Vibrations in solids

From first principles lattice dynamics to high temperature phase stability

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To my family

Abstract

In this thesis I introduce a new method for calculating the temperature dependent vibrational contribution to the free energy of a substitutionally disordered alloy that accounts for anharmonicity at high temperatures. This method exploits the underlying crystal symmetries in an alloy to make the calculations tractable. The validity of this approach is demonstrated by constructing the phase diagram via direct minimization of the Gibbs free energy of a notoriously awkward and technologically important system, $\text{Ti}_{1-x}\text{Al}_x\text{N}$. The vibrational entropy including anharmonic effects is shown to be large and comparable to the configurational entropy at high temperatures, and with its inclusion, the theoretical miscibility gap of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ is reduced from 6560 K to 2860 K, in line with atom probe experiments. A similar treatment of $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$ alloys suggests that mass disorder has a minimal effect on phase stability compared with chemical ordering. My method is also capable of demonstrating that $\text{Hf}_{1-x}\text{Al}_x\text{N}$, which is dynamically unstable at room temperature, is stabilised at high temperatures. Moreover I develop a new method of computing temperature dependent elastic constants for alloys from their phonon spectra, and show that for $\text{Ti}_{1-x}\text{Al}_x\text{N}$, the elastic anisotropy is found to increase with temperature, helping to explain the spinodal decomposition.

The effects of lattice dynamics on phase stability, mechanical, magnetic and transport properties on other materials are also examined. Four specific systems are discussed in detail. Firstly, in the case of CrN, lattice vibrations are shown to decrease the antiferromagnetic to paramagnetic phase transition temperature from 500 K to 380 K, in line with experimental evidence. Secondly, a temperature/pressure induced phase transition in AlN becomes much more facile than in the quasi-harmonic approximation, and the thermal conductivity of the rocksalt phase is shown to be much lower than that of the wurtzite phase, as a result of the increased anharmonicity in the rocksalt structure. Thirdly, the temperature dependence of elastic constants of TiN becomes more isotropic as the temperature increases. Finally, iron carbides are evaluated as potentially important phases at the Earth's core; specifically, calculating the Gibbs free energy of a recently discovered orthorhombic phase of Fe_7C_3 demonstrates that it is not stable relative to the known hexagonal phase at extreme pressure and temperatures.

Popular science summary

Solid materials can be described using a simple mathematical model from the theory of lattice dynamics. In a solid, atoms are arranged in a regular and repeating structure (a lattice), and the forces between them can essentially be modelled as springs. Despite the simplicity of this model, it is possible to derive a surprising amount of information on materials from it. One can determine which arrangements of atoms, or phases, form the stable microscopic structures that we encounter in the real world, their mechanical properties, including their compressibility, elasticity, how fast sound waves travel through them and how they behave as the temperature is increased. For example, such calculations can be compared against seismological (sound wave) data to determine the composition of the Earth's core.

By increasing the complexity of this model it is also possible to predict how solid materials behave at very high temperatures. In this thesis, I apply and extend these methods such that they can be used to model disordered materials called alloys, or solids in which a number of different elements are randomly distributed across the lattice. I use this new method to predict the properties of several materials, including titanium aluminium nitride alloy, which is used in hard coatings for cutting tools. I use lattice dynamics to explain the unique structural change that this alloy undergoes at high temperatures, causing it to harden.

Svensk sammanfattning

I denna avhandling introducerar jag en ny metod för att beräkna de temperaturberoende vibrationernas bidrag till den fria energin för oordnade legeringar, vilket kan förklara anharmoniska effekter vid höga temperaturer. För att göra beräkningarna mer lätthanterliga utnyttjar den här metoden den inneboende strukturella symmetrin för kristaller i en legering. Hur lämpligt det här tillvägagångssättet är visas genom att konstruera ett fasdiagram genom en direkt minimering av Gibbs fria energi, vilket görs för ett notoriskt besvärligt (men teknologiskt viktigt) system, nämligen $Ti_{1-x}Al_xN$. Jag visar att vibrationsentropin, inkluderat de anharmoniska effekterna, är stor och jämförbar med konfigurationsentropin vid höga temperaturer. Vidare visar jag att man, genom att inkludera dem, kan reducera $Ti_{1-x}Al_xN$ s teoretiska löslighetslucka från 6560 K till 2860 K, i linje med de experiment som gjorts med atomsondstomografi. Genom att behandla legeringarna $Zr_{1-x}Al_xN$ och $Hf_{1-x}Al_xN$ på samma sätt framstår det som troligt att en oordning i massan har en minimal effekt på fasttemperaturen jämfört med en kemisk sammansättning. Min metod kan även visa att $Hf_{1-x}Al_xN$, som är instabil vid rumstemperatur, stabiliseras vid höga temperaturer. Dessutom har jag utvecklat en ny metod för att beräkna de temperaturberoende elastiska konstanterna för legeringar utifrån deras fononspektrum, och visar detta för $Ti_{1-x}Al_xN$. Den elastiska anisotropin visas öka avhängigt av temperaturen, vilket förklarar det spinodala sönderfallet.

Vidare undersöks gitterdynamikens effekt på andra materials fastabilitet, samt deras mekaniska, magnetiska och transportegenskaper. Fyra specifika system diskuteras i detalj. Den här studien visar, för det första, att vibrationerna i gittret för CrN sänker övergångstemperaturen mellan den antiferromagnetiska och paramagnetiska fasen från 500 K till 380 K, vilket överensstämmer med existerande experimentella bevis. För det andra visar den att en fasövergång inducerad av temperatur eller tryck i AlN blir betydligt smidigare än i den kvasiharmoniska approximeringen, och att värmeledningsförmågan i bergsaltsfasen blir betydligt lägre som ett resultat av den ökade anharmoniciteten i bergsaltsstrukturen. För den tredje blir temperaturberoendet av TiNs elastiska konstanter mer isotropisk när temperaturen ökar. Slutligen utvärderas järnkarbider som potentiellt viktiga faser i jordkärnan; mer specifikt visas den, genom att beräkna Gibbs fria energi för en nyligen upptäckt ortorombisk fas av Fe_7C_3 , inte vara stabil relativ till den redan kända hexagonala fasen vid tryck och temperatur på extrema nivåer.

Populärvetenskaplig sammanfattning

Egenskaperna för fasta material kan undersökas genom att använda en mycket enkel matematisk modell som beskrivs inom gitterdynamik. I ett fast material ordnar sig atomerna i en regelbunden och repetitiv struktur (ett gitter), och krafterna mellan dem kan i hög grad modelleras som fjädrar. Trots att den här modellen är enkel kan den erbjuda en förvånande mängd information om olika material. Det är till exempel möjligt att avgöra vilken ordning av atomer, eller vilka faser, som formar den stabila mikroskopiska struktur som vi möter i den verkliga världen. Det är också möjligt att bedöma deras mekaniska egenskaper, inklusive deras volymändring vid tryck, elasticitet, hur snabbt ljudvågor färdas genom dem, och hur de påverkas när temperaturen höjs.

Genom att göra den här modellen mer komplex är det också möjligt att förutsäga hur fasta material beter sig vid mycket höga temperaturer. I den här avhandlingen använder jag mig av modeller från gitterdynamik som en metod för att undersöka material. Den metoden tillämpar jag, och utvecklar, så att de kan användas för att modellera oordnade material som legeringar, eller fasta material där ett antal olika element är slumpmässigt fördelade över gittret. Jag använder den här nya metoden för att förutsäga egenskaperna för flera material, bland annat legeringen titanaluminiumnitrid, som används i hårda skikt för skärverktyg. Genom att använda gitterdynamik kan jag förklara den unika strukturella förändringen i den här legeringen vid höga temperaturer, som får den att hårdna.

Zusammenfassung

In der vorliegenden Arbeit stelle ich eine neu entwickelte Methode zur Berechnung der temperaturabhängigen Vibrationsbeiträge zur freien Energie von ungeordneten Legierungen unter Berücksichtigung nicht-harmonischen Verhaltens bei hohen Temperaturen vor. Diese Methode nutzt bei der Berechnung die in der jeweiligen Legierung vorhandenen Kristallsymmetrien aus. Die Gültigkeit dieses Ansatzes wird durch die Konstruktion des Phasendiagramms des technologisch wichtigen komplexen Systems $Ti_{1-x}Al_xN$ unter direkter Minimierung der freien Gibbs Energie gezeigt. Es zeigt sich, dass die Vibrationsentropie durch Berücksichtigung nicht-harmonischer Effekte in ihrer Größe vergleichbar der Konfigurationsentropie bei hohen Temperaturen ist, und dass durch ihre Miteinbeziehung die theoretische Mischungslücke von 6560 K auf 2860 K reduziert wird, in Einklang mit experimentellen Atomsonden Messungen. Vergleichbares Anwenden der Methode auf die Legierungen $Zr_{1-x}Al_xN$ und $Hf_{1-x}Al_xN$ zeigt, dass eine Unordnung der atomaren Masse im Vergleich zu chemischer Unordnung nur einen minimalen Effekt auf die Stabilität der Phase hat.

Die von mir entwickelte Methode ist des Weiteren im Stande zu zeigen, dass $Hf_{1-x}Al_xN$ (dynamisch instabil bei Raumtemperatur) sich bei hohen Temperaturen stabilisiert. Weiterhin wurde eine neue Methode zur Berechnung von temperaturabhängigen elastischen Konstanten aus Phonon Spektren von Legierungen entwickelt und gezeigt, dass für $Ti_{1-x}Al_xN$ die elastische Anisotropie mit der Temperatur ansteigt und so die spinodale Entmischung erklärt wird. Die Effekte von Gitterdynamik auf Phasenstabilität, mechanische-, magnetische- und Transport Eigenschaften werden zusätzlich für vier spezifische Systeme im Detail untersucht, und es wird gezeigt, dass

- in Einklang mit experimentellen Ergebnissen die Gitterschwingungen in CrN die Temperatur des Phasenüberganges von antiferro- magnetischer- zu paramagnetischer Phase von 500 K auf 380 K reduziert;
- mit der hier vorgestellten Methode ein Druck/Temperatur induzierter Phasenübergang in AlN müheloser beschrieben werden kann als in der quasiperiodischen Näherung. Weiterhin wird gezeigt dass die thermische Leitfähigkeit in AlN als Resultat aus erhöhter nicht-Harmonizität in der NaCl-artigen Gitterstruktur herabgesetzt wird;
- die Temperaturabhängigkeit der elastischen Konstanten von TiN mit steigender Temperatur mehr und mehr isotrop wird;
- die mit der vorgestellten Methode berechnete freie Gibbs Energie der kürzlich entdeckten orthorhombischen Phase Fe_7C_3 nahelegt, dass sie gegenüber der bekannten hexagonalen Phase nicht stabil ist.

Preface

In this thesis I have summarized the results of my doctoral studies carried out in Nanostructured Materials division at the Department of Physics, Chemistry and Biology at Linköping University (Sweden) and the Functional Materials division at the Department of Materials Science and Engineering at Saarland University in Saarbrücken (Germany) between 2011 and 2015.

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Nina Shulumba
Linköping, December 2015

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NOTATION

notation

$a()$ function

a_i component i of vector $\mathbf{a}$

$a[]$ functional

$\{a\}$ set of all a

$\hat{a}$ operator

$\mathbf{a}$ vector

constants

Z atomic number

$\hbar$ reduced Planck constant

e electron charge

k_B Boltzmann constant

coordinates

$\mathbf{r}$ Cartesian coordinate

$\mathbf{R}$ lattice vector

$\mathbf{u}$ displacement from equilibrium position

$\mathbf{p}$ momentum

$\mathbf{f}$ force

masses

m_e electron rest mass

m mass of atom

operators

$\hat{H}$ Hamiltonian operator $\hat{H} = \hat{T} + V$

$\hat{T}_e$ electron kinetic energy operator

$\hat{T}_n$ nuclear kinetic energy operator

$\hat{V}_{ee}$ electron Coulomb interaction

$\hat{V}_{en}$ electron-nucleus Coulomb interaction

$\hat{V}_{nn}$ nuclear Coulomb interaction

phonon formalism

ω angular frequency

$\mathbf{G}$ reciprocal lattice vector

ϵ phonon eigenvector

$\mathbf{k}$ electron wave vector

$\mathbf{q}$ phonon wave vector

$\bar{n}$ Bose-Einstein distribution function

potentials

V_H Hartree potential

V_{eff} effective potential

V_{ext} external potential

thermodynamics

F Helmholtz free energy

G Gibbs free energy

T temperature

Λ thermal De Broglie wavelength

β thermodynamic beta

$\mathcal{Z}$ partition function

wavefunctions

Ψ many body wavefunction

n electron density

ABBREVIATIONS

AIMD	<i>ab initio</i> molecular dynamics
DFT	density functional theory
DLM-MD	disordered local moments molecular dynamics
HA	harmonic approximation
QHA	quasiharmonic approximation
SIFC-TDEP	symmetry imposed force constants temperature dependent effective potential method
SQS	special quasirandom structure
TDEP	temperature dependent effective potential method
UP-TILD	upsampled thermodynamic integration using Langevin dynamics

Nothing is impossible. Not if you
can imagine it. That's what being a
scientist is all about.

— Professor Hubert Farnsworth

No, that's what being a magical elf
is all about.

— Cubert Farnsworth

INTRODUCTION

First-principles computations have proven to be an invaluable tool in the design and characterisation of physically and technologically important materials. The physical properties of experimentally synthesised materials can be explained at the atomic level, and moreover, such computations give us the power to predict properties and stability even under extreme conditions of temperature and pressure, inaccessible to experiments. However, there are significant shortcomings in the existing methods. There is a tendency in the literature to rely on “static” calculations, i.e. calculations that neglect the impact of atomic vibrations, and thus the effect of temperature. Even when vibrations are included, accuracy is generally limited at high temperatures by the level of approximation used. In the harmonic approximation, the potential energy of the lattice is truncated as a second order Taylor expansion, which means that it only holds when the potential is approximately quadratic; this is not the case for anharmonic materials at any temperature. The quasiharmonic approximation includes the effects of thermal expansion, but is subject to the same failures.

Fortunately, it is possible to accurately and efficiently include the effects of anharmonicity using the temperature dependent effective potential method (TDEP).^{1,2} However, the precise effects of anharmonicity remain unclear. How is it affected by temperature? What is its relationship to chemical and mass disorder? How does it affect the physical properties of a material? This thesis is dedicated to answering these questions through the development of new methodology and case studies on some important and notoriously awkward systems. In the first instance, I look at some technologically important crystalline materials used in hard coatings, and continue by implementing a method of including configurational disorder in vibrational calculations on random alloys.

TiN, CrN and AlN are industrially important thin film coating materials that are expected to operate at high temperatures. However, they all have different temperature dependent behaviours that cannot be reproduced theoretically, for various reasons.

TiN is a member of a class of transition metal nitrides used as a wear-resistant hard coatings on cutting tools. Its bulk modulus is believed to be the highest of all stoichiometric compounds, and it has a very high melting temperature of 3223 K³ — however, it lacks thermal stability, and its hardness decreases rapidly with temperature,⁴ which is symptomatic of temperature dependence in the elasticity. Under the high temperature and pressure operating conditions of cutting tools, such coatings may undergo phase or microstructural changes that can improve or deteriorate them.^{5,4} I use finite-temperature first principles calculations to recover the temperature dependence of the elastic constants, and demonstrate that elastic anisotropy decreases as the temperature increases, which may explain the high temperature reduction in hardness.⁶

CrN is a hard ceramic generally used in protective coating applications.^{7,8,9,10,11} Crucially, it has been observed in two phases with distinct magnetic states: at ambient pressure, it adopts a paramagnetic rocksalt structure, and when cooled it changes to an antiferromagnetic orthorhombic structure, which can also be

stabilised at room temperature by the application of pressure.¹² By combining anharmonic vibrational free energy calculations as implemented in TDEP with locally disordered magnetic moments, I demonstrate that including a vibrational contribution to the free energy, in addition to the locally disordered magnetic contribution, the cubic paramagnetic phase is stabilised relative to the orthorhombic. This has the effect of reducing the temperature of the phase boundary to a more realistic value, in contrast with static calculations, which severely overestimate the transition temperature.¹³

AlN is a wide band gap semiconductor¹⁴ that is one of the best non-metallic thermal conductors, boasting a thermal conductivity that is approximately 80% of the thermal conductivity of copper at room temperature,¹⁵ making it an excellent heat-sink substrate for semiconductors. It is also an optical semiconductor in its own right, emitting light at the ultraviolet end of the spectrum when doped with silicon.¹⁶ Like other group III nitrides, AlN has been shown both experimentally and theoretically to undergo a pressure-induced phase transition from wurtzite to rocksalt at low temperatures,^{17,18} although its high temperature behaviour is less clear due to the failure of the quasiharmonic approximation.^{19,20,21,22,23} The rocksalt phase is metastable under ambient conditions, and can therefore only be synthesised in the form of thin films, for which it is difficult to measure the thermal conductivity. By reconstructing the pressure-temperature phase diagram, I demonstrate that the rocksalt phase is stabilised by temperature at lower pressure due to anharmonicity. Construction of phonon lineshapes shows that the rocksalt phase behaves much more anharmonically than the wurtzite phase at high temperatures. I also compute the thermal conductivity of the rocksalt phase by solving the Boltzmann transport equation, finding it to be much lower than for the wurtzite phase at all temperatures, which may have severe consequences for a heat sink operating at high temperatures, close to the phase transition.

