system from the saddle points on the PES to the $a^-a^-c^+$ minima.

In regards to the existence and nature of these low-energy paths, CaMnO_3 is very similar to the inorganic halide perovskites just discussed. With a major difference being that I have not identified one particular path with lower energy barriers than others. Instead, I found that the investigated paths all had similar energy barriers. For CaMnO_3 , I have also performed AIMD at a set of temperatures. In these AIMD simulations we explicitly observe hops of the system (Fig. 5.8) between different minima with tilts around all three axes, mainly $a^-a^-c^+$, but also other more complicated tilt patterns, which appear to correspond to more shallow minima on the full PES.

5.2.1 On the Nature and Theoretical Modelling of the Cubic Perovskite Phase

Experimentally, there is, as mentioned above, a substantial body of work pointing towards the fact that the cubic phase of, in particular many halide perovskites, is locally of a lower symmetry [79, 80, 82, 83]. The question of the nature of the disorder that produces this difference between average and local structure, in particular the extent of its spatial vs temporal component, remains, in my mind, unanswered. The model of high symmetry perovskite phases as time averaged structures, produced as a perfect defect free bulk fluctuating along the types of octahedral-tilting paths described

above, does not, of course, capture the full picture. At high temperatures, these type of octahedral tilting modes will certainly anharmonically couple to other vibrational modes, and the resulting fluctuations will certainly not be "clean" octahedral tilts, but will contain a combination of other modes of motion as well.

From a theoretical modelling point-of-view it may be instructive to think in terms of possible finite-size effects on the observed octahedral fluctuations in AIMD simulations. If the octahedra are taken to be essentially rigid, the fluctuations must involve the collective reorientation of whole planes of octahedra. On one hand, as the supercell size increases, more and more atoms have to participate in the octahedral reorientations, and one could then imagining these fluctuations to be "entropically suppressed" at large enough supercell sizes, while the periodic boundary conditions could help promote the fluctuations for smaller cells. On the other hand, the octahedral fluctuations are likely initiated by particularly large fluctuations of one, or a few, X atoms and the BX_6 octahedral network may then respond, with some probability, by a collective reorientation. The number of possible "initiators" of the collective reorientations would, in this case, grow with increasing supercell size. It is difficult to make quantitative predictions regarding these finite-size effects, due to the overwhelming computational cost of AIMD for large supercell-sizes, but it is worth to note that recent Monte Carlo simulations [84] in $12 \times 12 \times 12$ supercells, beyond the possibilities of conventional AIMD, found that the intermediate tetragonal phase in CsPbI_3 can emerge as the type of dynamical average discussed here.

In any case, if these types of dynamical octahedral reorientations are present in reality, their spatial extent will certainly be limited. Likely, they occur in smaller domains or at the domain boundaries [79]. To quantify the spatial and temporal extents needed to precisely observe the cubic phase in a diffraction experiment would be an interesting and challenging future line of investigation.

5.3 Anharmonicity and Ultra-Low Thermal Conductivity in Lead-Free Halide Double Perovskites

As mentioned in the introduction of this chapter, very impressive photovoltaic performances have been demonstrate in the Pb containing halide perovskites. They do, however, suffer from major drawbacks, the first being the presence of toxic Pb [6] and the second severe problems with long-term stability [85]. Many avenues are currently being explored in attempts to understand and solve these issues. A promising direction is found in the so-called *lead-free halide double perovskite* class of materials [6]. The basic idea is to replace the divalent Pb^{2+} cations with pairs of mono and trivalent cations, (Fig. 5.9 (a)), the most popular choices being Ag^+ , Bi^{3+} and In^{3+} . While the bandgaps of most currently known systems in this class are larger-than-optimal for photovoltaic applications, there exists a vast chemical space to explore [86] and the number of synthesised materials is rapidly growing [87].

The nature of the lattice dynamics in these materials is much less well-studied than for the single Pb-halide variants, but there are indications that they are, like the single Pb-halide variants, highly anharmonic with strong electron-phonon coupling [88].

In general, double perovskites are susceptible to the same kind of distortions as the single perovskites, in particular to octahedral tilting [89]. This appears to be true also for the halide double perovskite, where it was recently found [90] that $\text{Cs}_2\text{AgBiBr}_6$,

Figure 5.9: (a) Illustration of the cubic double perovskite crystal structure of $\text{Cs}_2\text{AgBiBr}_6$. (b) View along the out-of-phase tilting axis of the low temperature tetragonal, $a^-b^0b^0$, phase. Light green and brown spheres represent Cs and Br ions, respectively, while the Bi and Ag ions are located at the centers of pink and gray octahedra, respectively. (c) Static harmonic phonon dispersion relation and (partial) density of states (DOS) of $\text{Cs}_2\text{AgBiBr}_6$. Negative numbers denote imaginary frequencies. (d) 1D potential energy surface (PES) of three different octahedral tilting modes (see text for details), the inset is a zoom in of the low-energy part of the PES. (e) and (f) 2D $a^-b^+c^0$ PES of $\text{Cs}_2\text{AgBiBr}_6$ and CsPbBr_3 , respectively, as a function of the out-of-phase tilt a^- and in-phase tilt b^+ . The tilt amplitude is given as the offset of one Br ion in units of the lattice constant of the double perovskite (two times the lattice constants of the single perovskite in the CsPbBr_3 case). Image from Paper III.

the prototypical member of this family, has a cubic-to-tetragonal phase transformation upon cooling below ~ 122 K. This tetragonal phase have out-of-phase tilted octahedra around one axis, $a^0a^0c^-$, Fig. 5.9 (b).

In Paper III I have studied the lattice dynamics in $\text{Cs}_2\text{AgBiBr}_6$. Fig. 5.9 (c) shows its static harmonic phonon dispersion where, like in the single perovskite case we see imaginary frequencies, which are found to corresponds to modes of octahedral tilting. At the X -point the atomic displacements correspond to an in-phase tilt pattern, while at the Γ -point, the mode is mostly a pure out-of-phase tilt around a single axis, but with small tilts present also around the two other axes. At points between Γ and X , the atomic displacements corresponds to more complicated tilt-patterns with longer periodicity. Mapping out the PESs for a set of these modes yield double-well shaped potentials with very shallow minima, Fig. 5.9 (d). Moving to 2D, Fig. 5.9 (e) and (f) shows the $a^-b^+c^0$ PES² in $\text{Cs}_2\text{AgBiBr}_6$ and CsPbBr_3 , respectively. There is clearly a sharp difference in the topology of these PESs, while the $\text{Cs}_2\text{AgBiBr}_6$ is very flat, the CsPbBr_3 one has a set of minima offset from the origin³. This difference can, at least partly, be understood in terms of a closer-to-unity Goldschmidt tolerance factor (Eq. 5.1) in $\text{Cs}_2\text{AgBiBr}_6$ as compared to CsPbBr_3 .

As was discussed in the previous section, there are indications that the local atomic structure of the single Pb halide perovskites may be better described by a lower symmetry structure with tilted octahedra. This is commensurate with the existence of the deep minima offset from the cubic structure in their octahedral tilting PESs. The situation is different in $\text{Cs}_2\text{AgBiBr}_6$, where the PES is almost completely flat, which means that at temperatures comparable to room temperature, although there should be large anharmonic motion of the octahedra, the cubic tiltless structure should be the center of atomic oscillation for all relevant timescales.

With these considerations in mind, the lattice dynamics of the cubic structure in $\text{Cs}_2\text{AgBiBr}_6$ should be describable in a renormalized phonon picture. To this end I performed a set of AIMD simulations of $\text{Cs}_2\text{AgBiBr}_6$ for a range of temperatures and fitted a fourth order effective Hamiltonian in the framework of the TDEP method, as described in Section 4.2.2. The obtained spectral functions (Eq. 4.24) at 100 K and 300 K are shown in Fig. 5.3 (a), where we see that the unstable modes (Fig. 5.9 (c)) have been anharmonically stabilized. It is also clear that we have quite severe anharmonic broadening at room temperature (300 K), as evidenced by the highly diffuse modes around $\sim 2.2 - 3$ THz and the highest optical modes in the range $\sim 4.4 - 5$ THz. Fig. 5.3 (b) shows the temperature dependence of the square of the frequency of the soft octahedral tilting mode at the Γ point. I show both the "pure" TDEP case, i.e. the frequency obtained solely from the second order effective Hamiltonian, as well as the corresponding peaks in the spectral functions when using self energies $\Sigma_{\mathbf{q}\mathbf{s}}^{(3)}(\Omega)$ and $\Sigma_{\mathbf{q}\mathbf{s}}^{(3)}(\Omega) + \Sigma_{\mathbf{q}\mathbf{s}}^{(4)}$, respectively (cf. Section 4.2.1). It is seen that the fourth order, $\Sigma_{\mathbf{q}\mathbf{s}}^{(4)}$ correction is very significant and the full $\Sigma_{\mathbf{q}\mathbf{s}}^{(3)}(\Omega) + \Sigma_{\mathbf{q}\mathbf{s}}^{(4)}$ self energy yields a similar low temperature extrapolation as the pure TDEP case, while using only the $\Sigma_{\mathbf{q}\mathbf{s}}^{(3)}(\Omega)$ yields a significantly different result. The phonon collapse is thus predicted to happen at ~ 50 K, which agrees reasonably with the experimental transition temperature of ~ 122 K. The difference could, in principle, be partly related to the presence of defects in the experimental samples, but it is also well known that the precise frequencies of this type of soft optical modes are very sensitive to the computational setup, including cell

²Cs relaxation is included here, but the lattice vectors are kept fixed in their cubic state.

³As expected, of course, from the discussion in the previous section.

Figure 5.10: (a) Phonon spectral function, $S(\mathbf{q}, \Omega)$, of $\text{Cs}_2\text{AgBiBr}_6$ at 100 and 300 K. The solid discs at 300 K are Raman scattering results from Ref. [88]. (b) Frequency squared of the soft mode at the Γ -point with varying corrections, see text for details. The red and blue lines are second order polynomial fits, while the yellow line is merely a straight line to guide to the eye. The vertical black line indicates the experimental transition temperature [90]. Image from Paper III.

volume and XC-functional [91].

The fact that we find significant corrections originating from the fourth order *effective* IFCs deserve some further comment. Typically, with phonon-renormalization strategies based on "bare" IFCs, i.e. derivatives of the BO energy surface, such as the SCP approximation (Section 4.2.2), the effect of the bare fourth order IFCs are renormalized into the second order IFCs. Adding on top of this a $\Sigma_{\mathbf{q}s}^{(4)}$ correction obtained using the bare IFCs would thus not make sense. The TDEP case is different. Since the IFCs are fitted in a sequential fashion, the fourth order *effective* IFCs are fitted to describe the part of the forces that was not describable by the second and third order ones. Indeed, a large part of the correction from what would have been the *bare* fourth order IFCs, are already encoded into the second order *effective* IFCs. This implies that the *effective* fourth order IFCs largely contain information from higher-than-fourth order *bare* IFCs. The large correction that is seen for $\text{Cs}_2\text{AgBiBr}_6$ is thus a clear indicator of a very high degree of anharmonicity.

As it is now clear that $\text{Cs}_2\text{AgBiBr}_6$ is very anharmonic and is also very soft, its thermal conductivity, κ should be expected to be rather low. I have estimated κ through an iterative solution to the linearised phonon Boltzmann Transport Equation, as laid out in Section 4.2.3, including three-phonon and isotope scattering from the natural isotope-distribution, using the full temperature dependent IFCs. $\kappa(T)$ is shown in Fig. 5.11. The value of $\sim 0.33 \text{ Wm}^{-1}\text{K}^{-1}$ at 300 K puts it deep in the range of values normally refereed to as "ultra-low". It is also interesting to note that $\kappa(T)$ follows a non-standard temperature dependence $\sim T^{-0.5}$, different from the "standard" $\sim T^{-1}$.