Continuing on the theme of phase stability, high temperature effects are critical when considering the stability of phases in the context of planetary science and geoscience. The Earth's inner core is believed to be predominantly comprised of iron, but seismological measurements suggest that its density is up to 10% lower than a pure iron core.^{24,25} Alloying iron with lighter elements is the most likely explanation for this density shortfall, and it is likely that there is a significant amount of carbon at the Earth's core,²⁶ possibly in the form of hexagonal Fe_7C_3 . Recently, a new orthorhombic phase of Fe_7C_3 has been prepared in experiments, and it has a Poisson's ratio that is more similar to that of the Earth's core than any other phase.²⁷ Static calculations suggest that the new orthorhombic phase is more stable than the hexagonal below approximately 100 GPa, but it is not sufficient to merely consider zero temperature calculations when we are interested in stability at the Earth's core, which has a temperature in excess of 5000 K. As a first approximation, we compute the Gibbs free energy of both phases at experimental (150 GPa) and Earth's core pressures (360 GPa), finding that at 150 GPa the orthorhombic phase is marginally less stable but becomes more stable with increasing temperature, and at 360 GPa the hexagonal phase is significantly more stable, a trend that is not changed by increasing the temperature.²⁸ However, as a first approximation, these calculations do not

take anharmonicity into account, and at such high temperatures, anharmonicity is likely to have a decisive effect.

One particularly difficult problem is the finite-temperature modelling of random alloys, i.e. generally non-stoichiometric materials consisting of a crystalline lattice with atomic species randomly distributed across the sites. Special quasirandom structures²⁹ offer a convenient method of capturing the configurational entropy at zero temperature, but the vibrational contribution to the free energy is often neglected despite the fact that it has been shown that both contributions are of the same order of magnitude.^{30,31,32,33,34} I have developed a method extending TDEP which enables the computation of the free energies of random alloys taking into account both the configurational contribution and the fully anharmonic vibrational contribution including thermal expansion, and applied it to the notoriously awkward case of cubic $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys, for which lattice vibrations underpin an unusual and technologically useful isostructural decomposition.³⁵ $\text{Ti}_{1-x}\text{Al}_x\text{N}$ thin films used to coat cutting tools undergo age hardening at operating temperatures approaching 2000 K. This is caused by spinodal decomposition in which the alloy decomposes to form nanoscale domains of cubic TiN and AlN, through which extra stress is required to propagate dislocations.^{36,37,38} Static thermodynamic calculations have been unable to recover the miscibility gap for this process, but my new method has been used to reconstruct the phase diagram, demonstrating that vibrations cannot be neglected.

Anharmonicity is not only important in determining the phase stability of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys; it also has considerable influence on mechanical properties, in particular, elasticity. Elastic anisotropy controls the microstructural evolution³⁹ during the aforementioned spinodal decomposition. If the elasticity is isotropic, nanocrystalline domains are expected to grow roughly spherically, and in the presence of significant anisotropy, they become irregular and elongated,⁴⁰ which results in a higher hardness.⁴¹ In a perfectly harmonic crystal, the the elastic constants are temperature independent,⁴² thus any temperature dependence in the elastic constants must arise from anharmonicity. The most widely used method of computing elastic constants *ab initio* is the use of zero temperature density functional theory (DFT) calculations on distorted unit cells. Building on the method I use for computing vibrational free energies in alloys, I recycle the same fully anharmonic, finite temperature calculations to determine temperature and composition dependent elastic constants. I demonstrate that not only are the elastic constants in $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys temperature dependent, but also that the anisotropy leads to two possible strategies for creating harder alloys: controlling the composition or controlling the annealing temperature.

I use this method in a predictive way, to study two more alloys that are in practice very difficult to synthesise, cubic $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and cubic $\text{Hf}_{1-x}\text{Al}_x\text{N}$. By reconstructing their phase diagrams, I show that they only form a solid solution at high temperatures and low AlN concentrations. Moreover, $\text{Hf}_{1-x}\text{Al}_x\text{N}$ is dynamically unstable in a regime below 1000 K, but is stabilised at higher temperatures. Zr and Hf are in the same group of the periodic table as Ti, and serve to demonstrate the effect of increased mass disorder on the vibrational free energy. It turns out that in the case of these pseudobinary systems, mass

disorder has a minimal effect compared with chemical and thermal expansion considerations.

In this thesis, I introduce methods I have developed to determine the phase stability of alloys at high temperatures, to compute temperature dependent elastic constants for alloys and to include the contribution of paramagnetism in free energies. I have applied these methods to several industrially important systems, including $M_{1-x}Al_xN$ ($M = \text{Ti, Zr, Hf}$) alloys, TiN, AlN and CrN.

SOLID STATE THEORY

In principle any solid can be completely described quantum mechanically by solving the time-dependent Schrödinger equation.⁴³ I start with an introduction to the many body problem in the theory of quantum mechanics.

2.1 Many body problem

A non-relativistic system of N_e interacting electrons and N_n nuclei is described by the many body Hamiltonian operator:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{en}, \quad (2.1)$$

where $\hat{T}_e$ and $\hat{T}_n$ are the kinetic energies of the electrons and nuclei, and can be written,

$$\begin{aligned} \hat{T}_e &= - \sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \nabla_i^2 \\ \hat{T}_n &= - \sum_{k=1}^{N_n} \frac{\hbar^2}{2m_k} \nabla_k^2, \end{aligned} \quad (2.2)$$

where m_e and M_k are the mass of the electron and mass of the nucleus k respectively. Indices i and j run over the electronic degrees of freedom and k and l over the nuclei. The electron-electron Coulomb interactions $\hat{V}_{ee}$ and nuclear-nuclear interactions $\hat{V}_{nn}$ are given by,

$$\begin{aligned} \hat{V}_{ee} &= \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ \hat{V}_{nn} &= \frac{1}{2} \sum_{k \neq l}^{N_n} \frac{Z_k Z_l e^2}{|\mathbf{r}_k - \mathbf{r}_l|}, \end{aligned} \quad (2.3)$$

where e is the negative charge of the electron, $Z_{k,l}$ and $-eZ_{k,l}$ are the atomic number and positive charge of nuclei k and l , and $\{\mathbf{r}_i\}$ and $\{\mathbf{r}_k\}$ are electronic and nuclear positions. To simplify the notation, we implicitly include the spin coordinates σ_i for the electrons in $\{\mathbf{r}_i\}$. The potential energy of the interaction between electrons and nuclei is given by:

$$\hat{V}_{en} = - \sum_i^{N_e} \sum_k^{N_n} \frac{eZ_k}{|\mathbf{r}_i - \mathbf{r}_k|}. \quad (2.4)$$

The evolution of a system is described by the time-dependent Schrödinger equation,⁴³

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}, \quad (2.5)$$

where Ψ is a many body wavefunction that depends on the set of spatial coordinates of electrons and nuclei, and spin at each point in time.

$$\Psi = \Psi(\{\mathbf{r}_i\}, \{\mathbf{r}_k\}, t) \quad (2.6)$$

Again, the spin coordinates are implicit in $\mathbf{r}_i$. Since the many body Schrödinger equation (2.5) includes a large number degrees of freedom for electrons and nuclei it is very difficult to solve even for a system with a few particles, and can only be solved analytically for the hydrogen atom. Therefore, we must make a series of physically motivated approximations.

We require a convenient representation of the structure of solids. Solids are in reality complicated arrangements of atoms, but we can approximate them as a regular three dimensional array of atoms, a crystal lattice. This itself can be represented as a unit cell of a few atoms periodically repeated to infinity in all directions. I will discuss the mathematical formalism of the unit cell in chapter 5.

2.2 The adiabatic approximation

The first intuitive step towards solving of the equation (2.1) is to separate the nuclear and electronic parts of the potential energy. One of the first approximations to be made is the adiabatic approximation, in which we choose to decouple the nuclear and electronic wavefunctions due to the great difference in masses.⁴⁴

Since the kinetic energies of the nuclei are small due to the large mass of the nucleus in comparison to the electron ($m_e/M_k \approx 10^{-3}$) we can consider the kinetic energy of the nuclei ($\hat{T}_n$) as a perturbation to the rest of Hamiltonian (2.1), such that the nuclei oscillate around their equilibrium positions.⁴⁴ Then we can consider only the unperturbed terms of that Hamiltonian:

$$\hat{H}_0 = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{en}. \quad (2.7)$$

Since nuclei move much more slowly than electrons, we can say that for an arbitrary fixed configuration of the nuclei $\{\mathbf{r}_k\}$ at any time, the electronic configuration will be determined by the instantaneous nuclear configuration, and will relax to its ground state much more rapidly than the timescale of nuclear vibrations. Therefore in equation (2.7), the interaction term between electrons and nuclei $\hat{V}_{en}$ is treated as an external potential for each configuration of nuclei. The nuclear potential $\hat{V}_{nn}$ at this instantaneous configuration is then fixed for the electronic problem. This means that for the electrons, we can solve the time-independent Schrödinger equation for fixed nuclear positions, and that the electronic wavefunction depends on the position of the nuclei only parametrically via $\mathbf{r}_k$ at any given time:

$$\begin{aligned} \hat{H}_e \Psi_n(\{\mathbf{r}_i\}; \{\mathbf{r}_k\}) &= E_n \Psi_n(\{\mathbf{r}_i\}; \{\mathbf{r}_k\}) \\ \hat{H}_e &= \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en}. \end{aligned} \quad (2.8)$$

We assume that the solution of the clamped-nuclei part of the Hamiltonian, $\hat{H}_e$, is known at any specific configuration $\mathbf{r}_k$, and is a discrete spectrum for which the eigenfunctions are orthonormal:

$$\langle \Psi_m(\{\mathbf{r}_i\}; \{\mathbf{r}_k\}) | \Psi_n(\{\mathbf{r}_i\}; \{\mathbf{r}_k\}) \rangle = \delta_{mn}. \quad (2.9)$$

If we know all adiabatic eigenfunctions of the electronic part of total Hamiltonian for all nuclear coordinates, an exact solution of the full Schrödinger equation can be expanded in terms of set of eigenfunctions ϕ_l with nuclear wavefunctions as χ_l as temperature dependent coefficients:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{r}_k\}, t) = \sum_{l=0}^{\infty} \phi_l(\{\mathbf{r}_i\}; \{\mathbf{r}_k\}) \chi_l(\{\mathbf{r}_k\}, t). \quad (2.10)$$

This is Born's *ansatz* of the total wave function.⁴⁴ In the Born-Oppenheimer approximation, this expansion is truncated to a single term, and is the direct product of the electronic and nuclear wavefunctions:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{r}_k\}, t) \approx \phi_m(\{\mathbf{r}_i\}; \{\mathbf{r}_k\}) \chi_m(\{\mathbf{r}_k\}, t). \quad (2.11)$$

This representation means that vibrational (or nuclear) wavefunction is determined by the properties of only m^{th} electronic state, and that electronic transitions are not allowed by the motion of nuclei. By incorporating this ansatz into the time-dependent Schrödinger equation, we get a decoupled equation for nuclei:

$$\left[\hat{T}_n + \hat{V}_{nn} + E_m(\{\mathbf{r}_k\}) \right] \chi_m = i\hbar \frac{\partial \chi_m}{\partial t}. \quad (2.12)$$

From equation (2.12) we can see that the external potential for the nuclei is defined by the nuclear repulsion and by E_m , which is the expectation value of the electronic Hamiltonian at state m and fixed nuclear coordinates. By solving the stationary equation for the electrons for a set of configurations of the nuclei we can build a potential energy surface on which the atoms move.

The validity and breakdown of the Born-Oppenheimer approximation has been discussed in the literature. The difference in mass between an electron and a nucleus is equivalent to the condition that frequencies of electronic motion are much greater than lattice vibrations, or alternatively that electronic wavefunction should vary slowly with nuclear positions.⁴⁵ This condition is satisfied for semiconductors and insulators due to the large energy band gap and smaller vibrational frequencies; however, the validity of this approach for metallic systems and for systems containing light elements is still debated.^{46,47,48} Nevertheless, the Born-Oppenheimer approximation is in general sufficient for metals.

The main limitation of this approach is that it does not allow for the excitation of an electron from one nucleus to another. These excitations come from non-adiabatic terms, i.e. the full expansion in equation (2.10), and here they are neglected.

AB INITIO THEORY

3.1 Density functional theory

For a periodic system of even just a few atoms, solving the Schrödinger equation is an intractable problem. In density functional theory (DFT), the Schrödinger equation is recast by replacing the many body system with a simple auxiliary system of non-interacting particles. Hohenberg and Kohn⁴⁹ formalised what was to become modern density functional theory with the following theorems:⁵⁰

1. For a system of interacting particles in an external potential V_{ext} , the potential is *uniquely* defined (up to a constant) by the ground state particle density $n_0(\mathbf{r})$.
2. For any V_{ext} , a universal energy functional $E[n]$ can be defined in terms of the density. For any specific V_{ext} , the ground state energy can be found by minimising this functional.

In a system of N electrons, the spin-independent wavefunction is a function of $3N - 3$ coordinates, whereas the density is a scalar field in three dimensions, and is independent of the number of electrons. Thus by computing the density instead of the wavefunction, a considerable amount of computational effort can be saved. We can write the many body Hamiltonian as in chapter 2, as the sum of a fixed part $\hat{H}_0$, which includes the kinetic and nuclear potential energy of the system, and a term including the electronic potential energies of the system:

$$\hat{H} = \hat{H}_0 + \hat{V}. \quad (3.1)$$

Since the Hohenberg-Kohn ground state energy E^{HK} is uniquely determined by the electron density, it can be written in the following functional form:

$$E^{\text{HK}}[n(\mathbf{r})] = E_{\text{nn}} + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + F[n(\mathbf{r})] \quad (3.2)$$

$$= \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + G[n]. \quad (3.3)$$

Here, the functional F includes the internal energy (kinetic and potential) of the interacting system of electrons in an external potential V_{ext} . It is also convenient to separate the Coulomb interaction (the Hartree potential, V_{H}) from F . For the correct electron density n , the system will be in the ground state with energy E_g . The functional $E^{\text{HK}}[n(\mathbf{r})]$ can be minimised using the variational principle. A further assumption is required to solve equation (3.2), the Kohn-Sham ansatz.⁵¹ The real system of interacting electrons is replaced by an *auxiliary system* of non-interacting electrons with the same ground state density (by definition). Then $G[n]$ in equation (3.3) can be expressed as the sum of kinetic energies of the non-interacting system $T[n]$, and a functional $E_{\text{xc}}[n]$, the *exchange-correlation functional*, which is the remaining non-Coulombic electron-electron interaction:

$$G[n] = T[n] + E_{\text{xc}}[n]. \quad (3.4)$$

This gives us a set of Schrödinger-like equations:

$$\hat{H}_{\text{KS}}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \quad (3.5a)$$

$$\hat{H}_{\text{KS}} = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{\text{eff}}(\mathbf{r}) \quad (3.5b)$$

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}). \quad (3.5c)$$

The electron density can be recovered from the Kohn-Sham orbitals ψ_i using,

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (3.6)$$

The Kohn-Sham equations (3.5) can be solved using the method of Lagrange multipliers, subject to the constraint that $N_e = \int n(\mathbf{r})d\mathbf{r}$, i.e. the number of electrons remains constant. Since the electron density n appears on both sides of the equations, they must be solved self-consistently.

In principle, the Kohn-Sham equations are exact; the problem arises in determining the exchange-correlation functional $E_{\text{xc}}[n]$, for which there is no known analytic form. There are many ways of approximating it, but I will only mention two, both of which are derived from a Taylor expansion of the exchange-correlation energy of a free electron gas,⁵¹

$$E_{\text{xc}}[n] = \int \epsilon_{\text{xc}}(n)n d\mathbf{r} + \int \epsilon_{\text{xc}}^{(2)}(n)|\nabla n|^2 d\mathbf{r} + \dots, \quad (3.7)$$

where ϵ_{xc} is the exchange-correlation energy per electron. In the first approximation, we assume that the electron density varies slowly, since we can reasonably assume that exchange and correlation effects are short-ranged in solids. We can then truncate equation (3.7) after the first term to recover the local density approximation (LDA). In the next level of approximation, we include the gradient of the electron density in E_{xc} , which is in practice more complicated than simply including the second order of expansion in equation (3.7), hence the *generalised* gradient approximation (GGA). This is also known as semi-local DFT, since the density is required at position $\mathbf{r}$, and in an infinitesimal region surrounding $\mathbf{r}$.

There is no exchange-correlation functional that can be applied to any system without failing, nor is there any method of systematically generating new and more consistently accurate functionals. In general, semi-local approximations of E_{xc} suffer from the self-interaction error, i.e. the interaction of an electron with its own density; this can be mitigated to some extent using hybrid DFT, in which a fraction of Hartree-Fock exact exchange is included in the exchange-correlation energy. Very briefly, Hartree-Fock theory is a wavefunction-based approach to solving the Schrödinger equation, in which a wavefunction is represented as a single Slater determinant and the exchange energy is formally exact.

Another fundamental problem with the available approximate functionals is that they are unable to describe long-range dispersion interactions present in weakly bound, or highly correlated systems. A discussion of such effects goes beyond the scope of this thesis, since I am only interested in relatively dense systems, in which only the repulsive part of the potential is significant.