This non-standard behaviour of $\kappa(T)$ is another indicator of high anharmonicity. Indeed, when thermal conductivity is evaluated using IFCs that are constant w.r.t. temperature, as is often done, the temperature dependence of $\kappa(T)$ comes solely from

Figure 5.11: Temperature dependence of the lattice thermal conductivity of $\text{Cs}_2\text{AgBiBr}_6$, evaluated using the full temperature dependent IFCs (blue circles) and using the 100 K IFCs (red squares). The inset shows the spectral thermal conductivity (right axis) and Cs partial DOS (right axis) at 300 K. Image from Paper III.

the phonon population numbers (Bose-Einstein distribution). One then typically (rigorously in the high-T limit) obtain a $\sim T^{-1}$ dependence. If the IFCs are instead temperature dependent, as they are in the TDEP case, $\kappa(T)$ depends on temperature through the three-phonon scattering phase space (due to temperature dependent frequencies), which together with phonon population and third order IFCs yields temperature dependent lifetimes, and through temperature dependent group-velocities. This may result in a range of different T-dependencies, but several other highly anharmonic systems have also recently been found to have slower than T^{-1} dependencies [92, 93].

5.4 Nuclear Quantum Effects on Structure and Bonding in Methylammonium Lead Iodide

Methylammonium lead iodide, $\text{CH}_3\text{NH}_3\text{PbI}_6$ or MAPi, is the champion solar-cell material, and by far the most well-studied member, of the lead halide perovskite family of materials. MAPi undergoes two structural phase transitions upon heating. Its low-temperature phase is orthorhombic (Fig. 5.12) with orientally ordered MA-molecules and the octahedra tilted (roughly $a^-a^-c^+$) and distorted. It transforms to a tetragonal phase, with octahedra tilted as $a^0a^0c^-$ and dynamically disordered MA, at ~ 165 K and then into a (on average) cubic phase at ~ 327 K [94].

From a first-principles materials modelling point-of-view MAPi is a highly non-trivial system to deal with. This is due to range of physical phenomena which are of relevance in MAPi, but not in conventional semiconductors. These include extreme anharmonicity, both of the inorganic PbI_6 octahedral framework and of the MA cation [95, 96], strong electron-phonon coupling [97, 98] and large spin-orbit coupling (SOC) [99].

One further aspect that has been very sparsely addressed, but the importance of which cannot be *a priori* ruled out, is the effect of nuclear quantum effects (NQE), in particular on the light nuclei that make up the MA cation. Indeed, NQEs on light nuclei and on hydrogen bonds are known to be complex and potentially very large [100,

Figure 5.12: Crystal structure of the low temperature orthorhombic phase of MAPI. The Pb and I atoms are colored black and purple, respectively and the C, N and H atoms of the MA molecule are black light-gray and beige, respectively. Image adapted from Paper IV.

101], which implies that the interactions between the MA cation and the inorganic framework, mediated primarily by a set of $\text{N-H} \cdots \text{I}$ hydrogen bonds, is potentially susceptible to large renormalization by NQEs.

In Paper IV I have investigate the nature of NQEs in MAPI using path integral molecular dynamics (PIMD) (cf. Section 4.4). As the MA molecules contain light elements and strong, high frequency, bonds the NQEs are expected to be large on the intra-molecular bonding and vibration. This is indeed the case, as can be seen in Fig. 5.13, which shows intra-MA radial distribution functions (RDFs) from simulations with classical and quantum nuclei in the orthorhombic phase at 100 K. Besides the expected significant broadening of the peaks for the quantum nuclei as compared to the classical ones, a few interesting features can be noticed. Firstly one can note a significant increase in the non-Gaussian appearance of the peaks for the quantum nuclei. This is particularly true for the nearest-neighbor peak in the N-H RDF, and is a result of the quantum nuclei exploring the PES farther away from the minima, around which the harmonic approximation is valid, than the classical nuclei.

These large intra-MA NQEs are expected and, since the MA contributions to the electronic structure of MAPI are located away from the band edges, perhaps not that interesting by themselves. The interesting question is instead what effects NQEs have on the interaction between the MA and the inorganic PbI_6 octahedral framework. Towards this end, I performed several simulations of the tetragonal phase with both classical and quantum nuclei. It was found that the reorientational dynamics of the MA cations is significantly faster for classical as compared to quantum nuclei, which seems to indicate a stronger MA- PbI_6 interaction when NQEs are included.

Furthermore, upon inspecting the angular distribution of the Pb-I vectors, I find a significantly more spread distribution for the classical nuclei, as shown in Fig. 5.14. Indeed, at 300 K the Pb-I angular distribution around the c axis has a single peak distribution for the classical nuclei, indicating that the system wants to transform away from the $a^0a^0c^-$ tilt configuration into the tiltless $a^0a^0a^0$ configuration. One should be very careful in comparing this transition to the experimental tetragonal-to-cubic transition. This due to the restrictions of a rather small and fixed supercell, and the limited time that can be covered in the simulations. In particular the fixed supercell shape might be overly restrictive in this regard, considering the experimental observations of

Figure 5.13: Intra-molecular radial distribution functions for the MA cation in the orthorhombic phase at 100 K, obtained from AIMD simulations using classical (blue lines) and quantum nuclei (red lines). Image from Paper IV.

local symmetry breaking in the cubic phase. What my results clearly show, however, is that NQEs potentially have a large effect on the transition temperature in MAPI.

A further caveat is in place. It has been demonstrated that properties of MAPI [102], in particular the reorientational motion of the MA molecules, depend quite strongly on the the employed XC-functional. This likely means that the nature of the NQEs also depend sensitively on the choice of XC-functional. Compared to the PBE+TS [103] (see Paper VII) description used here, the NQEs might be either larger or smaller if another XC-approximation is employed. This has implications when judging the suitability of a certain XC-functional against experimental results. Indeed, it might be that a certain one gives good agreement with experiment when NQEs are not included due to a cancellation of errors between the neglect of NQEs and the XC-approximation. When NQEs are properly included, another one might instead yield better results.

Figure 5.14: Angular density distribution of the Pb-I bond vectors. ϕ represents the magnitude of the out-of-phase tilt in the $a^0a^0c^-$ tilt pattern of the tetragonal phase. Image from Paper IV.

Dynamics and Phase Stability of Dynamically Disordered Solids

In this chapter I will discuss vibrational properties and phase stabilities in a particular set of solids that will be referred to as *dynamically disordered*. Such systems can roughly be said to be those that possess, in some form, a characteristic long-range order of crystalline solids, but where equilibrium atomic positions cannot be statically assigned to each atom. Evidently, some of the perovskite systems discussed in the last chapter fit into this category. I am in particular going to focus on two classes of such materials, the first are the so-called superionic solids [3], or superionics, which are solid materials with very high rates of ionic conductivity, the second is solids with rotationally disordered molecules, where MAPI, discussed in the previous chapter, could be taken as an example.

Superionic solids are considered for a range of technological applications. Obviously, the high ionic conductivity makes them promising solid state electrolytes in batteries and fuel cells [3, 104]. They have, however, also shown promise in other applications, including thermoelectrics [105], since the presence of extreme anharmonicity typically results in low thermal conductivities, and as mechanocaloric materials [5, 106, 107], since the superionic transition is typically associated with a large entropy change and can be tuned by an external stress field. The nature of the transitions to the superionic phases in these systems are often grouped into two classes [3]. In type-I superionics the process is a discontinuous solid-solid phase transformation, AgI being the prototypical example, while for type-II superionics the process is a continuous increase of ionic conductivity within a pre-existing phase, such as in fluorite, CaF_2 , and many other fluorite-structured materials.

A second clear example of dynamically disordered solids are those that contain molecular units that become rotationally disordered as temperature is increased. These are sometimes referred to as "plastic" or "orientationally-disordered" crystals. Typically, the center-of-mass of these molecular units can be thought of as occupying some particular crystallographic equilibrium positions, but the individual atoms of the molecule cannot. Clearly, the high-temperature phases of hybrid organic-inorganic perovskites discussed in the last chapter belong to this group. These materials are, similarly to the superionics, highly promising as mechanocaloric materials, [5, 108–110] since their transformations from low-temperature ordered phases to high-temperature

rotationally disordered phases are often sensitive to external pressure and accompanied by a large increase in entropy.

Among the main issues hindering the use of these materials in the applications I have mentioned is the limited stability of their dynamically disordered phases. Often, the window of stability starts at a temperature above the operational temperature in the application and is typically quite narrow. From a computational point-of-view, modelling these order to dynamical-disorder phase transformations is challenging. This is largely because they are governed by a much more violent energy-entropy competition than standard solid-solid phase transformations. Furthermore, due to the absence of well-defined static equilibrium positions in the dynamically disordered phase, the standard phonon picture (Section 4.2) is of limited utility. This chapter is going to focus on theoretical modelling of the mechanisms and the critical temperature of these phase-transformations in a few select model-systems of interest.

6.1 Finite-temperature Lattice Dynamics and Superionic Transition in Ceria

Ceria, CeO_2 , is a fluorite structured oxide that has been quite intensively studied in regards to its suitable properties for applications in e.g. catalysis and solid oxide fuel cells (SOFC) [111]. Doping ceria with trivalent rare-earth ions such as Gd^{3+} or Sm^{3+} introduces charge-compensating oxygen vacancies into the structure and quite fast diffusion of O^{2-} therefore occurs at elevated temperature.

Fluorite structured materials often have a type-II superionic transition at around 80 % of their melting temperature. The connection between a soft phonon-mode and the superionic transition in fluorite structured materials was first proposed by Boyer [112] for the prototype CaF_2 system. This optical mode has B_{1u} symmetry and its atomic displacement pattern corresponds to [100]-chains of anions moving along the [001] directions, with nearest-neighbor chains moving in opposite directions, as shown in Fig. 6.1 for CeO_2 . Since this displacement pattern correlates with the expected [100] direction of diffusion, and since it critically softens upon volume expansion at volumes in the neighbourhood of the equilibrium values around the superionic transition temperature, it has been connected to type-II superionic transitions in a host of fluorite structured materials [113–115]. However, since these types of soft modes are highly susceptible to anharmonic renormalization, especially at the high temperatures where superionic transitions takes place, frequencies obtained by the quasiharmonic approximation (QHA) should be analyzed with caution. This issue has been studied in Paper V.

Fig. 6.2 shows the temperature dependence of the E_u and B_{1u} modes at the X-point in the QHA and TDEP descriptions. We see that while the QHA predicts the expected collapse of the B_{1u} mode, this mode remains far from critically soft in the TDEP description. The interpretation must thus be that while the QHA frequencies do certainly reveal the soft nature of the underlying PES, and could as such be a suitable descriptor in screening for superionicity [116], they are likely rather far from the corresponding quasi-particle frequencies that would be probed by e.g. inelastic neutron scattering. These quasi-particles are, of course, susceptible to anharmonic renormalization and should thus be expected to correspond more closely to the TDEP frequencies.

Figure 6.1: Atomic displacements of the B_{1u} phonon mode at the X point in fluorite structured CeO_2 . Alternating (110) planes of the O ions move in opposite directions along the [001] direction. Green and red spheres represent Ce and O ions, respectively. The octahedral interstitial site is shown as a black sphere. Image adapted from Paper V.

Figure 6.2: Frequency of the B_{1u} (circles and solid lines) and E_u modes (diamonds and dashed lines) at the X point in CeO_2 , as calculated using TDEP (red and black) and QH (blue) vs temperature. The inset shows the QH phonon dispersion at a volume corresponding to ~ 2300 K. The vertical line at 2150 K corresponds to the superionic transition temperature, T_c . Image from Paper V.