3.2 Practical implementation of DFT

In crystalline systems, the natural representation for electronic wavefunctions (or Kohn-Sham orbitals) is plane waves, which are periodic by definition (as opposed to Gaussian-type basis sets). Bloch's theorem states that a wavefunction can be expanded in plane waves with a exponential wave-like component and a cell-periodic component f ,

$$\psi_j(\mathbf{r}) = f_j(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (3.8)$$

where $\mathbf{k}$ is a wave vector in reciprocal space. The cell-periodic component can be expanded as follows:

$$f_j(\mathbf{r}) = \sum_{\mathbf{G}} c_j(\mathbf{k} + \mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}. \quad (3.9)$$

Here, $\mathbf{G}$ are reciprocal space lattice vectors, and c are coefficients to be determined. The electronic wavefunction becomes a sum of such plane waves:

$$\psi_j(\mathbf{r}) = \sum_{\mathbf{G}} c_j(\mathbf{k} + \mathbf{G})e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (3.10)$$

Since we are working in reciprocal space, coefficients c with small kinetic energies $\frac{\hbar^2}{2m}|\mathbf{k} + \mathbf{G}|^2$ have a larger contribution to the expansion, so the expansion can be truncated. The maximum kinetic energy must be determined on a per system basis. This is very convenient in practice, since the precision of a DFT calculation using a plane wave basis set is determined by one parameter, the plane wave cutoff.

So far, we have assumed full translational symmetry of the unit cell. The most mathematically convenient way to express this as a boundary condition for the unit cell is Born-von Kármán, or cyclic boundary conditions. We require that the wavefunction has the periodicity of the lattice,

$$\begin{aligned} \psi(\mathbf{r} + \mathbf{R}) &= \psi(\mathbf{r}) \\ e^{i\mathbf{R}\cdot\mathbf{G}} &= 1, \end{aligned} \quad (3.11)$$

where $\mathbf{G}$ is a lattice vector. When transformed to reciprocal space subject to this condition, the wavefunction solutions are all reduced to the first Brillouin zone, $\psi(\mathbf{k}) = \psi(\mathbf{k} + \mathbf{G})$. Since an infinite periodic lattice retains its periodicity when Fourier transforming to reciprocal space, it is sufficient to determine the wavefunctions in the reciprocal unit cell, or equivalently the first Brillouin zone. In practice, it is impossible to perform a continuous sampling of the Brillouin zone, and a numerical quadrature has to replace any integral. The nodes of this quadrature are called "k-points", and calculations must be converged with respect to the density of this k-point grid.

There are two problems with using a plane wave basis set. Firstly, plane waves are cell-dependent, so it is just as expensive to treat systems with large amounts of vacuum (such as slabs) as it is to treat bulk systems. The second is that core electrons have wavefunctions that vary extremely rapidly near atomic nuclei, and therefore require high frequency plane waves (i.e. a high cutoff) in the expansion. Moreover, valence electrons must also oscillate rapidly in the

core region to maintain orthogonality. These problems can be overcome since core electrons can be replaced with a smooth external potential, or pseudopotential (the plane-wave pseudopotential, or PW-PP method).

In my work, I only use the projector-augmented wave (PAW) method⁵² as implemented in VASP.^{53,54,55,56} This involves dividing the wavefunction into two parts: a partial wave expansion close to the core region, within an “augmentation sphere”, and an envelope function outside the sphere. The partial wave expansion deals with the problems of expanding wavefunctions close to atomic cores. The all-electron wavefunctions are transformed to “pseudo-wave” functions via a linear transformation:⁵⁶

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\psi}_n \rangle, \quad (3.12)$$

$\tilde{\psi}_n$ are the pseudo-wavefunctions, i refer to atomic sites and $\tilde{p}_i$ are projector functions. $|\phi_i\rangle - |\tilde{\phi}_i\rangle$ is the difference between the partial core all electron wavefunctions and pseudo-wavefunctions. This difference is designed to become zero outside an augmentation sphere, centered on the atomic sites. This transformation requires that orthonormality is maintained, so the projectors are subject to the following constraint:

$$\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij}. \quad (3.13)$$

The projectors are localised in the augmentation region. It can be shown that the frozen core PAW and PW-PP methods are essentially the same; however there are some differences in implementation and efficiency.⁵²

I have mentioned that no universal density functional has been developed, and there is no systematic way of improving the approximation of the exchange-correlation functional. There is a huge number of approximations, but their use is generally situational; there is no single functional that works well for all systems. In this work, I only use the Perdew-Burke-Ernzerhof (PBE) GGA functional,⁵⁷ which has been shown to give good results for most systems. However, it still suffers from the shortcomings of the generalised gradient approximation, namely self-interaction error, a poor reproduction of dispersive interactions, overestimating lattice constants and a systematic underestimate of band gaps for semiconductors. The last of these is particularly problematic when we want to know the band gap of semiconductors such as AlN (see section 9.6), and is a result of using a single-electron Hamiltonian; however I am mainly interested in the qualitative trends in the band gap with respect to temperature, so its absolute value is not important.

3.3 Born-Oppenheimer molecular dynamics

Molecular dynamics is a method of simulating the real-time evolution of a system of atoms at finite temperatures, and is important in the study of dynamical and thermodynamic properties of materials. Returning to the solution of the many body problem in chapter 2, recall that the motions of electrons and phonons were decoupled in the Born-Oppenheimer approximation. The electronic part was reduced to a solution of the time-independent Schrödinger equation at given configurations of the nuclei $\{\mathbf{r}_k(t)\}$. Since the nuclei move relatively slowly, they can be considered to be classical particles. Moreover, the time dependence of the electronic structure depends only parametrically on the classical motion of the nuclei. Then the equations of motion of the nuclei are described by Newtonian mechanics,

$$\begin{aligned}\dot{\mathbf{r}}_k &= \frac{\mathbf{p}_k}{m_k} \\ \dot{\mathbf{p}}_k &= \mathbf{f}_k,\end{aligned}\tag{3.14}$$

where $\mathbf{p}_k$ and $\mathbf{f}_k$ are the momentum of atom k and the force acting on it respectively. The potential energy is computed as the solution of the stationary electronic Schrödinger equation using density functional theory; this is the most computationally expensive part of the simulation. The forces can then be calculated using the Hellmann-Feynman theorem:⁵⁸

$$\mathbf{f}_k = -\langle \Psi | \nabla_{\mathbf{r}_k} \hat{H}_e | \Psi \rangle.\tag{3.15}$$

Once all forces acting on all atoms have been computed, we can numerically integrate the equations of motion. The natural choice is a symplectic integrator that conserves the internal energy of the system. Drift in all quantities is possible as a result of numerical integration, but should be minimal. There are several algorithms available,^{59,60,61,62} of which I will only mention the commonly used velocity Verlet algorithm,⁶³ in which trajectories, velocities and forces are computed simultaneously. Expanding the atomic coordinate $\mathbf{r}_k$ around time t , we have expressions for the positions and velocities at the next time step, and can then compute the forces.

$$\begin{aligned}\mathbf{r}_k(t + \delta t) &= \mathbf{r}_k(t) + \dot{\mathbf{r}}_k(t)\delta t + \frac{1}{2}\ddot{\mathbf{r}}_k(t)\delta t^2 + \mathcal{O}(t^4) \\ \dot{\mathbf{r}}_k(t + \delta t) &= \dot{\mathbf{r}}_k(t) + \frac{\ddot{\mathbf{r}}_k(t) + \ddot{\mathbf{r}}_k(t + \delta t)}{2}\delta t + \mathcal{O}(t^2).\end{aligned}\tag{3.16}$$

At finite temperature the physical observables are ensemble averages. Integrating over all possible states of the system is impossible, but the ergodic principle⁵⁹ states that as long as the system has no memory of its initial state, the ensemble average can be replaced by a time average:

$$\langle A \rangle = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{t=1}^N A(t),\tag{3.17}$$

which means that if the system is allowed to evolve with time it will eventually visit every possible state. Any molecular dynamics algorithm must satisfy the ergodicity principle to provide meaningful observables.

So far I have only addressed how a system of N particles will evolve over time in volume V and with total energy E , i.e. in the microcanonical (NVE) ensemble. Since I am interested in equilibrium thermodynamics at constant temperature, the canonical ensemble, defined by constant temperature T , volume V and number of particles N , is more useful. A thermostat is required to maintain the temperature, since temperature is not defined in the absence of a heat bath; there are several available, including the Andersen and Nosé-Hoover thermostats⁵⁹ the former being based on stochastic processes. An alternative to molecular dynamics is sampling configuration space using Langevin dynamics, which is a set of stochastic differential equations.

In the case of the Andersen thermostat, a fictitious heat bath with a fixed temperature is coupled to the system. This coupling can be described by impulsive forces that act on randomly chosen particles, resetting their momenta to a random value drawn from the appropriate distribution. In the limit of infinitely long trajectories averaged over collisions with heat bath, the correct canonical ensemble is recovered, in which microstate probabilities for different configurations are reflected in the distribution of kinetic and potential energies. The disadvantage is equilibration time: since the collisions are chosen randomly, they form sharp discontinuities in the trajectories that can be severe for the relatively small simulation cells of Born-Oppenheimer molecular dynamics.

The Nosé-Hoover thermostat⁶⁴ works by connecting the simulation to a thermal bath via an extended Lagrangian. It corresponds to an integration regulator where the kinetic energy of the system is driven towards a desired value, defined by a temperature T_{set} , through a friction term:

$$\begin{aligned} m_i \ddot{\mathbf{r}}_i &= -\mathbf{f}_i - \xi m_i \dot{\mathbf{r}}_i \\ Q \dot{\xi} &= \sum_i m_i \dot{\mathbf{r}}_i^2 - 3k_B T_{\text{set}}. \end{aligned} \quad (3.18)$$

The effective mass controls the rate of heat exchange between the system and heat bath. An excessively small Q results in large fluctuations and therefore slow convergence, and large fluctuations recover the microcanonical ensemble. The Nosé-Hoover thermostat works when Q is chosen to reproduce the equilibrium dynamics of the system.

In Langevin dynamics, the temperature is maintained through modifications of Newton's equation of motion to a set of stochastic differential equations:

$$\begin{aligned} \dot{\mathbf{r}}_k &= \frac{\mathbf{p}_k}{m_k} \\ \dot{\mathbf{p}}_k &= \mathbf{f}_k + \gamma_k \mathbf{p}_k + \mathbf{f}_k, \end{aligned} \quad (3.19)$$

where γ_k is a friction coefficient and $\mathbf{f}_k$ is a random force from collisions with fictitious particles that is related to γ_k with dispersion σ_k :

$$\sigma^2 = \frac{2m_k \gamma_k k_B T}{\Delta t}. \quad (3.20)$$

For small friction coefficients these equations of motion recover stochastically perturbed Newtonian trajectories corresponding to a canonical ensemble. Care

must be taken, since a too large friction coefficient will lead to completely stochastic motion with unphysical trajectories.

In all cases, it is a huge advantage to initialise the system in a configuration with positions and velocities such that the equilibration time is minimised or eliminated, as in section 6.6.

3.3.1 DISORDERED LOCAL MOMENTS MOLECULAR DYNAMICS (DLM-MD)

Computing the free energy of a material with a paramagnetic phase is a very challenging task, due to the implementational difficulty in coupling magnetic and phonon interactions, not to mention the practical difficulties in describing a paramagnetic state. In principle, we need to include full magnon-phonon coupling in finite temperature *ab initio* calculations to compute the free energy accurately; however, since paramagnetism is an excited electronic property poorly captured by density functional theory, we must make certain approximations. In the disordered local moments molecular dynamics (DLM-MD)⁶⁵ method the paramagnetic state is modelled using collinear spins, and the magnetic moments are randomly distributed over the magnetic atoms, with a new set of random moments chosen every N_{flip} time steps. The net magnetism is constrained to be zero, and it is assumed that this captures some of the magnon-phonon coupling. It should be noted that this is not true magnon-phonon coupling, but is the effect of infinite temperature magnetic disorder on the trajectories, and consequently the vibrational free energy, as discussed in section 9.2.2.

PHASE STABILITY

4.1 Gibbs free energy

When there is more than one possible phase for a combination of elements, the equilibrium phase is defined as the one with the lowest thermodynamic potential energy. At a specific temperature and pressure, this potential is the Gibbs free energy G :

$$G = U - TS + PV, \quad (4.1)$$

where U , T , S , P and V are the internal energy, temperature, entropy, pressure and volume respectively.

In the context of atomistic simulation, these quantities can be accessed either directly or indirectly; in the particular case of the canonical ensemble (constant number of atoms, volume and temperature), we can consider the Helmholtz free energy, F :

$$F = U - TS. \quad (4.2)$$

By computing the Helmholtz free energy over a volume/temperature grid and interpolating to get a smooth function, the pressure can be calculated as the derivative of F with respect to volume,

$$P = - \left. \frac{\partial F}{\partial V} \right|_T, \quad (4.3)$$

and then the Gibbs free energy can be determined. Even though this decomposition seems straightforward, some of these quantities can only be computed indirectly.

The internal energy can be computed in the framework of DFT, from the static atomic configuration. The effect of temperature can be added by performing *ab initio* molecular dynamics (AIMD) simulations, from which we can extract the ensemble averages of the potential $\langle U_{\text{MD}} \rangle$ and kinetic $\langle E_k \rangle$ energies, which contribute to the Helmholtz free energy:

$$F = \langle U_{\text{MD}} \rangle + \langle E_k \rangle - TS_{\text{vib}}. \quad (4.4)$$

However, the vibrational entropy S_{vib} is not directly accessible from the simulations. These quantities can be computed using the TDEP method as in section 6.3.

In the case of ordered structures, there are only two contributions to the entropy: vibrational and electronic (if we ignore magnetism). In the case of alloys, the situation is considerably more complicated. They are substitutionally disordered, which means we must also take the configurational entropy into account, and this is manifested as chemical disorder and mass disorder. These have the additional effect of making the computation of the vibrational contribution more challenging. Solving the problem of the vibrational contribution requires the theory of lattice dynamics, and will be discussed further in chapters, 5, 6 and 9.

4.2 *Configurational entropy in alloys*

I now turn to the issue of substitutional disorder in random alloys. In this thesis, I use the term alloy to describe a crystalline “parent lattice” on which elements are randomly distributed. In contrast with ordered structures, which are modelled via the repetition of relatively small unit cells, a disordered alloy lacks any symmetry beyond its parent lattice, and in principle can only be described with an infinite lattice. The configurational entropy is derived from the number of ways of arranging the different species on the parent lattice, and is infinite in the case of an infinite lattice. In practice, it is necessary to use a supercell that captures the short range disorder and some of the long range disorder. As a result of this substitutional disorder, alloys are very difficult and computationally expensive to model from first principles. This difficulty arises from the lack of periodicity (despite the periodicity of the parent lattice), which means that in a thermodynamic description, one must consider a huge number of different microscopic configurations. This can be simplified by considering only short range ordering and pair interactions. Taking the example of a binary alloy containing two species of atom, A and B, there are three possible pair interactions: A–A, A–B and B–B. To get the best possible representation of an alloy, it is necessary to place the atomic species such that correlations between the pairs are minimised. In practice, this can be achieved using the method of special quasirandom structure (SQS).²⁹

The mean field approximation⁶⁶ defines the maximum possible number of configurations at a given concentration c , resulting in the configurational entropy S_{conf} ,

$$S_{\text{conf}} = k_{\text{B}}(c \ln c + (1 - c) \ln(1 - c)). \quad (4.5)$$

For a binary alloy, this is maximised for $c = 0.5$, i.e. a 50/50 combination of components. Note that the configurational entropy is temperature independent in the mean field approximation. The actual number of states can be computed using the cluster expansion method,⁶⁷ which more accurately describes short range ordering effects, including the temperature dependence.

4.3 Phase diagrams

In a crystalline system with more than one competing phase, it is convenient to show their regions of stability in a phase diagram. Each region corresponds to the phase with the minimum Gibbs free energy in pressure-temperature space (figure 4.1 a), i.e. the regions in which different phases are stable. Alloys, on the other hand, can be non-stoichiometric, and can therefore have a continuum of compositions. The phase stability of each composition is determined by the Gibbs free energy of mixing of its components. Alloy phase stabilities are generally represented on a temperature/concentration phase diagram at a constant pressure (figure 4.1 b). The alloy is stable in the solid solution region, but there may be many different phases coexisting in the (metastable) miscibility gap.

FIGURE 4.1: Schematic illustrations of phase diagrams. a) Pressure-temperature phase diagram for two phases A and B, of the same composition b) Temperature-concentration phase diagram for an alloy at a fixed pressure.

4.3.1 METHODS OF CONSTRUCTING PHASE DIAGRAMS

For stoichiometric crystalline systems, the phase diagram reconstruction is simply a case of finding the intersection lines of the Gibbs free energy surfaces of the relevant phases, and finding which phases have the minimum energies in the intervening regions. I will discuss the construction of the phase diagram for an alloy, which is more general.

In the case of binary alloys, the temperature-concentration phase diagram is traditionally plotted using a graphical method called the common tangent construction.^{68,69} The Gibbs free energy of mixing for alloy components A and B is given by,

$$\begin{aligned} G_{\text{mix}} &= G_{\text{AB}} - (x_A G_A + x_B G_B) \\ x_A + x_B &= 1, \end{aligned} \quad (4.6)$$

where G_{AB} is a solid solution. G_{mix} is plotted against concentration, where x_{AB} is the fraction of component A in a solid solution. A common tangent is constructed on the plot as in figure 4.2. The points where the tangent meets the free energy curve elsewhere to form a common tangent identify the extrema of the region in which the two components (A and B) do not form a solid solution. The lever rule can be used to determine whether any composition decomposes to the equilibrium minima at a specific temperature. This process is complicated by situations in which the Gibbs free energy is not continuous, such as

FIGURE 4.2: Illustration of the common tangent construction. The free energy of a composition x_{AB}^o is minimised by existing in a mixture of compositions x_{AB}' and x_{AB}'' . The relative amount of each composition in the composition x_{AB}^o is found using the "lever rule". G_{mix} is minimised by moving a tangent along the curve until it forms a tangent with another part of the curve.

the presence of dynamical instabilities, but this is not an insurmountable problem. It may, however, fail at extreme concentrations (x close to 0 and 1).

In this thesis, I use the formulation of Gibbs:^{70,71} I reconstruct the phase diagram by direct minimisation of the Gibbs free energy.^{72,73,74} This procedure does not require interpolation of the derivative of the Gibbs free energy, which can make it more straightforward. The problem is reduced to a nonlinear optimization subject to certain constraints, a well known mathematical method.⁷⁵

A system of N atoms of j different species can be arranged in many different ways, with states denoted i . Moreover, the relative quantities of each species can vary between states. In order to simplify the constraints, we define a finite grid of compositions,

$$\rho_i = \left(\frac{N_1}{N}, \frac{N_2}{N}, \dots, \frac{N_j}{N} \right). \quad (4.7)$$

A global state vector, $\mathbf{X}$, gives the composition of each state, $0 \leq X_i \leq 1$, and is roughly analogous to a structural density of states. The energy of a global configuration $\mathbf{X}$ is then,

$$G_{\text{global}} = \mathbf{X} \cdot \mathbf{G} = \sum_i X_i G_i. \quad (4.8)$$

Where G is a vector with components G_i , the Gibbs free energy of state i . We want to minimise G_{global} with respect to $\mathbf{X}$, subject to the constraints (4.9) that the number of atoms is fixed (4.10) and that all states must have a positive occupation (4.11). Mathematically, these can be expressed as,

$$\mathbf{A}\mathbf{X} = \mathbf{B}, \quad (4.9)$$

where,

$$B_j = N_j, \quad (4.10)$$

and

$$A_{ji} = \rho_{ij}. \quad (4.11)$$

In matrix form, this reduces to,

$$\min_{\mathbf{X}} \mathbf{X} \cdot \mathbf{G} \quad \text{subject to} \quad \mathbf{A}\mathbf{X} = \mathbf{B}, 0 \leq X_i \leq 1. \quad (4.12)$$

In order to construct the phase diagram, we repeat this procedure over a range of temperatures in the regime of interest. This is a convenient methodology since no assumptions about phase transitions are necessary, and the constraints are easy to identify. There is also no need to define G across the entire concentration interval if we have a many phase system, which removes complications such as the presence of dynamically unstable phases. It also has no problems at the concentration extrema. However, minimising the Gibbs free energy and the common tangent construction should in principle return the same result.

A major problem with the atomistic approach is that it becomes intractable for systems with large numbers of components. There is an alternative approach called CALPHAD (computer coupling of phase diagrams and thermochemistry),⁷⁶ which is used to construct and predict concentration and temperature dependent phase diagrams. The general idea is that if the Gibbs free energies of the components of a solid solution are known, then one can construct models to find the Gibbs free energy of the mixture. Analytical expressions for the Gibbs free energies are constructed in the form of low order polynomials, for which the coefficients are determined from available experimental and possibly theoretical (*ab initio*) data. Phase diagrams are constructed in temperature-concentration space, where the phase boundaries are the intersection of Gibbs free energy surfaces for different phases. Moreover, the mathematical expressions for the Gibbs free energy can be extrapolated to regimes where data is unavailable, giving it considerable predictive power.

However, the CALPHAD method assumes that the difference in vibrational entropy between two crystal structures is small or zero,⁷⁶ and although this is often reasonable, it only works when the entropy is well defined. This means that CALPHAD may encounter problems for dynamically unstable systems, where the Gibbs free energy is no longer a continuous function. Although there are sometimes problems reconciling CALPHAD and *ab initio* calculations, this may be an instance where they complement each other, and *ab initio* results for enthalpies and vibrational free energies can be used to parameterise CALPHAD models.

LATTICE DYNAMICS

The ultimate goal of this thesis is to determine which phase is the most stable for a given material whose composition may vary, at different temperatures and pressures — and to do this it is necessary to compute Gibbs free energies. This can be achieved using the theory of lattice dynamics, which is concerned with the collective motions of atoms, or vibrations, in solids, and in turn can be used to describe how a solid behaves as a function of temperature. Lattice dynamics is also crucial for understanding mechanical properties of materials at finite temperatures, such as elastic constants, elastic moduli, thermal properties such as thermal expansion and heat capacity, and transport properties, namely thermal conductivity. Since the time of Einstein, Debye, Born and von Kármán this field has expanded significantly with the ability to implicitly include the effects of anharmonicity in *ab initio* calculations. Therefore, in this chapter I will start with an introduction of the classical theory of lattice dynamics, in which atomic nuclei are treated as classical particles. This makes use of the harmonic approximation (HA), in which the potential energy of the lattice is truncated as a second order Taylor expansion. Then I introduce a quantum mechanical description, in which lattice vibrations are treated as quasi-particles (phonons).

5.1 Potential energy and force constants

In this section I introduce the basic of the lattice dynamics using the notation of Horton and Maradudin.⁴⁴ The fundamental theory of lattice dynamics was originally described by Born and von Kármán, starting with the assumption that the crystal is infinite and has a perfect periodicity, such that we can represent an entire crystal using a small unit cell. The unit cell is defined by three basis (lattice) vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. The position of any lattice point can be described using $\mathbf{r}$, which is a linear combination of the basis vectors. Let us define the origin in any unit cell as,

$$\mathbf{r}(l_1, l_2, l_3) = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3, \quad (5.1)$$

where $l_{1,2,3}$ are integers. The equilibrium positions of N atoms in the unit cell with respect to the origin of the unit cell can be described by a set of vectors $\{\mathbf{r}(\kappa)\}$ for the κ^{th} atom in the unit cell. The position of an atom is written as,

$$\mathbf{r}(l\kappa) = \mathbf{r}(l) + \mathbf{r}(\kappa). \quad (5.2)$$

A displacement $\mathbf{u}(l\kappa)$ of an atom ($l\kappa$) from its ideal lattice position must increase the potential energy of the lattice. A situation with all atoms displaced, as a result of thermal disorder, can be quantified by Taylor expanding the potential energy, provided it is determined by the instantaneous positions of the atoms alone, i.e. $U = U(\{\mathbf{u}\})$. The expansion in terms of Cartesian components

of displacements u_α is given by:⁷⁷

$$\begin{aligned}
 U = & U_0 + \sum_{l\kappa\alpha} \Phi_\alpha(l\kappa) u_\alpha(l\kappa) + \frac{1}{2!} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(l\kappa; l'\kappa') u_\alpha(l\kappa) u_\beta(l'\kappa') \\
 & + \frac{1}{3!} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{l''\kappa''\gamma} \Phi_{\alpha\beta\gamma}(l\kappa; l'\kappa'; l''\kappa'') u_\alpha(l\kappa) u_\beta(l'\kappa') u_\gamma(l''\kappa'') + \dots
 \end{aligned} \tag{5.3}$$

Here, α , β , and γ are indices for the Cartesian coordinates and u_α , u_β , and u_γ are the Cartesian components of the displacement of the atom $l\kappa$, and U_0 is the potential energy of the static lattice. The coefficients of the Taylor expansion are the derivatives of the potential energy with respect to displacement, and are called the Born-von Kármán force constants, which are expressible as tensors of increasing rank:

$$\Phi_\alpha(l\kappa) = \left. \frac{\partial U}{\partial u_\alpha(l\kappa)} \right|_{\mathbf{u}=0} \tag{5.4a}$$

$$\Phi_{\alpha\beta}(l\kappa; l'\kappa') = \left. \frac{\partial^2 U}{\partial u_\alpha(l\kappa) \partial u_\beta(l'\kappa')} \right|_{\mathbf{u}=0} \tag{5.4b}$$

$$\Phi_{\alpha\beta\gamma}(l\kappa; l'\kappa'; l''\kappa'') = \left. \frac{\partial^3 U}{\partial u_\alpha(l\kappa) \partial u_\beta(l'\kappa') \partial u_\gamma(l''\kappa'')} \right|_{\mathbf{u}=0}. \tag{5.4c}$$

The physical meaning of the force constants can be explained very simply, as follows. The first-order force constant $\Phi_\alpha(l\kappa)$ (5.4a) is simply the force on atom $l\kappa$. The second order force constant (5.4b) is the relationship between the force in the Cartesian α direction acting on the atom $l\kappa$, when atom $l'\kappa'$ is displaced in direction β , as in figure 5.1 a). A similar interpretation works for the higher order force constants, for example, third order force constants in figure 5.1 b).

The second order force constant matrix $\Phi_{\alpha\beta}$ has 3×3 elements, and the third order force constant matrix is a third rank tensor containing $3 \times 3 \times 3$

FIGURE 5.1: Illustration of a) second and b) third order force constants on a lattice. The second order force constant $\Phi_{\alpha\beta}$ is the force constant determining the coupling between atoms $l\kappa$ and $l'\kappa'$, with the strength of the interaction determined by the length of the displacements $\mathbf{u}$. The third order force constant is similar, but involves the interaction of three atoms.

elements. Note that the derivatives in equation (5.4) must be evaluated at the equilibrium positions. The equilibrium position is defined by Born and Huang as the position of the atoms where there are no forces acting on any atom in the crystal; this configuration should correspond to the vanishing of all stresses in the crystal. Applying this constraint to the force constants matrices, we see that the first derivative in equation (5.4) a) has to be equal to zero.

For practical applications, the infinite number of force constants needs to be reduced to a manageable set. The translational symmetry of the lattice allows us to shift the position of all atoms by a lattice vector without changing the energy. This can be written,

$$\Phi_{\alpha\beta}(l\kappa; l'\kappa') = \Phi_{\alpha\beta}((l+k)\kappa; (l'+k)\kappa') \quad (5.5)$$

$$\Phi_{\alpha\beta\gamma}(l\kappa; l'\kappa'; l''\kappa'') = \Phi_{\alpha\beta\gamma}((l+k)\kappa; (l'+k)\kappa'; (l''+k)\kappa''), \quad (5.6)$$

where k is an integer. The derivatives in (5.4) are commutative, which makes the force constants symmetric under permutation of the Cartesian and atomic indices α, β, γ and $l\kappa, l'\kappa', l''\kappa''$

$$\Phi_{\alpha\beta}(l\kappa; l'\kappa') = \Phi_{\beta\alpha}(l'\kappa'; l\kappa) \quad (5.7)$$

$$\begin{aligned} \Phi_{\alpha\beta\gamma}(l\kappa; l'\kappa'; l''\kappa'') &= \Phi_{\gamma\alpha\beta}(l''\kappa''; l\kappa; l'\kappa') = \Phi_{\beta\gamma\alpha}(l'\kappa'; l''\kappa''; l\kappa) = \\ &= \Phi_{\gamma\beta\alpha}(l''\kappa''; l'\kappa'; l\kappa) = \Phi_{\beta\alpha\gamma}(l'\kappa'; l\kappa; l''\kappa'') = \Phi_{\alpha\gamma\beta}(l\kappa; l''\kappa''; l'\kappa'). \end{aligned} \quad (5.8)$$

We also know that rigidly translating the crystal an arbitrary amount – equivalent to giving all the atoms the same displacement $\mathbf{u}$ – should leave the energy unchanged. This leads to the following constraints:

$$\sum_{l\kappa} \Phi_{\alpha}(l\kappa) = 0 \quad (5.9)$$

$$\sum_{l\kappa} \Phi_{\alpha\beta}(l\kappa; l'\kappa') = \sum_{l'\kappa'} \Phi_{\alpha\beta}(l\kappa; l'\kappa') = 0 \quad (5.10)$$

$$\begin{aligned} \sum_{l\kappa} \Phi_{\alpha\beta\gamma}(l\kappa; l'\kappa'; l''\kappa'') &= \sum_{l'\kappa'} \Phi_{\alpha\beta\gamma}(l\kappa; l'\kappa'; l''\kappa'') = \\ &= \sum_{l''\kappa''} \Phi_{\alpha\beta\gamma}(l\kappa; l'\kappa'; l''\kappa'') = 0. \end{aligned} \quad (5.11)$$

All lattices belong to one of the 230 lattice space groups. The force constants should be invariant under these symmetry operations: If operation S takes atom lk to LK , the force constants tensors transforms as:

$$\Phi_{\alpha}(LK) = \sum_{\lambda} S_{\alpha\lambda} \Phi_{\lambda}(l\kappa) \quad (5.12)$$

$$\Phi_{\alpha\beta}(LK; L'K') = \sum_{\lambda\mu} \sum_{\beta\mu} S_{\alpha\lambda} S_{\beta\mu} \Phi_{\lambda\mu}(l\kappa; l'\kappa') \quad (5.13)$$

$$\Phi_{\alpha\beta\gamma}(LK; L'K'; L''K'') = \sum_{\lambda\mu\nu} S_{\alpha\lambda} S_{\beta\mu} S_{\gamma\nu} \Phi_{\lambda\mu\nu}(l\kappa; l'\kappa'; l''\kappa''). \quad (5.14)$$

Here S is the proper or improper rotation part of a symmetry operation belonging to the space group of the lattice. The final symmetry to consider is that

giving the lattice an infinitesimal rotation in an arbitrary direction should leave the energy invariant. This manifests as,

$$\sum_{l'\kappa'} \Phi_{\alpha\beta}(l\kappa; l'\kappa') (r(l'\kappa')_{\gamma} - r(l\kappa)_{\gamma}) = 0, \quad (5.15)$$

for the second order force constants. The symmetries of the force constants are important since the symmetries of a crystal are an implicit part of lattice dynamics. The symmetry helps to reduce the number of force constants, making calculations of the dynamical properties numerically possible. For the following sections, I adopt a shorter notation by contracting the indices l, κ to a single index i , denoting an atom.

5.2 Harmonic approximation

I now discuss one of the most widely used approximations, highlighting when it is applicable and under which circumstances it fails. In the harmonic approximation the potential energy of the lattice (5.3) is expanded only to the second order. Expansion terms beyond second order are therefore described as “anharmonic” contributions, and anharmonicity can be included by taking higher orders of expansion in potential energy, including phonon-phonon interactions which are important for thermal conductivity. I will discuss this in section 6.4.

5.2.1 EQUATIONS OF MOTION

When the atoms in a crystal vibrate, the kinetic energy of the crystal can be written by summing over the Cartesian components α of the momentum $p_{\alpha}(l\kappa)$, of the κ th atom with mass M_{κ} in the l th unit cell. This results in the following vibrational Hamiltonian:

$$\hat{H} = U_0 + \sum_{i\alpha} \frac{p_{i\alpha}^2}{2m_i} + \frac{1}{2} \sum_{ij\alpha\beta} \Phi_{\alpha\beta}^{ij} u_{i\alpha} u_{j\beta}. \quad (5.16)$$

The equations of motion for the harmonic vibrational Hamiltonian are the time derivatives of the atomic displacements and momenta in a Cartesian basis α :

$$\dot{u}_{i\alpha} = \frac{\partial \hat{H}}{\partial p_{i\alpha}} = \frac{p_{i\alpha}}{m_i} \quad (5.17)$$

$$\dot{p}_{i\alpha} = -\frac{\partial \hat{H}}{\partial u_{i\alpha}} = -\sum_{j\beta} \Phi_{\alpha\beta}^{ij} u_{j\beta}. \quad (5.18)$$

The equation of motion for each atom is then written,

$$m_i \ddot{u}_{i\alpha} = -\sum_{j\beta} \Phi_{\alpha\beta}^{ij} u_{j\beta}. \quad (5.19)$$

For a crystal containing N atoms in a unit cell, we have to solve $3N$ equations of motion, one for each Cartesian direction α . The natural basis in which to solve the equations of motions is plane waves, since they are periodic functions

and are thus commensurate with periodic boundary conditions. We use a plane wave ansatz for the equations of motion:

$$u_{i\alpha} = \frac{1}{m_i} \sum_{\mathbf{q}} A_{\mathbf{q}} \epsilon_{\mathbf{q}}^{i\alpha} e^{i\mathbf{q} \cdot \mathbf{r} - \omega t}. \quad (5.20)$$

Here the displacements are expressed as a sum of plane waves, or normal modes, each with wave vector $\mathbf{q}$ and frequency ω . ϵ is a polarisation vector, and $A_{\mathbf{q}}$ the normal mode amplitude. Substituting this into equation 5.19 and exploiting the orthogonality of planes waves gives,

$$\omega^2 \epsilon = D(\mathbf{q}) \epsilon, \quad (5.21)$$

where $D(\mathbf{q})$ is the dynamical matrix, the Fourier transform of force constant matrix, where each 3×3 submatrix (corresponding to a pair of atoms in the unit cell) of the full $3N \times 3N$ matrix is given by,

$$D_{ij}^{\alpha\beta}(\mathbf{q}) = \sum_i \frac{\Phi_{\alpha\beta}^{ij}}{\sqrt{m_i m_j}} e^{i\mathbf{q} \cdot \mathbf{r}}. \quad (5.22)$$

Here double sum over i and j is avoided since the force constants do not depend on the absolute position, but only on the relative positions of the atoms, as expressed in equation (5.5). Equation (5.21) will then have a non-trivial solution if the following determinant is zero:

$$|D_{ij}^{\alpha\beta}(\mathbf{q}) - \omega^2 \delta_{\alpha\beta} \delta_{ij}| = 0. \quad (5.23)$$

The $3N$ solutions $\omega_s(\mathbf{q})$ of equation (5.21) are called branches, and are collectively called the phonon dispersions (figure 5.2).

The frequencies have the same periodicity as the reciprocal lattice, hence it is convenient to limit the solution to all vectors $\mathbf{q}$ in the first Brillouin zone. Three of these are branches are described as acoustic, with $\omega(\mathbf{q}) \rightarrow 0$ as $\mathbf{q} \rightarrow 0$, and $3N - 3$ are optical, with $\omega(\mathbf{q}) \rightarrow \text{constant}$ as $\mathbf{q} \rightarrow 0$. Since the dynamical matrix is Hermitian, the eigenvalues, which are the vibrational frequencies ω^2 , can only be positive. Imaginary frequencies are indicative of a dynamical instability of the crystal, and in this case, displacements will change exponentially instead of periodically. Without loss of generality, we can contract the notation for phonon mode s at wave vector $\mathbf{q}$ to a single index λ .