6.2 Phase Stability of Dynamically Disordered Bi_2O_3 and Li_2C_2

The fact that the dynamically disordered solids that we treat in this chapter do not have well defined static equilibrium positions makes phonon based techniques difficult to apply. Hence, the phonon-thermodynamics techniques of Section 4.3.1 cannot be straightforwardly applied to investigate phase stabilities in these materials. This necessitates the use of more advanced free energy techniques. Using the "standard" thermodynamic integration (Eq. 4.54) is, for the same reason, more complicated than in dynamically ordered crystals.

In Papers VI and VII I lay out a somewhat different method to investigate phase stabilities in a subset of the dynamically disordered crystals. The basic observation is that many dynamically disordered phases have closely related (real or artificial) (meta)stable ordered variants that are related by simple homogeneous deformations. Indeed, the high-T superionic δ -phase of Bi_2O_3 is closely related to the metastable tetragonal β -phase [117], as illustrated in Fig. 6.3. Similarly, the high-T phase of Li_2C_2 , which has rotationally disordered C_2 dimers, can be simply connected to the low-T orthorhombic phase [118], as also displayed in Fig. 6.3.

Using this basic observation, it is then possible to derive an expression for the change in the free energy along such deformation paths, which can be evaluated through a series of AIMD simulations. Indeed, the general form of the differential of F for a rotationally invariant crystal was shown in Eq. (4.61), and is reproduced here,

$$dF(\{\mathbf{X}, \boldsymbol{\eta}\}, T) = -SdT + V(\mathbf{X})\boldsymbol{\tau} : d\boldsymbol{\eta}. \quad (6.1)$$

Integrating Eq. (6.1) at constant temperature, along with some straightforward algebraic manipulation (see Supplemental Information in Paper VI for details) yields the following general expression for the free energy change along a path parametrized by λ ,

$$\Delta F(\lambda) = \int_0^\lambda V(\lambda')\boldsymbol{\sigma}(\lambda')\mathbf{h}^{-T}(\lambda') : \frac{\partial \mathbf{h}(\lambda')}{\partial \lambda'} d\lambda', \quad (6.2)$$

where $\boldsymbol{\sigma}$ and $\mathbf{h}$ are as in Section 4.3.2, i.e. the Cauchy stress and the matrix with the supercell lattice vectors as columns, respectively.

Eq. (6.2) can now be used to calculate free energy differences between two phases as follows:

1. Find approximate zero stress configurations $\mathbf{h}(0)$ and $\mathbf{h}(1)$ corresponding to the two phases between which the free energy difference is to be calculated.
2. Set up a series of supercells $\mathbf{h}(\lambda)$ that connects these endpoints, the connection can be made in one or several separate steps. In the simplest case one may take a linear interpolation between the endpoints.
3. Run AIMD for these supercells to obtain $\boldsymbol{\sigma}(\lambda)$, and numerically perform the integral.

This provides the free energy difference and since the internal energy is readily available from AIMD simulations, the entropy difference can also be extracted. Additionally, an upper bound to the free-energy barrier is obtained.

Figure 6.3: Illustrations of deformation paths between ordered and dynamically disordered phases. (Top row) Deformation path from the tetragonal β -phase to the superionic δ -phase of Bi_2O_3 . (Bottom row) Deformation path from the low-temperature ordered orthorhombic phase to the dynamically disordered high-temperature cubic phase of Li_2C_2 .

6.2.1 Phase Stability of Superionic δ -Bi₂O₃

The high temperature δ -phase of Bi₂O₃ is the the fastest know solid oxide-ion conductor [119], and could thus be extremely suitable as the electrolyte in a solid oxide fuel-cell. Unfortunately, this superionic phase is only stable from ~ 1003 K up to the melting point at ~ 1100 K, and a lot of work, including doping [117] and thin-film growth [120], has been done in order to attempt to stabilize it down to room temperature while retaining the high ionic conductivity.

At ambient conditions Bi₂O₃ crystallizes in the monoclinic α -phase, which remains stable up to the α - δ phase transformation at 1003 K. Upon cooling down from the δ -phase, Bi₂O₃ typically does not return to the α phase, but instead transforms into the tetragonal β -phase or the cubic γ -phase [117]. The cubic δ -phase can be thought of, on average, as a defective fluorite structure, where 25 % of the O-sites are vacant and the metastable β -phase is an ordered variant of the δ -phase, with O vacancies ordered as displayed in Fig. 6.5 (a).

In paper VI I have investigated the phase stability of δ -Bi₂O₃ using the stress-strain TI methodology. The integration from β to δ is carried out in two steps: Starting from the β structure, the c axis is first contracted towards its value in the δ -phase. In the second step, the a and b axis are expanded to their values in the δ -phase, where $a/c = \sqrt{2}$, which corresponds to a tetragonal representation of the cubic phase. This splitting of the path in two is done because it is highly unlikely that the disorder, that should appear at some point on the full deformation path, will set in as a results of compression of the ordered β -phase, i.e. we should expect it to set in on the second part of the deformation path.

At 900 K, the stress behaves as expected on this first part of the deformation path, showing an approximately linear decrease in σ_{33} , yielding a quadratic increase in the free-energy, see Fig. 6.5 (c) and (d). On the second part of the deformation path, we find the onset of diffusional disorder among the O ions at the first point, starting from around ~ 35 ps into the simulation. The diffusional disorder of the O ions is seen through the behavior of the stress. Indeed, upon this expansion of the a and b axes, we find a decrease of σ_{11} and σ_{22} , rather than the expected increase, indicating that the presence of the O ion disorder makes it thermodynamically preferable to further expand a and b . A snapshot of atomic positions and velocities from this point is used as the starting point for the subsequent simulations. I also go back and perform an additional ~ 110 ps of simulation time at the previous point, to check that the disorder does not, in fact, set in earlier along the path.

In the end, we see that this disorder of the O ions explicitly produces a minimum in free energy in the δ -phase, located ~ 6 meV/f.u. lower than the β -phase at 900 K, with a small upper-bound to the free energy barrier of ~ 2 meV/f.u. . Fig. 1(e) shows the change in internal energy U along the deformation path where it is seen that, at the point where the disorder sets in, there is a large increase in U because the system is breaking out of its low energy ordering. However, as pointed out above there is a simultaneous decrease in F , indicating an even larger increase in entropy, due to the disorder among the O ions.