FIGURE 5.2: Phonon dispersions of rocksalt AlN at zero temperature. The unit cell contains 1 Al atom and 1 N atom, resulting in 3 acoustic and 3 optical branches.

5.2.2 THE QUANTUM-MECHANICAL REPRESENTATION

In the previous section, we treated the vibrations of atoms classically, by solving Newton's equations of motion. Quantum-mechanically, vibrational normal modes can be represented as quasi-particles called phonons, carrying quanta of energy. It is important to derive the equations of motion quantum mechanically, since the Helmholtz free energy should be derived using Bose-Einstein statistics. We note that our normal mode transformation in equation (5.20) is a sum over the eigenfunctions of independent harmonic oscillators. This allows us to write the position and momentum operators in terms of creation and annihilation operators:⁷⁸

$$\hat{u}_{i\alpha} = \sqrt{\frac{\hbar}{2Nm_i}} \sum_{\lambda} \frac{\epsilon_{\lambda}^{i\alpha}}{\sqrt{\omega_{\lambda}}} e^{i\mathbf{q} \cdot \mathbf{r}_i} (\hat{a}_{\lambda} + \hat{a}_{\lambda}^{\dagger}) \quad (5.24)$$

$$\hat{p}_{i\alpha} = \sqrt{\frac{\hbar m_i}{2N}} \sum_{\lambda} \sqrt{\omega_{\lambda}} \epsilon_{\lambda}^{i\alpha} e^{i\mathbf{q} \cdot \mathbf{r}_i - \pi/2} (\hat{a}_{\lambda} - \hat{a}_{\lambda}^{\dagger}) . \quad (5.25)$$

Rearranging, we have,

$$\hat{a}_{\lambda} = \frac{1}{\sqrt{2N\hbar}} \sum_{i\alpha} \epsilon_{\lambda}^{i\alpha} e^{-i\mathbf{q} \cdot \mathbf{r}_i} \left(\sqrt{m_i \omega_{\lambda}} \hat{u}_{i\alpha} - i \frac{\hat{p}_{i\alpha}}{\sqrt{m_i \omega_{\lambda}}} \right) \quad (5.26)$$

$$\hat{a}_{\lambda}^{\dagger} = \frac{1}{\sqrt{2N\hbar}} \sum_{i\alpha} \epsilon_{\lambda}^{i\alpha} e^{i\mathbf{q} \cdot \mathbf{r}_i} \left(\sqrt{m_i \omega_{\lambda}} \hat{u}_{i\alpha} - i \frac{\hat{p}_{i\alpha}}{\sqrt{m_i \omega_{\lambda}}} \right) . \quad (5.27)$$

In terms of these operators, the vibrational Hamiltonian can be written in a simple form:

$$\hat{H} = \sum_{\lambda} \hbar \omega_{\lambda} \left(\hat{a}_{\lambda}^{\dagger} \hat{a}_{\lambda} + \frac{1}{2} \right) . \quad (5.28)$$

Since $\hat{a}_{\lambda}^{\dagger} \hat{a}_{\lambda}$ are commutative operators, the vibrational Hamiltonian becomes a sum of uncoupled harmonic quantum oscillators. It is often useful to work not with the phonon dispersion relations, which describe individual normal mode frequencies, but with the phonon density of states $g(\omega)$, for example, if we have a large number of atoms in the unit cell and there are too many normal modes to display in a dispersion diagram. The phonon density of states is the number of states with frequency ω ,

$$g(\omega) = \frac{1}{2\pi^3} \int_{\text{BZ}} \delta(\omega - \omega_{\lambda}) d\lambda, \quad (5.29)$$

and can be used to determine thermodynamic quantities, as described in the next section.

5.2.3 THERMODYNAMIC POTENTIALS

The thermodynamic potentials of a crystal can directly be derived from the partition function within the harmonic approximation:

$$\mathcal{Z} = \text{tr} \left[e^{-\beta \hat{H}} \right], \quad (5.30)$$

where β is the inverse temperature $1/k_B T$. Equation (5.30) can be evaluated easily when $\hat{H}$ is a sum of uncoupled oscillators:

$$\mathcal{Z} = \prod_{\lambda} \frac{\exp(-\beta \hbar \omega_{\lambda})}{1 - \exp(-\beta \hbar \omega_{\lambda})}. \quad (5.31)$$

The Helmholtz free energy can be expressed as a function of $\mathcal{Z}$,

$$\begin{aligned} F &= -k_B T \ln \mathcal{Z} = \sum_{\lambda} \frac{\hbar \omega_{\lambda}}{2} + k_B T \ln [1 - \exp(-\beta \hbar \omega_{\lambda})] \\ &= \int_0^{\infty} g(\omega) \frac{\hbar \omega}{2} + g(\omega) k_B T \ln [1 - \exp(-\beta \hbar \omega)] d\omega, \end{aligned} \quad (5.32)$$

where $g(\omega)$ is the phonon density of states as in equation (5.29). The Helmholtz free energy includes zero-point energy as a result of the quantum mechanical representation of the harmonic Hamiltonian. The vibrational entropy can be derived naturally from Helmholtz free energy by differentiation with respect to temperature at constant volume:

$$S = - \left. \frac{\partial F}{\partial T} \right|_V. \quad (5.33)$$

The free energies are used to determine phase stability, as discussed earlier in chapter 4.

5.3 Shortcomings of the harmonic approximation

The harmonic approximation is generally quite successful in determining the phonon dispersion relations, specific heat, and free energies, but fails under certain conditions. The approximation of non-interacting quasiparticles is quite limited, since they are subject to the principle of superposition. Each phonon added to the system will be identical to the existing ones, and is unaffected by them. If we consider heating the crystal as adding quanta of thermal energy (a phonon), then in the high-temperature limit, the energy required to excite an additional phonon is independent of the temperature, which is unphysical, and can have severe repercussions. There is no thermal expansion, and phonon lifetimes and therefore thermal conductivity are infinite. Furthermore, the vibrational entropy from the harmonic approximation can be rather different than the measured. To remedy this, it is possible to extend the existing framework and consider phonons as interacting quasiparticles. This is called anharmonicity, and is discussed in chapter 6.

ANHARMONICITY

In order to overcome the limitations of the harmonic approximation, it is necessary to include anharmonic effects. The first type of anharmonicity is thermal expansion, and is included in calculations via the quasiharmonic approximation. To include further levels of anharmonicity, we need to use more sophisticated methods such as the temperature dependent effective potential method. These extensions to the theory of lattice dynamics are discussed in this chapter.

6.1 Quasiharmonic approximation

In general, phonon frequencies change with temperature, but this is not captured in the harmonic approximation. If we want to include anharmonic effects, we must consider higher order terms of the potential energy expansion in equation (5.3), which is a challenging task. The first correction is to consider the change in a harmonic potential as a result of thermal expansion, which is the basis of the quasi-harmonic approximation.^{79,80} In this approximation, the potential energy expansion is still harmonic, but the structure and therefore the potential energy surface can vary with temperature, resulting in a frequency shift. The temperature dependence of the phonon modes is described by their volume dependence, i.e. $\omega(V, T) \approx \omega(V(T))$. From the definition of the Helmholtz free energy in equation (5.32), we can express it as a function of volume V and temperature T ,

$$F = U_0(V) + \sum_{\lambda} \frac{\hbar\omega_{\lambda}(V)}{2} + k_B T \ln [1 - \exp(-\beta\hbar\omega_{\lambda}(V))], \quad (6.1)$$

where U_0 is the energy of the static lattice at volume V . The equation of state within the quasiharmonic approximation (QHA) is,

$$P = - \left. \frac{\partial F(V)}{\partial V} \right|_T. \quad (6.2)$$

By substituting (6.2) into (6.1) we have,

$$P = - \left. \frac{\partial U_0(V)}{\partial V} \right|_T + \frac{1}{V} \sum_{\lambda} \gamma_{\lambda}(V) \left(\frac{\hbar\omega_{\lambda}(V)}{2} + \hbar\omega_{\lambda}(V)\bar{n}_{\lambda} \right) \Big|_T, \quad (6.3)$$

where $\bar{n}$ is the Bose-Einstein distribution function and γ is the mode Grüneisen parameter. Grüneisen's parameter quantifies the relative change of a phonon frequency with respect to a volume change:

$$\gamma_{\lambda}(V) = - \frac{\partial \omega_{\lambda}(V)}{\partial V} \frac{V}{\omega_{\lambda}(V)}. \quad (6.4)$$

It can be measured experimentally, encodes information on the response to volume change, and is used to estimate the stiffness of bonds. It can be computed via distortions of the unit cell (chapter 7), making it a useful comparison between experiment and theory. It can also be used to calculate the isothermal

bulk modulus by including the effect of pressure on phonon frequencies. The explicit effects of temperature on phonons can be seen only if phonon-phonon interactions are included. This can be done perturbatively,⁸¹ or as I will describe in the next section, using the temperature dependent potential energy surface that gives the correct frequency shift resulting from both thermal expansion and intrinsic anharmonicity.

6.2 *Anharmonicity in phonon calculations*

In order to include anharmonic effects beyond thermal expansion, we either need to expand the potential energy beyond the second order, or alternatively use a harmonic potential that is explicitly temperature dependent (figure 6.1). There are several existing methods for performing anharmonic phonon calculations on ordered structures, but none that allow the treatment of substitutionally disordered structures in a tractable way. I will briefly discuss the available methods, and will later go into detail about my modifications to the TDEP method that enable the modelling of random alloys in section 9.3.1.

A method proposed by Monserrat et al.⁸² involves exploring the Born-Oppenheimer potential energy surface in configuration space, along the directions of the normal modes as calculated within the harmonic approximation. Then, decoupled equations for individual phonons are solved using the vibrational self-consistent field (VSCF) method.⁸³

The stochastic self-consistent harmonic approximation (SSCHA) method^{84,85} is based on the SCHA method of Hooton,⁸⁶ in which the difference in free energies between a harmonic model Hamiltonian and a “real” Hamiltonian is minimised to find an analytic best fit for the real Born-Oppenheimer energy surface. The real Hamiltonian is a harmonic Hamiltonian plus a perturbative term, and is solved self-consistently. In the SSCHA method, thermally excited states are generated stochastically from a Bose-Einstein distribution, such that the zero-point motion is also captured. The SSCHA improves on previous self-consistent schemes such as SCAILD,^{87,88} in that it is a rigorous minimization of the free energy. It does not assume that the harmonic normal modes are fixed with respect to temperature, an approximation inherent in VSCF and SCAILD that has proven to have severe unwanted consequences.^{84,85}

Another option is thermodynamic integration,^{59,89} which is formally exact and includes all forms of anharmonicity in free energy calculations, but is computationally expensive. In this work, I have used the temperature dependent effective potential method, which I describe in more detail below. I also use thermodynamic integration to benchmark my new method (section 9.3.1), and therefore discuss it later.

6.3 *The temperature dependent effective potential method (TDEP)*

The established method of including anharmonicity into calculations is to include terms beyond second order in the potential energy expansion in (5.3). This is problematic in two ways: firstly, when the expansion is carried out to order n , it is necessary to solve the resulting n -body problem, which rapidly becomes intractable. Secondly, there is no guarantee that a Taylor expansion

FIGURE 6.1: Illustration of potential energies at zero temperature and a temperature dependent effective (average) potential (adapted from Romero et al.⁹⁰).

of the Born-Oppenheimer surface is convergent, since there are many singular points, e.g. when two atoms sit on top of each other. The temperature dependent effective potential method TDEP^{1,2} circumvents these issues by keeping the analytical form of the model Hamiltonian, and fitting it directly to the Born-Oppenheimer potential energy surface, sampled at finite temperature. This is illustrated in figure 6.1. I will outline how to determine the effective interatomic interactions up to third order, but the procedure is general and can be extended to even higher orders.

6.3.1 SECOND AND THIRD ORDER FORCE CONSTANTS

Starting with a lattice dynamical model Hamiltonian expanded to the cubic term of the potential energy, the anharmonic Hamiltonian is expressed,

$$\begin{aligned} \hat{H} = & U_0 + \sum_{i\alpha} \frac{p_{i\alpha}^2}{2m_i} + \frac{1}{2!} \sum_{ij} \sum_{\alpha\beta} \Phi_{\alpha\beta}^{ij} u_{i\alpha} u_{j\beta} + \\ & + \frac{1}{3!} \sum_{ijk} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}^{ijk} u_{i\alpha} u_{j\beta} u_{k\gamma}. \end{aligned} \quad (6.5)$$

As discussed in section 5.1, within the Born-von Kármán model, the force constants should obey the symmetry operations in equations (5.5)–(5.14). We can then derive a symmetry-irreducible expression for forces acting on the atoms, starting with:

$$f_{i\alpha} = \sum_j \sum_{\beta} \Phi_{\alpha\beta}^{ij} u_{j\beta} + \frac{1}{2} \sum_{jk} \sum_{\beta\gamma} \Phi_{\alpha\beta\gamma}^{ijk} u_{j\beta} u_{k\gamma}. \quad (6.6)$$

The second and third order force constant matrices are populated with 3^2 and 3^3 unknown variables respectively, collectively called θ_s , where the index s runs from 1 to the total number of variables in all force constant tensors. These tensors only include force constants for atoms which lie within a cutoff radius r_c , defined by size of the supercell. Many of the unknowns θ_s will be symmetry-equivalent. For example, in the case of the second order force constants, consider the first three coordination shells in an fcc lattice:

$\mathbf{r}_{ij}$	Φ original	Φ symmetrised
$\begin{pmatrix} a/2 \\ a/2 \\ 0 \end{pmatrix}$	$\begin{pmatrix} \theta_1 & \theta_2 & \theta_3 \\ \theta_4 & \theta_5 & \theta_6 \\ \theta_7 & \theta_8 & \theta_9 \end{pmatrix}$	$\begin{pmatrix} \theta_1 & \theta_2 & 0 \\ \theta_2 & \theta_1 & 0 \\ 0 & 0 & \theta_3 \end{pmatrix}$
$\begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix}$	$\begin{pmatrix} \theta_{10} & \theta_{11} & \theta_{12} \\ \theta_{13} & \theta_{14} & \theta_{15} \\ \theta_{16} & \theta_{17} & \theta_{18} \end{pmatrix}$	$\begin{pmatrix} \theta_4 & 0 & 0 \\ 0 & \theta_5 & 0 \\ 0 & 0 & \theta_5 \end{pmatrix}$
$\begin{pmatrix} a \\ a/2 \\ a/2 \end{pmatrix}$	$\begin{pmatrix} \theta_{19} & \theta_{20} & \theta_{21} \\ \theta_{22} & \theta_{23} & \theta_{24} \\ \theta_{25} & \theta_{26} & \theta_{27} \end{pmatrix}$	$\begin{pmatrix} \theta_6 & \theta_7 & \theta_8 \\ \theta_7 & \theta_6 & \theta_8 \\ \theta_8 & \theta_8 & \theta_9 \end{pmatrix}$

Note that the force constant matrices in each coordination shell have the same irreducible components, just transformed according to equation (5.13). The total number of independent variables is reduced to just nine, but this will naturally depend on the symmetries of the system of interest. An analytical form of the forces as a function of symmetry inequivalent components θ_s can be derived:

$$F_\alpha^i = \sum_s \theta_s c_s^{i\alpha}(\mathbf{u}), \quad (6.7)$$

where $c_s^{i\alpha}(\mathbf{u})$ are the coefficients of θ_s , and are polynomial functions of all displacements in the supercell within the cutoff radius. Note that equations (6.6) and (6.7) are equivalent. It must be emphasised that these functions have different forms for different crystals, but that the derivation of TDEP is general. It is more convenient to express the forces of the model Hamiltonian H from (6.7) in matrix form:

$$\mathbf{F}_H = \boldsymbol{\Theta} \bar{\mathbf{C}}(\mathbf{u}). \quad (6.8)$$

The matrix $\bar{\mathbf{C}}$ is now the matrix of coefficients $c_s^{i\alpha}$, and $\boldsymbol{\Theta}$ is a vector, the elements of which are θ_s . In order to find $\boldsymbol{\Theta}$, we first need to compute forces and their corresponding atomic displacements in a real system. This can be achieved using a number of methods, but *ab initio* methods are preferred due to their accuracy and transferrability. These include such Born-Oppenheimer molecular dynamics, DLM-MD or the small displacement method. Once the forces and displacements have been computed, the difference between these forces and forces from the model Hamiltonian is minimised to recover $\boldsymbol{\Theta}$. Atomic displacements are generated by propagating the system in real time using the classical equations of motion in *ab initio* molecular dynamics simulations. At each time step, the displacements of atoms from their equilibrium positions

and the associated forces are computed:

$$\begin{aligned}
 \min_{\Theta} \Delta \mathbf{F} &= \frac{1}{N_t} \sum_{t=1}^{N_t} \left| \mathbf{F}_t^{\text{MD}} - \mathbf{F}_t^{\text{H}} \right|^2 = \\
 &= \frac{1}{N_t} \sum_{t=1}^{N_t} \left| \mathbf{F}_t^{\text{MD}} - \bar{\mathbf{C}}(\mathbf{U}_t^{\text{MD}}) \Theta \right|^2 = \\
 &= \frac{1}{N_t} \left\| \begin{pmatrix} \mathbf{F}_1^{\text{MD}} \\ \vdots \\ \mathbf{F}_{N_t}^{\text{MD}} \end{pmatrix} - \begin{pmatrix} \bar{\mathbf{C}}(\mathbf{U}_1^{\text{MD}}) \\ \vdots \\ \bar{\mathbf{C}}(\mathbf{U}_{N_t}^{\text{MD}}) \end{pmatrix} \Theta \right\|^2.
 \end{aligned} \tag{6.9}$$

The difference in forces is minimised using a least-square solution for matrix Θ :

$$\Theta = \begin{pmatrix} \bar{\mathbf{C}}(\mathbf{U}_1^{\text{MD}}) \\ \vdots \\ \bar{\mathbf{C}}(\mathbf{U}_{N_t}^{\text{MD}}) \end{pmatrix}^+ \begin{pmatrix} \mathbf{F}_1^{\text{MD}} \\ \vdots \\ \mathbf{F}_{N_t}^{\text{MD}} \end{pmatrix}. \tag{6.10}$$

Now Θ can be substituted back into $\Phi_{\alpha\beta}^{ij}$ and $\Phi_{\alpha\beta\gamma}^{ijk}$, giving us the second and third order force constants. Both the second and third order force constants are extracted from the same forces and displacements without the need for additional calculations.