Once the free energy difference between the β - and δ -phases has been obtained, this can be connected to the low temperature thermodynamically stable α -phase by "conventional" free energy techniques. We calculate the β and α free energies using the TDEP technique, and obtain the temperature dependence of the δ phase free energy using a temperature-energy thermodynamic integration.

Figure 6.5: Illustration of the deformation from the ordered β (a) to the disordered δ (b) phases of Bi_2O_3 . (c) Diagonal components of the Cauchy stress on the deformation path at 900 K. Free energy (d) and internal energy (e) changes along the deformation path. Image from Paper VI.

The obtained α - δ transition temperature is 1010 K, which agrees very well with the experimental result of 1003 K. This very good agreement is clearly partly fortuitous considering the inherent approximations in the simulations, including the XC-functional, finite simulation time, the finite- and defect-free supercells and the TDEP approximation. However, our obtained transition enthalpy of ~ 0.32 eV/f.u. also agrees well with the experimental value of ~ 0.31 eV/f.u. [121], which indicates that our methodology accurately captures the violent energy-entropy competition that governs the phase stability of superionic solids.

6.2.2 Order to Dynamic-Disorder Transformation in Li_2C_2

Li_2C_2 offers a very "clean" example of a transition from a state of order to one of rotational molecular disorder [118]. At ambient conditions Li_2C_2 is found in an orthorhombic phase with C_2 dimers ordered along one crystallographic axis, as illustrated in Fig. 6.6. Upon heating, it transforms into a cubic phase where the C_2 dimers are dynamically disordered with preferential alignment along the $[110]$ directions, as illustrated in Fig. 6.6.

In Paper VII, I performed stress-strain TIs between these two phase at 600 and 650 K, results are shown in Fig. 6.7. Similarly to the Bi_2O_3 case, the stabilizing entropy is captured by the behaviour of the stress on the deformation path. This can most clearly be seen for the σ_{yy} , where the onset of the C_2 dimer disorder causes a switch from decreasing to increasing behaviour along the deformation path. It is interesting to note that both phases appear to be local minima on the PES, both above and below the thermodynamic transformation temperature, which we can estimate to be 611 K. This agrees with the experimental observation of coexistence between the two phases over a relatively broad temperature range [118]. It is not clear exactly where the experimental thermodynamic transition temperature is, but the first appearance of an XRD reflection corresponding to the high temperature phase upon heating is at around 693 K [118], so our theoretical estimate for the thermodynamic transition temperature is likely somewhat underestimated, although in fair agreement, considering the inherent approximations. It thus appears that the stress-strain TI methodology is suitable to study phase transitions in systems with rotationally disordered molecules.

The energy difference between the orthorhombic and cubic phases are ~ 82 and 71 meV/f.u. at 600 and 650 K, respectively. This reveals the interesting fact that energy difference between the two phases, in fact, decreases with increasing temperature, which will be discussed further in the next section.

6.2.3 On the Partitioning and Nature of the Entropy of Dynamically Disordered solids

An interesting question is how one should conceptualize the entropy of these dynamically disordered solids. It is quite common in the context of solid materials to think of the total entropy as being partitioned into a vibrational and a configurational part, i.e., to write $S_{\text{tot}} = S_{\text{vib.}} + S_{\text{conf.}}$. There is, however, nothing fundamental about this partitioning, it is made out of conceptual and computational convenience. The model is then that there exists a set of minima on the underlying PES that accessible to the system and is the source of $S_{\text{conf.}}$. Each minima has a well-defined contribution to $S_{\text{vib.}}$, and "jumps" between these minima are rare with respect to the timescales inherent

Figure 6.6: Illustration of the deformation path (parametrized by λ) from the orthorhombic (left) and the disordered cubic (right) phase with the supercells used in this work. Li and C atoms are colored green and brown, respectively. In the cubic phase a snapshot of the positions of C atoms are taken from an AIMD simulation, in order to illustrate the rotational disorder of the C_2 dimers, while the Li atoms are in displayed in their high-symmetry postitions. The conventional orthorhombic unit cell is illustrated by filled black lines. The Cartesian reference coordinate system, $\{\mathbf{x}, \mathbf{y}, \mathbf{z}\}$, used in our simulations is indicated by black vectors and letters, while the coordinate system, $\{\mathbf{x}', \mathbf{y}', \mathbf{z}'\}$, aligned with the conventional orthorhombic cell is displayed in red. $\mathbf{z}$ and $\mathbf{z}'$ are collinear and directed out of the figure. The spheres at the bottom represent the angular distribution of the C_2 dimers over AIMD simulations at 600 K. Bright colors and dark colors correspond to high density and low density, respectively. Image from Paper VII.

Figure 6.7: Results of the stress-strain thermodynamic integration on the deformation path from the ordered orthorhombic phase at $\lambda = 0$ to the dynamically disordered cubic phase at $\lambda = 1$. The top panel shows the free energy change along the deformation path at 600 K (solid blue line) and 650 K (dashed red line). Middle and lower panel shows the diagonal components of the Cauchy stress in the coordinate system $\{\mathbf{x}', \mathbf{y}', \mathbf{z}'\}$ aligned with the conventional orthorhombic unit cell, at 600 and 650 K, respectively. Image from Paper VII.

to determining $S_{vib.}$. The implicit underlying assumption is thus that $S_{vib.}$ and $S_{conf.}$ are associated with significantly different timescales. This is certainly the way the entropy of an alloy is typically conceptualized. For "standard" alloys, the timescale associated with $S_{conf.}$ is that of atomic diffusion, which, in most systems, is many orders-of-magnitude larger than that associated with $S_{vib.}$, and the entropy-partitioning is therefore appropriate. However, for systems where the timescales associated with what would commonly be conceptualized as vibrational and configurational entropies start to overlap, there is, formally, no clear physical basis for partitioning the entropy in this way.