The advantage of this procedure is that using Born-Oppenheimer molecular dynamics in the canonical ensemble results in an explicitly temperature dependent potential energy surface. In the TDEP method, the vibrational Hamiltonian in equation (6.5) is defined for each temperature and volume, and the second and third order force constants implicitly include all orders of anharmonicity. The quadratic form of the vibrational Hamiltonian and corresponding second order force constants are used to calculate the Helmholtz free energy. The expansion of the vibrational Hamiltonian up to third order can be used to derive important anharmonic properties of the crystals such as phonon lifetimes, which in turn can be used to compute lattice thermal conductivity.

6.3.2 FREE ENERGY

In section 6.3.1, I described the general idea of calculating force constants in combination with *ab initio* molecular dynamics; it should be noted that other methods can be used to compute the force constants. I now show how to extract free energies which are required for determining phase stabilities. In free energy calculations, only the second order term of the lattice Hamiltonian is required. In the canonical (NVT) ensemble, the Helmholtz free energy can be expressed in terms of the internal energy and entropy,

$$\begin{aligned}
 F &= U - TS = \\
 &= \underbrace{U_{\text{el}} - TS_{\text{el}}}_{F_{\text{el}}} + \underbrace{U_{\text{vib}} - TS_{\text{vib}}}_{F_{\text{vib}}},
 \end{aligned} \tag{6.11}$$

i.e. the Helmholtz free energy is a sum of electron (el) and phonon (vib) contributions to the free energy (for clarity, we do not consider magnetic or configurational entropy at the moment). I use a series of snapshots, or time steps, from

canonical ensemble molecular dynamics simulations to construct the TDEP potential. Just as the forces from the model Hamiltonian should match the forces of the real system, the potential energy is required to match between the model and real systems:

$$\langle U_{\text{MD}} \rangle = \langle U_{\text{TDEP}} \rangle . \quad (6.12)$$

In the TDEP formalism, the potential energy is given by

$$U_{\text{TDEP}}(t) = U_0 + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} \Phi_{\alpha\beta}^{ij} u_{i\alpha}(t) u_{j\beta}(t) . \quad (6.13)$$

Combining equations (6.12) and (6.13), the anharmonic correction term U_0 is given by,

$$U_0 = \left\langle U_{\text{MD}}(t) - \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} \Phi_{\alpha\beta}^{ij} u_{i\alpha}(t) u_{j\beta}(t) \right\rangle , \quad (6.14)$$

which gives the final expression for the TDEP free energy:

$$F_{\text{TDEP}} = U_0 + F_{\text{vib}} . \quad (6.15)$$

Note that in equation (6.14), the harmonic potential energy is subtracted, and in (6.15) it is added again. (It is implicitly included in F_{vib} , see chapter 5.) This has the benefit of recovering the correct low-temperature quantum behaviour: we remove the thermal energy classically and add it back quantum mechanically. Born-Oppenheimer molecular dynamics obeys Maxwell-Boltzmann statistics, while a real quantum mechanical system obeys Bose-Einstein statistics. This step is essentially a quantum mechanical correction, and adds the phenomena of zero-point motion and zero-point energy.

Performing one NVT molecular dynamics simulation gives us the Helmholtz free energy at that volume and temperature. By performing multiple simulations on a volume/temperature grid, it is possible to interpolate, giving the force constants as a smooth function of volume and temperature. This can be transformed to a Gibbs free energy surface, and then the lines along which the Gibbs free energy surfaces for different phases intersect are the phase boundaries in pressure-temperature (or volume-temperature) space.

6.3.3 HOW DOES TDEP WORK?

The TDEP formalism is closely related to traditional lattice dynamics,⁹¹ with some key differences. The force constants defined in Chapter 5 have strict interpretations as derivatives of the Born-Oppenheimer potential energy surface. In the TDEP formalism they are more akin to coefficients in a polynomial fit. The strength of the formalism lies in the *lack* of transferability: a traditional approach would calculate coefficients at $T = 0$ K, and extrapolate results to finite temperature. In contrast, in the TDEP formalism, the force constants are calculated at fixed temperatures, and are interpolated to get a smooth function. The difference can be viewed as extrapolation in the case of the former, versus interpolation of finite temperature properties for the latter.

6.4 Phonon lifetimes and lattice thermal conductivity

In the harmonic approximation (section 5.2), phonons do not interact. As a result, a phonon will have an infinite lifetime once it is excited, which is unphysical and leads to an infinite thermal conductivity. It also clashes with direct experimental observations of phonon dispersions: they have finite linewidths^{92,90} and finite lifetimes.

Phonons are usually measured via inelastic X-ray or neutron scattering.^{93,32} In an idealised experiment, the one-phonon neutron cross section would be measured as,⁸¹

$$\sigma_{\lambda}(\omega) \propto \frac{\omega_{\lambda} \Gamma_{\lambda}(\omega)}{\left[\omega^2 - \omega_{\lambda}^2 - 2\omega_{\lambda} \Delta_{\lambda}(\omega) \right]^2 + 4\omega_{\lambda}^2 \Gamma_{\lambda}^2(\omega)}. \quad (6.16)$$

Here ω_{λ}^2 are the eigenvalues of the dynamical matrix, $\Delta_{\lambda}(\omega)$ and $\Gamma_{\lambda}(\omega)$ are the real and imaginary parts of the frequency dependent self-energy, and $\hbar\omega$ is a probing energy. Equation (6.16) can be interpreted with the help of the example in figure 6.2. The energy axis is the probing energy, and the intensity represents the likelihood of exciting a phonon with energy $\hbar\omega$ and momentum $\mathbf{q}$. We can interpret the cross section, or phonon lineshape, as the broadened and shifted phonon frequencies. The term “broadening” is used in the sense of a spectral representation: non-interaction quasiparticles are represented as Dirac δ -functions, but in the interacting case these are replaced by distributions with finite widths. Given the third order force constants, the phonon self-energy can be calculated:^{79,81}

$$\Gamma_{\lambda}(\omega) = \frac{\hbar\pi}{16} \frac{V}{(2\pi)^3} \sum_{\lambda'\lambda''} |\Psi_{\lambda\lambda'\lambda''}|^2 \Delta_{\mathbf{q}\mathbf{q}'\mathbf{q}''} \times \{ (n_{\lambda'} + n_{\lambda''} + 1) \delta(\omega - \omega_{\lambda'} - \omega_{\lambda''}) + 2(n_{\lambda'} - n_{\lambda''}) \delta(\omega - \omega_{\lambda'} + \omega_{\lambda''}) \}. \quad (6.17)$$

The imaginary part of the self energy is a sum over all possible three-phonon interactions $\lambda\lambda'\lambda''$, n_{λ} are the Bose-Einstein thermal occupation factors counting the number of phonons in each mode, and the delta-functions in momentum and energy ensure that these are conserved. This is true of all three phonon processes, i.e.

$$\mathbf{q} \pm \mathbf{q}' + \mathbf{q}'' = \mathbf{G} \quad (6.18)$$

$$\omega \pm \omega' = \omega'', \quad (6.19)$$

where either two phonons combine into a third, or one phonon decays into two others. The momentum is conserved up to a reciprocal lattice vector $\mathbf{G}$. The expression for the self-energy is then an integral over the allowed processes, weighted by how many phonons are in each of the different modes, with the scattering strength determined by the three-phonon matrix element:

$$\Psi_{\lambda\lambda'\lambda''} = \sum_{ijk} \sum_{\alpha\beta\gamma} \frac{\epsilon_{\alpha i}^{\lambda} \epsilon_{\beta j}^{\lambda'} \epsilon_{\gamma k}^{\lambda''}}{\sqrt{m_i m_j m_k} \sqrt{\omega_{\lambda} \omega_{\lambda'} \omega_{\lambda''}}} \Phi_{ijk}^{\alpha\beta\gamma} e^{i(\mathbf{q} \cdot \mathbf{r}_i + \mathbf{q}' \cdot \mathbf{r}_j + \mathbf{q}'' \cdot \mathbf{r}_k)}. \quad (6.20)$$

FIGURE 6.2: Example of a line-shape for rocksalt AlN system at 1500 K.

FIGURE 6.3: An example of phonon lifetimes in rocksalt AlN at 1500 K, calculated from the third order force constants using TDEP. Low frequency phonons have longer lifetimes.

The real part is conveniently calculated via a Kramers-Kronig transform (it can of course be expressed in a similar way as the imaginary part^{79,81}):

$$\Delta_\lambda(\omega) = \frac{1}{\pi} \int \frac{\Gamma_\lambda(\omega')}{\omega' - \omega} d\omega'. \quad (6.21)$$

While the derivation of these results is tedious,⁷⁹ the interpretation is straightforward in limiting cases. If we assume that $\Gamma \ll \omega$ and $\Delta \ll \omega$, equation (6.16) reduces to a Lorentzian,

$$\sigma_\lambda(\omega) \approx \frac{\Gamma_\lambda}{\pi} \frac{1}{(\omega - \omega_\lambda - \Delta_\lambda)^2 + \Gamma_\lambda^2}, \quad (6.22)$$

centered at the second-order frequencies ω_λ , shifted by the real part of the self-energy and broadened to a full-width half maximum of $2\Gamma_\lambda$. This is the spectral representation; a Fourier transform to the time domain gives us

$$\mathcal{F}\{\sigma_\lambda(\omega)\} = \exp(i[\omega_\lambda + \Delta_\lambda]t) \exp(-2\Gamma_\lambda t), \quad (6.23)$$

which is a damped plane wave with lifetime $\tau_\lambda = 1/2\Gamma_\lambda$. Thus determining the phonon self-energy via third order force constants allows the calculation of the phonon lifetimes (figure 6.3).

6.4.1 LATTICE THERMAL TRANSPORT

Heat transport can be determined by solving the inelastic phonon Boltzmann equation.⁹⁴ By applying a temperature gradient ∇T_α in direction α , the phonon current is given by the group velocities of the phonon modes λ and non-equilibrium phonon distribution function n_λ :

$$J_\alpha = \frac{1}{V} \sum_\lambda \hbar \omega_\lambda v_{\lambda\alpha} n_{\lambda\alpha}. \quad (6.24)$$

Assuming the thermal gradient is small, the non-equilibrium distribution function can be linearised as,

$$n_{\lambda\alpha} \approx \bar{n}_\lambda - v_{\lambda\alpha} \tau_{\lambda\alpha} \frac{d\bar{n}_\lambda}{dT} \frac{dT}{d\alpha}. \quad (6.25)$$

Inserting this into equation 6.24, and exploiting the fact that the equilibrium occupation carries no heat, we arrive at,

$$J_\alpha = \frac{1}{V} \sum_\lambda \hbar \omega_\lambda \frac{d\bar{n}_\lambda}{dT} v_{\lambda\alpha} v_{\lambda\alpha} \tau_{\lambda\alpha} \frac{dT}{d\alpha}. \quad (6.26)$$

Utilizing Fourier's law, $J = \kappa \nabla T$, and identifying the phonon heat capacity,

$$c_\lambda = \hbar \omega_\lambda \frac{d\bar{n}_\lambda}{dT}, \quad (6.27)$$

we arrive at,

$$\kappa_{\alpha\beta} = \frac{1}{V} \sum_\lambda c_\lambda v_{\alpha\lambda} v_{\beta\lambda} \tau_{\beta\lambda}, \quad (6.28)$$

which can be interpreted as follows: the heat transported by each phonon will depend on how much heat it carries, how fast it travels, and how long it lives. The phonon-phonon induced lifetime can be determined from the self-energy Γ_λ (6.17). In addition, one must consider the scattering with mass impurities (isotopes), and the boundaries of the sample.^{95,96,97,98}

Inserting these lifetimes directly into equation (6.28) will result in the relaxation time approximation, in which all scattering processes are treated as contributing to thermal resistance. This is actually incorrect, since normal three-phonon process for which $q + q' + q'' = 0$ cannot influence the heat current since there is no change in momentum. Only so-called Umklapp processes for which momentum is not conserved, i.e. $q + q' + q'' = G$ can. To correctly account for this, one should iteratively solve the linearised phonon Boltzmann equation, starting from the relaxation time approximation and determining the non-equilibrium occupation functions,⁹⁵ as employed in section 9.5 to compute the thermal conductivity of AlN.

6.5 Thermodynamic integration

In order to determine the relative stabilities of two phases, or two states of the system, their Helmholtz free energies must be compared. All information on the potential energy can be directly extracted from molecular dynamics simulations (as a canonical ensemble average over the phase space) but this does not apply to the entropy. The partition function $\mathcal{Z}$,

$$\mathcal{Z} = \frac{1}{\Lambda^{3N} N!} \int \exp(-\beta U(\{\mathbf{r}\})) d\{\mathbf{r}\}, \quad (6.29)$$

can be used to compute the Helmholtz free energy via $F = -k_B T \ln \mathcal{Z}$. However, the partition function is not in the form of a canonical average over phase space, and cannot be calculated explicitly. It is therefore necessary to use thermodynamic integration to compute the Helmholtz free energy.⁵⁹ Given a reference phase (or state) with a known internal energy U_{ref} and free energy F_{ref} , and a phase of interest (“in”) whose internal energy U_{in} can be calculated, one can determine the free energy difference $\Delta F = F_{\text{in}} - F_{\text{ref}}$. This can be replaced by an integration over the ensemble average of the internal energies along a path. This path is defined by a “switching” parameter λ (the Kirkwood coupling parameter method),⁹⁹ which takes a value from 0 (the reference state) to 1 (the state of interest).

This can be introduced by linearly mixing the Hamiltonians:

$$H(\lambda) = (1 - \lambda)H_{\text{ref}} + \lambda H_{\text{in}} = T + (1 - \lambda)U_{\text{ref}} + \lambda U_{\text{in}}, \quad (6.30)$$

where the kinetic energy part T is unaffected by the mixing, and the mixing only enters into the potential energy part. Inserting this into equation (6.29) and differentiating with respect to λ gives,

$$\frac{\partial F}{\partial \lambda} = \left\langle \frac{\partial U}{\partial \lambda} \right\rangle = \langle U_{\text{in}} - U_{\text{ref}} \rangle, \quad (6.31)$$

which enables the calculation of the free energy difference as:

$$\Delta F = F_{\text{in}} - F_{\text{ref}} = \int_0^1 \langle U_{\text{in}} - U_{\text{ref}} \rangle d\lambda. \quad (6.32)$$

The term on the right hand side is an ensemble average of the system with Hamiltonian $H(\lambda)$. Given a known Hamiltonian for the reference system then we can always calculate the energy for the unknown system. However, the potential must be parameterised such that it is continuous and it is possible to take a numerical derivative at any point.

Computing the phase diagram like this is computationally expensive, since calculations must be performed for many points in pressure-temperature space, and every temperature-volume point requires a set of Born-Oppenheimer molecular dynamics calculations. In practice, to achieve accuracy in these calculations one can use the upsampled thermodynamic integration using Langevin dynamics (UP-TILD).⁸⁹ A set of uncorrelated snapshots with energies computed at the gamma point only is chosen and upsampled using a more dense k-point mesh:

$$\left\langle \frac{\partial U}{\partial \lambda} \right\rangle \Big|_{\lambda}^{\text{high}} = \left\langle \frac{\partial U}{\partial \lambda} \right\rangle \Big|_{\lambda}^{\text{low}} + \langle \Delta E \rangle|_{\lambda}, \quad (6.33)$$

where the difference $\langle \Delta E \rangle|_\lambda$ is

$$\langle \Delta E \rangle|_\lambda = \frac{1}{M} \sum_{u=1}^M (E_u^{\text{low}} - E_u^{\text{high}}), \quad (6.34)$$

and energies E_u^{low} and E_u^{high} are the differences between total energies for AIMD snapshot u and the total energy of the system when all atoms are at their equilibrium positions.

$$E_u^{\text{c,tot}} = E_u^{\text{c}} - E_u^{\text{eq}} \quad (6.35)$$

Here, the superscripts stand for low and high accuracy respectively. Although UP-TILD is more efficient compared with running the entire AIMD simulation with a dense k-point grid, it is still computationally expensive, and it gives only the difference between energies at a specific volume and temperature. Construction of the Helmholtz free energy surface using this procedure would require many AIMD simulations.

6.6 Preparation of the cell

Born-Oppenheimer molecular dynamics is a real space method, and we need to describe collective motions of atoms that may have vibrational wavelengths much larger than the length of the unit cell. For this reason, we need to use a supercell in practice.

Born-Oppenheimer molecular dynamics can be expensive for many reasons. Firstly, it is necessary to deal with relatively large supercells which may contain more than 100 atoms. Secondly, it is necessary to compute the electronic ground state at every time step, which is the most time consuming part of the simulation. Thirdly, the cell must be fully equilibrated. Finally, the precision of the calculations is statistically linked to the number of configurations used: any property A for which we want to calculate the ensemble average $\langle A \rangle$ must be converged with respect to the number of uncorrelated time steps.

To minimise the equilibration time, the simulation supercell is initialised in a thermally excited state, by setting the initial velocities and displacement amplitudes according to the Maxwell-Boltzmann distribution.¹⁰⁰ For a given simulation cell of N_a atoms, we determine the $3N_a$ commensurate normal modes within the harmonic approximation, and calculate the eigenvectors ω_s and eigenvalues ω_s^2 . In the given cell, we can use the normal mode transformation from equation (5.20) to express the instantaneous positions and velocities,

$$u_{i\alpha} = \sum_{s=1}^{3N_a} \epsilon_{i\alpha}^s A_s \quad (6.36)$$

$$\dot{u}_{i\alpha} = \sum_{s=1}^{3N_a} \omega_s \epsilon_{i\alpha}^s A_s, \quad (6.37)$$

where the normal mode amplitudes A_s will be determined by the following boundary conditions: we require a set of positions and velocities that correspond to a canonical ensemble. We choose A_k so that they are normally dis-

tributed around their mean value,

$$\langle A_s \rangle = \sqrt{\frac{\hbar(2n_k + 1)}{2M_j\omega_k}} \approx \frac{1}{\omega_k} \sqrt{\frac{k_B T}{m_j}}, \quad (6.38)$$

where the approximate result is in the classical limit, $\hbar\omega \ll k_B T$. The appropriate distribution of atomic positions and velocities is given by,

$$u_{i\alpha} = \sum_{s=1}^{3N_a} \epsilon_{i\alpha}^s \langle A_s \rangle \sqrt{-2 \ln \xi_1} \sin 2\pi\xi_2 \quad (6.39)$$

$$\dot{u}_{i\alpha} = \sum_{s=1}^{3N_a} \omega_s \epsilon_{i\alpha}^s \langle A_s \rangle \sqrt{-2 \ln \xi_1} \cos 2\pi\xi_2. \quad (6.40)$$

Here, $0 < \xi_n < 1$ represents a uniform distribution of random numbers, which can be transformed to a normal distribution of random numbers using the standard Box-Muller transform. This also ensures that the velocities are phase shifted by $\pi/4$ with respect to the displacements.

Choosing the mean amplitudes in the classical limit gives us a snapshot in time from a canonical Maxwell-Boltzmann ensemble (within the harmonic approximation), which results in a starting point that reduces the time until equilibration by orders of magnitude.¹⁰⁰ Choosing the Bose-Einstein distribution instead gives us the opportunity to investigate the effect of quantum thermal disorder (harmonically) at low temperatures, akin to the SSCHA method.^{84,85}

In order to minimise the electronic relaxation time, we sample the Brillouin zone at the gamma point only. This is followed an upsampling procedure analogous to upsampled thermodynamic integration,⁸⁹ in which the electronic ground state is recomputed for a subset of molecular dynamics snapshots for a denser k-point mesh. Together, these procedures dramatically reduce the computational time.

6.7 Vibrational entropy in alloys

It is often claimed that the configurational disorder results in the largest entropic contribution to the free energy of an alloy, while the vibrational contribution is often neglected; however, they are comparable.^{30,31,32,101,34} When I discussed lattice dynamics in chapter 5, the derivation of the equations of motion was applicable only to ordered crystalline systems due to the imposition of symmetry. This will obviously not work in alloys due to their substitutional disorder, and although there are methods of including vibrations quasiharmonically, there is no way of including anharmonicity as described in section 6.2. In principle, one can overcome the issue of periodicity and disorder by using a SQS supercell (section 6.6) with TDEP or thermodynamic integration, but in practice this would be hugely computationally expensive.

Since the dynamical matrix for alloys is generally computationally intractable, it is necessary to make some approximations. The first way of doing this is by making approximations to the force constants. The bond proportion effect¹⁰¹ is based on the observation that the forces between atoms change with chemical

ordering. At a very basic level, in an ordered structure, there are strong chemical bonds between unlike atomic species with high vibrational frequencies. However, introducing substitutional disorder results in weaker bonds between like species that shift the frequencies in the phonon spectrum down, and lower free energies. The bond length is generally anticorrelated with its strength, which can in turn be related approximately to the force constants. Thus it is possible to come up with a model approximating force constants from average bond strengths based on whether the atoms involved are the same species, from which free energies of mixing can be computed.

For a rough estimate of the vibrational contribution to the free energy, one can use very basic approximations such as the Debye model, for which the highest frequency is determined by a single temperature, or the Einstein model, in which all of the atoms vibrate with the same frequency.

The final approach I will mention is the coherent potential approximation (CPA), in which the density of states can be computed by replacing the real environment of a phonon which cannot be treated analytically with an effective medium described by a “coherent potential.” Any atomic site is defined by a Green’s function, and all aspects of disorder (mass, chemical) are perturbations to the function. This method fails since it is only a single site mean field approximation.¹⁰² It has been improved to the itinerant coherent potential approximation (ICPA), which includes local environmental mass and force constant disorder, i.e. it goes beyond a simple average.^{103,104}

In spite of their success, these methods all have limitations. Running any phonon calculation on an SQS is currently computationally intractable due to the number of unknowns in the force constant matrix. The Debye and Einstein approximations are useful estimates, but are woefully inaccurate compared with *ab initio* methods. The ICPA makes a very convincing case, since in principle it accounts for all forms of disorder, but it requires the force constants as an input, and they must be calculated separately. I chose to extend the TDEP method, due to its implementational transparency and the simplicity of the underlying concepts. This method is described in section 9.3.1.

MECHANICAL PROPERTIES

Experimentally, it is convenient to measure macroscopic mechanical properties of materials such as bulk and shear modulus.¹⁰⁵ Real materials have complicated microstructures that are impossible to describe using first principles atomistic calculations, so from a theoretical perspective we concentrate on single crystal properties, for which the mechanical properties are described by the elastic constants. The elastic constants can be defined either in the long wave limit of phonons^{106,79,80} or as coefficients in an expansion of the potential energy.

7.1 Elasticity and lattice dynamics

The long wavelength limit corresponds to the atoms in a crystal moving coherently as a plane wave with vanishing frequency, and thus very small wave vectors $\mathbf{q}$. Waves with small $\mathbf{q}$ are sound waves, and have frequencies that are determined by the macroscopic elastic constants. Analogously, the frequencies of all normal modes of a crystal are determined by the force constants, thus the macroscopic elastic constants can be related to the microscopic force constants, and the elastic constants can therefore be calculated from atomistic calculations of the interatomic force constants.^{106,79,80}

In the continuous limit, the atomic displacements vary slowly from cell to cell, and can be described as a continuous displacement field $\mathbf{u}(\mathbf{x})$, that takes values $\mathbf{u}_i$, at site i centered at $\mathbf{r}_i$. The equations of motion for these long wavelength elastic waves are,⁸⁰

$$\rho \ddot{u}_\alpha = - \sum_{\beta\gamma\delta} C_{\alpha\beta\gamma\delta} \frac{\partial^2 u_\beta}{\partial x_\gamma \partial x_\delta} \bigg|_{\mathbf{x}=0}, \quad (7.1)$$

where $C_{\alpha\gamma\beta\lambda}$ are the second order macroscopic elastic constants and ρ is the density. Relating equations (7.1) and (5.19) is possible in the limit of small $\mathbf{q}$, giving the following relations between elastic constants and force constants:

$$C_{\alpha\beta\gamma\delta} = D_{\alpha\beta\gamma\delta} + D_{\beta\gamma\alpha\delta} - D_{\beta\delta\alpha\gamma}, \quad (7.2)$$

where

$$D_{\alpha\beta\gamma\delta} = -\frac{1}{2V} \sum_{ij} \Phi_{ij}^{\alpha\beta} r_\gamma r_\delta, \quad (7.3)$$

and V is the volume of the unit cell. Crystal symmetries constrain the relations between elastic constants in a similar manner to the force constants in equations (5.5)–(5.14), reducing the number of elements in the elastic tensor depending on the symmetry of the cell. Note that $C_{\alpha\beta\gamma\delta}$ is invariant under the transformation from $\alpha\beta \longleftrightarrow \gamma\delta$. Taking all symmetry conditions into account, the number of independent elastic constants is in general reduced from 3^4 to 21. This number can be reduced further depending on the symmetry of the unit cell; for example, for a cubic system, there are 3 independent elastic constants.

Returning to the equation of motion for sound waves, in analogy to the dynamical matrix and equation of motion, we seek a plane wave solution of equation (7.1) with phase velocity v , leading to an eigenvalue problem for $\rho v^2(\mathbf{q})$

expressed in the Christoffel equation,¹⁰⁷

$$|\Gamma_{\alpha\beta} - \rho v_{\mathbf{q}}^2 \delta_{\alpha\beta}| = 0, \quad (7.4)$$

where

$$\Gamma_{\alpha\beta} = \sum_{\gamma\delta} C_{\alpha\beta\gamma\delta} \frac{q_\gamma q_\delta}{q^2}, \quad (7.5)$$

is the Christoffel matrix, which depends on direction of the wave vector $\mathbf{q}$. For each direction there are three solutions for $v_{\mathbf{q}}^2$: one longitudinal wave (v_p) with a polarization vector parallel to the wave vector and two transverse waves (v_{s_i}) with perpendicular polarisation vectors. Christoffel's equation is often used to determine sound wave velocities from elastic constants, but this could equally be achieved using the slope of the acoustic branches at small $\mathbf{q}$ close to the Γ point in the Brillouin zone.

7.2 Stress and strain

According to Hooke's law, stress in a material will cause a deformation which is given by the shear strain tensor η ,

$$\eta_{\alpha\beta} = \eta_{\beta\alpha} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right), \quad (7.6)$$

where the derivatives denote an extension u per unit length x in perpendicular directions α and β . In the linear elasticity regime, the strain is sufficiently small that Hooke's law applies. Equation (7.6) can then be interpreted as follows: if a force is applied in direction α then a shear stress appears in a normal direction β . Taking into account rotational and translational symmetries of the crystal only 6 independent stresses remain, of which three are shear and three are normal stresses. The stress components can be expressed as a linear combination of the deformation components, or strains,

$$\sigma_{\alpha\beta} = \sigma_{\beta\alpha} = \sum_{\gamma\delta} C_{\alpha\beta\gamma\delta} \eta_{\gamma\delta}, \quad (7.7)$$

where the deformations are small. Since the deformations are small, any internal stress in the crystal can be treated independently of the external stress. The elastic energy is a useful link between the atomistic description in first principles calculations, and the macroscopic elastic constants, and can be expressed,

$$E = \frac{1}{2} \sum_{\alpha\beta} \sum_{\gamma\delta} C_{\alpha\beta\gamma\delta} \eta_{\alpha\beta} \eta_{\gamma\delta}, \quad (7.8)$$

where E is the elastic energy density per unit volume. This expression can be used to compute elastic constants from small distortions of a unit cell.

7.3 Shortcomings of static elastic constants

The definitions of the elastic constants above are derived from the harmonic approximation, and are therefore subject to its failures. To understand how

temperature and pressure affect the elastic constants, it is necessary to consider the relation between elastic constants and the thermodynamics potentials. The elastic constants can be expressed as derivatives of the thermodynamic potentials;¹⁰⁸ for isentropic (adiabatic) deformations of a crystal, the components of the stress tensor are the derivative of the internal energy with respect to stress at constant entropy per unit mass:

$$C_{\alpha\beta\gamma\delta}^S = \rho \left. \frac{\partial^2 U}{\partial \eta_{\alpha\beta} \partial \eta_{\gamma\delta}} \right|_S. \quad (7.9)$$

The isothermal elastic coefficients are the derivatives of the Helmholtz free energy at constant temperature per unit mass:

$$C_{\alpha\beta\gamma\delta}^T = \rho \left. \frac{\partial^2 F}{\partial \eta_{\alpha\beta} \partial \eta_{\gamma\delta}} \right|_T. \quad (7.10)$$

In the zero temperature limit, the adiabatic and isothermal elastic constants are the same. For a static lattice, the adiabatic and isothermal elastic constants can be calculated using first-principles calculations. The difference between the zero temperature elastic constants and the room temperature elastic constants is insignificant, and potentially smaller than the systematic error arising from the LDA and GGA exchange-correlation approximations (section 3.1).

Calculating finite temperature elastic constants is a challenging task since atomic motion must be considered. Finite temperature elastic constants can be calculated by using *ab initio* molecular dynamics simulations by either calculating temperature dependence of stresses, or through the temperature dependence of the phonon dispersions, as in section 9.4. Once the elastic constants have been computed, they can be used to derive many macroscopic mechanical properties, including bulk, shear and Young's modulus, anisotropy and Poisson's ratio.¹⁰⁵

EXPERIMENTAL VERIFICATION

8.1 Atom probe tomography

Atom probe tomography is an experimental technique which can be used to construct a three-dimensional map of a material at the atomic scale.^{109,110}

It is based on the field evaporation and successive removal of single atoms at the apex of a needle-shaped specimen. These atoms are accelerated towards a detector via an electric field, as in figure 8.1. The atoms are ionised by the simultaneous effect of a standing (DC) electrostatic field and either high voltage or laser pulses on the surface of the specimen, and are then evaporated by a high electric field.¹¹¹

A position-sensitive detector is used to record the x and y coordinates of each single impact, and a time-of-flight mass spectrometer enables the identification of the nature of the ions. These data are finally used to generate a three-dimensional reconstruction. The space-resolved reconstructed map can be used to measure the global and local composition of the specimen, and to identify microstructures including domains, defects, dislocations and diffusion into boundaries.¹¹²

High intensity electric fields of the order of 20–40 V/nm are required to evaporate atoms from sample. In order to maintain a high electric field, there must be certain constraints on the size and shape of the tip: it must be a sharp needle with a diameter of around 50 nm at the apex. A focused ion beam (FIB) was used to construct a tip from the thin film, since it offers excellent control of size and shape for a site-specific specimen.^{113,114}

FIGURE 8.1: Schematic of an atom probe tomography experiment. Atoms are evaporated from a sample tip and accelerate towards a detector using a pulsed local electrode or laser pulse. The time of flight (TOF) and x - y coordinates are used to reconstruct the sample in 3D. The reconstruction in this figure is from the actual $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ sample used in my experiment, and was done using 10.6 million ions, of which 50 000 Al ions are pictured.

CONTRIBUTIONS TO THE FIELD

9.1 *Introduction*

So far, I have to a large extent concentrated on methods of calculating the vibrational contribution to the free energy. However, in order to determine phase stability it is necessary to take into account all contributions, including electronic energy and entropy, configurational entropy, and magnetic energy and entropy (if applicable). Some (or all) of these contributions are included depending on the complexity of the system and the level of approximation.

In the first instance, I discuss several crystalline systems of industrial interest, and continue by looking at some random alloys. Most of these are grown as hard coating thin films for use as cutting tools. They include TiN, CrN and AlN, all of which have simple crystal structures such as rocksalt and wurtzite. CrN is particularly interesting because it is magnetic; it has an antiferromagnetic orthorhombic phase which is stable at low temperatures, and a cubic paramagnetic phase that is stable at high temperatures.

AlN is a product of decomposition of many alloy systems; and the wurtzite phase is unusual in having one of the highest thermal conductivities of non-metals, and is used as a heatsink substrate and in ultraviolet LEDs. AlN also forms pseudobinary alloys when mixed with transition metal nitrides. In particular $\text{Ti}_{1-x}\text{Al}_x\text{N}$ has a high hardness and undergoes spinodal decomposition at high temperatures, resulting in age-hardening. For this reason, other group IV pseudobinary alloys are also of interest, owing to the possibility that they may be subject to a similar phenomenon, so I also study $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$. The components form metastable alloys (i.e. are immiscible) at low temperatures, but a solid solution at high temperatures. By reconstructing the phase diagram from first principles, it is possible to find the solid solution regions, and help to explain why cubic/metastable $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$ thin films are so difficult to grow.

Finally, I also consider the case of iron carbide, which is potentially important at the Earth's core since carbon alloying may explain why its density is lower than that of pure hexagonal close-packed iron. The details of the potential phases are the subject of much debate.

9.2 Phase stability in crystalline solids

9.2.1 ALUMINIUM NITRIDE

Wurtzite AlN is a wide band gap semiconductor with an unusually high thermal conductivity of $319 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. It undergoes a pressure-induced phase transition to a rocksalt-like phase at high pressures. The phase diagram has been computed in the quasiharmonic approximation, but the pressure and temperature range is limited by dynamical instability at large (zero temperature) cell volumes.^{10,22} TDEP calculations are therefore ideal for predicting its properties.

The reconstructed phase diagram (figure 9.1) shows the effect of anharmonicity at high temperatures: the region in which the wurtzite phase is stable closes, and the rocksalt phase becomes thermodynamically stable at around 3200 K. The melting point of AlN is unknown, but is estimated at around 3000–3500 K, so it is unclear whether this phase transition will occur.

Intrinsic anharmonicity also affects the thermal expansion of AlN, which leads to a divergence from the quasiharmonic values. The cell volume is plotted as a function of temperature in figure 9.2, demonstrating that the TDEP cell volumes increase much more rapidly as a function of temperature than the QHA volumes, and that this effect is much more pronounced for the rocksalt phase, suggesting that it may be subject to more anharmonicity.

FIGURE 9.1: Phase diagram of AlN, showing the ambient pressure wurtzite phase and the high pressure/temperature rocksalt phase. Including anharmonicity has the effect of closing the phase boundary, stabilising rocksalt AlN at high temperatures and ambient pressure.