In order to check for this, one should compare a characteristic "hopping-time", i.e. the average time the system stays in one minima, to the vibrational period of a characteristic phonon mode in the system, or more stringently, to a characteristic phonon-lifetime. These two characteristic times should be significantly different for the partitioning to be appropriate. This is certainly not true for the Bi_2O_3 and Li_2C_2 systems described above. In fact, an implicit assumption in the TI methodology is that the timescale that can be simulated is long enough to capture the relevant entropy contribution associated with the dynamic disorder. If the different timescales would be so vastly different as they are in the "standard" alloy example, the TI methodology would clearly not capture the "configurational" entropy part.

It is furthermore interesting to think more closely about what the mechanism of stabilization for these dynamically disordered phases actually is. It is, of course, clear that the reason that these phases appear at high T is that they possess a much larger entropy than other, ordered, phases. However, looking for instance at the energy dif-

ference between the ordered and dynamically disordered phases of Li₂C₂, they are ~ 82 and 71 meV/f.u. at 600 and 650 K, respectively. This reveals the interesting fact that the energy difference between the two phases, in fact, decreases with increasing temperature, which, together with the known free energy difference further shows, perhaps counter-intuitively, that the entropy difference is also decreasing with temperature, albeit more slowly.

This implies that the proper way of conceptualizing the appearance of the dynamically disordered phase in Li₂C₂ upon heating is that it appears once the energy difference between the phases decreases enough so that its free energy drops below that of the ordered phase. Thus it is, at least in the case of Li₂C₂, not correct to think of the entropy in dynamically disordered phase as rapidly growing until it becomes large enough to induce a phase transformation. This can be understood as follows: the entropy associated with the dynamical disorder is required to "mechanically" stabilize (i.e. to produce a free energy local minimum) the dynamically disordered phase in the first place. When this disorder has "entered", its associated entropy does not grow rapidly with temperature. Instead, once the energy of the competing, ordered, phase increases enough in energy as a result of the increased temperature, the dynamically disordered phase will be stabilized.

CHAPTER 7

Conclusion and Outlook

This thesis has dealt with theoretical studies of solid materials that are highly anharmonic. I have focused on two classes, not mutually exclusive, of such systems. The first are systems with perovskite-related crystal structures, which are notoriously complicated, in particular in relation to their anharmonic dynamics. I have attempted to, at least in part, rationalize the experimentally observed differences in average and local atomic structures of the high temperature phases in select oxide and halide perovskites. I have further studied the anharmonic lattice dynamics in the lead-free halide double perovskite $\text{Cs}_2\text{AgBiBr}_6$, where I rationalize the experimentally observed phase transformation and find that the anharmonicity aids in producing ultra-low thermal conductivity. Next, I showed that the influence of the quantum nature of the nuclei is potentially of high relevance for important properties of the champion photovoltaic lead halide perovskite, methylammonium lead iodide (MAPI).

The second part of the thesis dealt with dynamically disordered solids. These are systems which possess some type of long-range order, as is characteristic of a crystalline solid, yet all atoms in the system cannot be statically assigned equilibrium positions. The two subclasses of interest were the superionics, i.e. solids with very high rates of ionic diffusion, and solids that contain rotationally disordered molecules. The main focus was the mechanism, and critical temperature, of the order to dynamical-disorder phase transformations in these systems. A select few model systems of interest was treated. Firstly, I critically investigated the proposed connection between a particular phonon-mode and the type-II superionic transition in fluorite-structured CeO_2 , done on the basis of quasi-harmonic phonon calculations. I show that anharmonic effects are clearly of relevance.

I then lay out a method to investigate the phase stability of certain dynamically disordered phases. The method is based on the observation that the dynamically disordered phases can often be connected to (meta)stable ordered variants by simple deformation paths. The free energy can then be obtained by a stress-strain thermodynamic integration along such deformation paths. The method is applied to superionic Bi_2O_3 and rotationally disordered Li_2C_2 , and results in satisfactory comparison to experiments are obtained.

The underlying motivation for the materials studied in this thesis have mostly come

from the field of energy materials, be it the halide perovskites, highly relevant for a host of optoelectronic applications or superionic solids, envisioned as solid state electrolytes in batteries and fuel cells. I hope to have shown clearly that, in this field in particular, accurate modelling beyond some of the commonly employed approximations, including harmonic lattice dynamics (also with simple perturbative additions), the assumption of equal local and average atomic structure, or the classical nuclei approximation, will often be required if predictive accuracy is to be obtained.

7.1 Outlook and Future work

It is evident that, as the requirements on proposed materials for future technological applications becomes more and more stringent, these materials also become increasingly more complex. This, in turn, puts increasingly high requirements on the accuracy of the theoretical and computational models used to understand and predict relevant materials. To eventually reach such accuracy entails, when necessary, to abandon overly simplified theoretical models, such as those mentioned above, that may have been highly effective and successful for simpler materials.

In this thesis I have, of course, only scratched the surface in respect to performing calculations beyond these approximations. In some cases, the main purpose have not necessarily been to make realistic prediction, but rather to point out the deficiency of one these simplified models. A vast amount of work clearly needs to be done in all areas touched in the thesis for anything close to full understanding.

In some general sense, this thesis has dealt with the *understanding* of how and why certain physical phenomena, associated with high degrees of anharmonicity, appear, and there is as mentioned a virtually unlimited amount of work to do in this regard. However, a perhaps in some sense more interesting, and certainly more ambitious, line of research is to attempt to reach a good understanding of how properties related to high anharmonicity can be controlled and tuned towards a desired behaviour for technological applications.

When it comes to precise future lines of research, there are many directions to build from on the work performed in this thesis. Indeed, in connection to each of the topics touched, there are interesting open questions. In the interest of brevity I will mention one particularly interesting topic, which combines many of the challenges presented in this thesis. This is the study of rotationally disordered molecular crystals in regards to their use as barocaloric materials in future solid-state cooling devices [5]. Such a theoretical study would require predicting the temperature and pressure dependence of an order to dynamical-disorder phase transformation, which as should be clear from the present thesis is highly challenging. Furthermore, these systems contain many light elements and the phase transformation should, for the material to be useful, occur somewhere around room temperature. NQEs are thus likely to be substantial. In particular, the effect of NQEs on the phase transformation is an interesting question. As should be evident, this is a highly ambitious and challenging line of research, but as it combines many of the interesting issues raised in this thesis, also very exciting.

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CHAPTER 8

List of Included Publications and my Contributions

- [I] **Nature of the Octahedral Tilting Phase Transitions in Perovskites: A Case Study of CaMnO_3**
Johan Klarbring and Sergei I. Simak
Physical Review B **97**, 024108 (2018).
I conceived the project, performed the calculations and wrote the majority of the manuscript.
- [II] **Low-Energy Paths for Octahedral Tilting in Inorganic Halide Perovskites**
Johan Klarbring
Physical Review B **99** 104105 (2019).
I did everything.
- [III] **Anharmonicity and Ultra-Low Thermal Conductivity in Lead-Free Halide Double Perovskites**
Johan Klarbring, Olle Hellman, Igor A. Abrikosov and Sergei I. Simak
Submitted
I conceived the project, performed the calculations and wrote the majority of the manuscript.
- [IV] **Impact of Nuclear quantum effects on the structure and bonding of $\text{CH}_3\text{NH}_3\text{PbI}_3$**
Johan Klarbring, Sergei I. Simak and Olle Hellman
In Manuscript
I jointly conceived the project, performed the calculations and wrote the majority of the manuscript.
- [V] **Finite temperature lattice dynamics and superionic transition in ceria from first-principles**
Johan Klarbring, Natalia V. Skorodumova, and Sergei I. Simak
Physical Review B **97**, 104309 (2018)
I jointly conceived the project, performed the calculations and wrote the majority of the manuscript.

- [VI] **Phase Stability of Dynamically Disordered Solids from First Principles**
Johan Klarbring and Sergei I. Simak
Physical Review Letters **121**, 225702 (2018).

I jointly conceived the project, did the theoretical work, performed the calculations and wrote the majority of the manuscript.

- [VII] **Ab initio Determination of Phase Stabilities of Dynamically Disordered Solids: rotational C_2 disorder in Li_2C_2**
Johan Klarbring, Stanislav Filippov, Ulrich Häussermann and Sergei I. Simak
In Manuscript

I conceived the project, performed the calculations and wrote the majority of the manuscript.

CHAPTER 9

Related, not included publications

- [1] **Ionic conductivity in Gd-doped CeO₂: Ab initio color-diffusion nonequilibrium molecular dynamics study**
Johan O Nilsson, Olga Yu Vekilova, Olle Hellman, Johan Klarbring, Sergei I Simak and Natalia V Skorodumova
Physical Review B **93**, 024102 (2016).
- [2] **Ionic conductivity in Sm-doped ceria from first-principles non-equilibrium molecular dynamics**
Johan Klarbring, Olga Yu Vekilova, Johan O Nilsson, Natalia V Skorodumova and Sergei I Simak
Solid State Ionics **296**, 47-53, (2016).
- [3] **Superioniclike diffusion in an elemental crystal: bcc titanium**
Davide G. Sangiovanni, Johan Klarbring, Daria Smirnova, Natalia V. Skripnyak, Davide Gambino, Matous Mrovec, Sergei I. Simak and Igor A. Abrikosov
Physical Review Letters **123**, 105501, (2019).
- [4] **Temperature-induced phase transition and Li self-diffusion in Li₂C₂: A first-principles study**
Stanislav Filippov, Johan Klarbring, Ulrich Häussermann, Sergei I Simak
Physical Review Materials **3**, 023602, (2019).
- [5] **Thermochromic Lead-Free Halide Double Perovskites**
Weihua Ning, Xin-Gang Zhao, Johan Klarbring, Sai Bai, Fuxiang Ji, Feng Wang, Sergei I Simak, Youtian Tao, Xiao-Ming Ren, Lijun Zhang, Wei Huang, Igor A Abrikosov and Feng Gao
Advanced Functional Materials **29**, 1807375, (2019).

- [6] **Unraveling Hidden Mg–Mn–H Phase Relations at High Pressures and Temperatures by in Situ Synchrotron Diffraction**
Kristina Spektor, Wilson A Crichton, Sumit Konar, Stanislav Filippov, Johan Klarbring, Sergei I Simak, Ulrich Häussermann
Inorganic chemistry **57**,1614-1622, (2018).
- [7] **Analysis of Dihydrogen Bonding in Ammonium Borohydride**
Stanislav Filippov, Jakob B Grinderslev, Mikael S Andersson, Jeff Armstrong, Maths Karlsson, Torben R Jensen, Johan Klarbring, Sergei I Simak and Ulrich Häussermann
The Journal of Physical Chemistry C **123**, 28631-28639, (2019).
- [8] **Na–Ni–H Phase Formation at High Pressures and High Temperatures: Hydrido Complexes $[\text{NiH}_5]^{3-}$ Versus the Perovskite NaNiH_3**
Stanislav Filippov, Jakob B Grinderslev, Mikael S Andersson, Jeff Armstrong, Maths Karlsson, Torben R Jensen, Johan Klarbring, Sergei I Simak and Ulrich Häussermann
ACS Omega **2020**
- [9] **The effects of microstructure, Nb content and secondary Ruddlesden–Popper phase on thermoelectric properties in perovskite $\text{CaMn}_{1-x}\text{Nb}_x\text{O}_3$ ($x=0-0.10$) thin films**
E Ekström, A le Febvrier, F Bourgeois, B Lundqvist, J Palisaitis, PO Å Persson, O Caballero-Calero, MS Martín-González, J Klarbring, SI Simak, F Eriksson, B Paul, P Eklund
RSC Advances **10**, 7918-7926, (2020)

CHAPTER 10

Papers

Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

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