FIGURE 9.2: Comparison of volume as a function of temperature computed within the QHA and anharmonically using TDEP. Beyond approximately 2000 K, intrinsic anharmonicity begins to affect thermal expansion. The rocksalt phase undergoes significantly more thermal expansion at high temperatures, suggesting it is affected by a greater degree of intrinsic anharmonicity than wurtzite.

There is a significant divergence between the thermal expansions treated quasiharmonically and with TDEP at high temperatures. The difference due to *intrinsic* anharmonicity is almost twice as large in the case of the rocksalt phase as manifested at 3500 K in figure 9.2. This difference may explain the change in the phase boundary at high temperature.

9.2.2 CHROMIUM NITRIDE

Chromium nitride is an industrially used ceramic coating that has two main phases of interest. At low temperatures, it adopts an antiferromagnetic orthorhombic structure, and at high temperatures a paramagnetic cubic structure. Modelling the cubic phase is difficult because it is necessary to simultaneously include vibrations, and the high temperature paramagnetic contribution in the free energy. We achieved this using the DLM-MD method (section 3.3.1) in combination with TDEP.

TDEP was used to extract phonon dispersions for both phases. In the case of the orthorhombic phase, the AIMD simulations were performed with spin-polarised DFT to include the effect of antiferromagnetism, while DLM-MD was used to treat the paramagnetic cubic phase. In the cubic phase, the magnetic moments were generated randomly, and forced to undergo spin flips by substitution with another random state, with a time period of 10 fs. It was also shown that the potential energy was converged for this spin flip period.

A complete description of the paramagnetic state requires the contribution of the magnetic entropy, which can be approximated as a mean field at high temperatures.^{116,117} The magnetic entropy is interpreted as the orientational disorder of the spin alignments for a Heisenberg-like system in which the spins are collinear, and is used here as a first approximation for the case of CrN.

Including only the electronic and magnetic contributions to the free energy, the orthorhombic phase is stable at low temperatures. The effect of adding the vibrational contribution to the free energy in both phases is to shift the phase boundary to lower temperatures, closer to the experimental values (figure 9.3). Although we did not capture the true paramagnetic state, we have made a first

approximation at including the paramagnetic contribution to the free energy in combination with fully anharmonic vibrations, and used them to reconstruct the phase diagram.

9.2.3 IRON CARBIDE

The solid inner core of the Earth is believed to be predominantly comprised of iron, but seismological observations suggest that the density of iron is too high to account for the sound velocities. The most likely reason for this density mismatch is the presence of elements lighter than iron in the core. Cosmological and thermodynamic considerations suggest that one of the most likely candidates is carbon. Both cementite Fe_3C and hexagonal Fe_7C_3 have been suggested as potentially important phases, but recently a newly discovered orthorhombic phase of Fe_7C_3 was experimentally synthesized at pressures of up to 200 GPa with a Poisson's ratio comparable to that of the Earth's core. Experiments are not capable of reaching the conditions of the Earth's core (350 GPa, 5000–7000 K), but simulations are capable of determining the phase stability.

The Gibbs free energies of the hexagonal and orthorhombic phases were computed in the quasiharmonic approximation with the aim of making a first estimate of whether the new orthorhombic phase would be competitive at the conditions of the Earth's core. In figure 9.4, it can be seen that at 150 GPa, the two phases are essentially degenerate, within the typical error bars of first principle calculations (approximately 5 meV/atom). As the temperature increases the orthorhombic phase is stabilised with respect to the hexagonal phase. However it is difficult to determine at which temperature the quasiharmonic approximation breaks down, so it is dangerous to extrapolate this result to high temperatures. At 360 GPa, however, the hexagonal phase is more stable by a clear margin, in excess of 50 meV/atom, increasing with temperature. This

FIGURE 9.4: Gibbs free energies of hexagonal (h-) and orthorhombic (o-) Fe₇C₃ at 150 GPa and 360 GPa. The lower panel shows the difference in free energies between the two phases. At 150 GPa, the free energies are within the error bars of *ab initio* calculations and the phases are essentially degenerate, although it appears that the orthorhombic phase is stabilised by temperature. However, the hexagonal phase is clearly favoured at 360 GPa.

suggests that the new orthorhombic phase is unlikely to be of any importance at the Earth's core.

I have made some preliminary calculations using TDEP, and including intrinsic anharmonicity appears to dramatically change the picture, as can be seen in figure 9.5. Compared with my other calculations on crystalline structures, these iron carbide calculations are extremely challenging, since the orthorhombic structure has such a large unit cell.

There are 80 atoms in the unit cell of orthorhombic Fe₇C₃, and I used a $1 \times 3 \times 1$ supercell, which contains 168 Fe atoms and 72 C atoms. This results in 336 960 unknowns in the force constant tensor in equation (6.8), which reduces to 660 symmetry-irreducible unknowns. There are many other difficulties when dealing with a unit cell of this size, such as force convergence, convergence with respect to the k-point grid and the amount of computer time required to perform the AIMD simulations.

FIGURE 9.5: Predicted phase diagram for Fe_7C_3 , including the hexagonal ($\text{h-Fe}_7\text{C}_3$) and orthorhombic ($\text{o-Fe}_7\text{C}_3$) phases, calculated using TDEP. When intrinsic anharmonicity is included, the orthorhombic phase is strongly stabilised at the temperature and pressure of the Earth's core (330–360 GPa, 5000–7000 K). There is also a regime in which Fe_7C_3 decomposes to Fe_2C and Fe_3C .

At 360 GPa, the hexagonal phase is still stable at low temperatures; however, with anharmonicity, the orthorhombic phase is stabilised at high temperatures, to the extent that it may have a role to play at the Earth's core. Zero temperature structure prediction calculations suggest that a previously unknown composition, Fe_2C , will be thermodynamically stable at 350 GPa.¹¹⁸ They also suggest that hexagonal Fe_7C_3 will decompose as follows at 350 GPa:

To test whether this is feasible at high temperatures, I also computed the Gibbs free energy surface of the sum of the two decomposition phases and added it to the phase diagram, which shows that there is a narrow regime at roughly the pressure of the Earth's core but lower temperatures, in which this decomposition occurs.

9.3 Phase stability in alloys

The high computational cost of vibrational free energy calculations makes constructing the phase diagram of an alloy a challenging task. This is traditionally done via quasiharmonic phonon calculations using zero Kelvin equilibrium structures. However, this approximation breaks down at high temperatures, as I have demonstrated for crystalline AlN and Fe₇C₃. A similar effect is expected for alloys.

In this section, I describe my method of calculating free energies for alloys and its application to some example systems. I start by discussing how to include configurational disorder in a TDEP calculation, and continue to detail the approximations used to make the *ab initio* vibrational calculations tractable.

9.3.1 THE SIFC-TDEP METHOD

9.3.1.1 Description

I have developed a new method that enables the computation of the vibrational contribution to the free energies for a randomly disordered alloy. This method is based on TDEP, which relies heavily on crystal symmetries to be computationally efficient. Briefly, it employs special quasirandom structures (SQS)²⁹ to model the substitutional disorder, and the force constants are given by symmetry of the parent lattice.

The first step is to generate a substitutionally disordered alloy configuration by distributing atoms on the sites of a SQS.²⁹ These atoms interact with effective force constants which have full symmetry of the underlying crystal lattice, which reduces the computational expense. The lattice vibrations are described by a model Hamiltonian constructed using the temperature dependent effective potential (TDEP) method,^{1,2} as described in section 6.3. The model Hamiltonian (6.5) is truncated at the second order and the translational and spatial symmetry (section 5.1) of the underlying crystal lattice are imposed by treating the components of the alloy as symmetry equivalent. The real interactions are computed using DFT and mapped to effective interactions expressed by the interatomic effective alloy force constants $\tilde{\Phi}_{ij}$. The model Hamiltonian can be written,

$$\hat{H} = U_0 + \sum_{i\alpha} \frac{p_{i\alpha}^2}{2m_i} + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} \tilde{\Phi}_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta}, \quad (9.2)$$

where $\mathbf{p}_i$ and $\mathbf{u}_i$ are the momentum and displacement of atom i . As in section 6.3, U_0 is a renormalised ground state energy that implicitly contains anharmonicity, and additionally in this case, the thermal effects of substitutional disorder. Obtaining $\tilde{\Phi}_{ij}$ is no different to calculating the effective force constants for an ordered system, described in detail in section 6.3: we minimize the difference in forces and energy between the model Hamiltonian (9.2) and the real system, in this case Born-Oppenheimer molecular dynamics of a disordered alloy. These effective force constants $\tilde{\Phi}_{ij}$ are defined at fixed volume, concentration and temperature, in contrast to the normal TDEP force constants, which are defined at fixed volume and temperature.

Given the effective force constants $\tilde{\Phi}_{ij}$, we require the phonon density of states to determine the vibrational free energy. To account for mass disorder, we use the effective force constants in a new, larger supercell, where the atoms interact via $\tilde{\Phi}_{ij}$, but have the correct masses. The species are distributed according to a SQS, where pair correlations are subject to the same distance cutoff as the force constants. Obtaining phonon frequencies and free energies for this cell is straightforward (see section 5.2.1), and converging the effect of mass disorder is as simple as increasing the cell size.

The new approach is called symmetry imposed force constants temperature dependent effective potential method (SIFC-TDEP). Note that the accuracy of the free energy calculations can always be improved, for example, by using a more complex model Hamiltonian. This can be achieved using an expansion of the pairwise force constants AB, BC, AC... resulting in different force constants for different pairs of species; however, this is not necessary for our test case, the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloy.

FIGURE 9.6: Convergence of vibrational free energy of $\text{Zr}_{0.5}\text{Al}_{0.5}\text{N}$ at 1500 K with respect to a) SQS size b) q-point grid density for a fixed SQS. In this case, the calculation is converged for a SQS of dimension $5 \times 5 \times 5$, and for a $15 \times 15 \times 15$ q-point grid.

9.3.1.2 Practical procedure

A SIFC-TDEP calculation can be performed using the following procedure:

1. Generate a SQS cell, optimizing the short-range order parameters that would represent the most random alloy.
2. Perform static DFT calculations to get initial volume grid for the potential energy, by fitting the equation of state at 0 K. This is just an initial grid; at higher temperatures, the equilibrium volume will change according to thermal expansion. The atoms should be positioned at their equilibrium positions, therefore for each volume we statically relax the SQSs at to ensure that the net forces acting on atoms are zero. If they are not zero, the displacements extracted from AIMD will lead to incorrect force constants, and possibly even bogus imaginary frequencies.
3. Equilibrate the molecular dynamics simulations. This can be achieved with by running AIMD for a few hundred time steps and computing initial phonon dispersions to generate thermalised cells, as described in section 6.6.
4. Perform a set of canonical ensemble *ab initio* molecular dynamics calculations on the chosen temperature-volume grid. It is important to relax the SQS structures using the electronic temperature corresponding to the AIMD simulations.
5. From these simulations, choose a subset of uncorrelated samples and recalculate their energies at a higher accuracy.
6. When the simulations are converged, extract a set of potential energies, forces and displacements for each time step. From these, compute force constants as described in section 6.3, by minimizing the difference in forces between real and model systems as in TDEP equations (6.7)–(6.10).
7. Map the effective force constants to the SQS and calculate the frequencies and phonon density of states. The size of the SQS and q-point grid must be converged with respect to the free energies as in figure 9.6. We now have the force constants as a function of volume and temperature. In principle, these can be used to compute free energies within the extrema of the chosen volume/temperature grid. However, it is useful to interpolate the force constants between the grid points to get the free energy as a smooth function of volume, temperature and concentration. The interpolated force constants are then mapped back to the SQS. The computational cost of this procedure is negligible.
8. The procedure to this point results in the Helmholtz free energy including anharmonic term U_0 . By taking the numerical derivative of the Helmholtz free energy with respect to the volume at constant temperature as described in chapter 4, we can compute the Gibbs free energy and thermal expansion for the composition or phase of interest.

9.3.1.3 Benchmark test

To check the validity of this approach, I implemented the formally exact method of thermodynamic integration (described in detail in section 6.5) in VASP.^{53,54,55,56} Thermodynamic integration is based on the Kirkwood coupling theorem.^{59,99}

$$F_r = F_m + \underbrace{\int_0^1 \langle U - U_m \rangle_\lambda d\lambda}_{\Delta F}, \quad (9.3)$$

where U_m and U are potential energies of model and real systems respectively. Equation (9.3) is formally exact for phase equilibria in alloys at relevant temperatures. In practice, calculating ΔF can be very difficult,⁸⁹ so my general strategy is to choose the model system with the smallest possible ΔF , ideally within the error bars of *ab initio* calculations.

The implementation involves mixing interatomic forces at each time step in a molecular dynamics simulation with a parameter λ , then calculating on-the-fly potential energies for the model Hamiltonian. At each time step, the difference in potential energies was taken and time-averaged. Langevin dynamics was used to control the temperature and break the mode-locking. The numerical integration over coupling parameter λ was carried out over 5 discrete steps, and the AIMD simulations were run for $\sim 100\,000$ time steps with k-point sampling at the Gamma point only. A set of uncorrelated snapshots was selected from AIMD and upsampled to high accuracy with a $3 \times 3 \times 3$ k-point mesh to ensure convergence for ΔF using the UP-TILD method.

To ensure that the free energies obtained from the SIFC-TDEP method were correct, thermodynamic integration was performed for a single composition of the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ test system ($\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$) at the equilibrium volume corresponding to 1500 K. From the inset of figure 9.7 it can be seen that the full TDEP vibrational free energy lies slightly above the single thermodynamic integration point, within 5 meV/atom (i.e. less than the typical systematic error for

FIGURE 9.7: Vibrational free energy of $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ computed using SIFC-TDEP and zero temperature force constants, including a single point computed using thermodynamic integration. The UP-TILD data point is within 5 meV/atom of the SIFC-TDEP curve, which is within the error bars of *ab initio* calculations.

DFT calculations). Moreover, the harmonic free energy calculated at the zero-temperature equilibrium volume has a significantly higher value. This benchmark test demonstrates that my method is useful.

9.3.2 THE PHASE DIAGRAM OF TITANIUM ALUMINIUM NITRIDE

In order to demonstrate the viability of SIFC-TDEP, I used it to describe the decomposition thermodynamics of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys,^{36,119} a system for which lattice vibrations underpin an unusual and technologically useful isostructural decomposition.³⁵ Metastable cubic $\text{Ti}_{1-x}\text{Al}_x\text{N}$ undergoes spinodal decomposition at high temperatures to form nano-scale domains of cubic TiN and AlN, through which extra stress is required to propagate dislocations,^{36,120,38} which results in age-hardening. This makes $\text{Ti}_{1-x}\text{Al}_x\text{N}$ thin films ideal for coating cutting tools. Remarkably, the calculated values for the maximum temperature of the miscibility gap vary between approximately 6050 and 9000 K,^{5,67} depending on the methodological details, and as low as 3790 K within the Debye-Grüneisen approximation.¹²¹ These are well above the dissociation temperatures of TiN and AlN. However, cutting tools may reach temperatures of up to 1300 K,¹²² at which point thermal expansion and anharmonic vibrations could be of considerable importance. Existing studies either neglect or use an incomplete description of the vibrational contribution to the free energy, since the methodological challenges and computational efforts required to calculate the phonon spectra of a substitutionally disordered solid using *ab initio* approaches are considerable. The stable phase for an alloy is defined as the one with the lowest Gibbs free energy of mixing. SIFC-TDEP was employed to calculate the Gibbs free energy of mixing for a range of fixed compositions. SIFC-TDEP is capable of coping with compositions that are dynamically unstable under certain

FIGURE 9.8: Phase diagram of $\text{Ti}_{1-x}\text{Al}_x\text{N}$. The dotted line shows the change in the miscibility gap if vibrations are not included.

temperature regimes, such as in the case of $\text{Hf}_{1-x}\text{Al}_x\text{N}$, which will be discussed later. Returning to the ideas introduced by Gibbs,^{70,71} it is possible to numerically minimize the Gibbs free energy of mixing as described in section 4.3.1.

The Helmholtz free energy can be decomposed into vibrational (“vib”), configurational (“config”) and electronic terms (“el”):

$$F = U - TS = F_{\text{el}} + F_{\text{vib}} + F_{\text{config}}. \quad (9.4)$$

The vibrational contribution is often neglected in calculations of the phase diagrams since configurational entropy related to configurational disorder in alloys is the largest contribution after the mixing enthalpy (i.e. the internal energy at constant pressure). One can consider configurational disorder as a function of temperature⁶⁷ but its variation is minimal, justifying the use of the mean field configurational entropy. Including the temperature dependence of the vibrational entropy shifts the miscibility gap, lowering it from 6560 K to 2860 K, by a factor of more than two. This dramatic effect can be explained by opposite signs of the vibrational free energy of mixing with respect to the mixing enthalpy, and is discussed in section 9.3.4. However, only a combination of these effects can significantly change the regions of stability on phase diagram. In figure 9.8, I show the phase diagrams when both both configurational and vibrational entropy are included, contrasted with the effect of only including configurational entropy. The combination of those effects lowers the miscibility gap.

This result raises the question of whether it is exclusively the vibrational energy that suppresses the miscibility region, or whether it is the effect of anharmonicity. The anharmonicity can be decomposed into a thermal expansion term and the anharmonic terms arising from the temperature dependence of the potential resulting from higher order expansion terms. In SIFC-TDEP, the model is limited to a harmonic fit to an anharmonic potential, but still captures this anharmonicity. Figure 9.9 demonstrates the huge effect of the latter contribution, and that the quasiharmonic approximation is not sufficient at high temperatures. The quasiharmonic terms explicitly includes only thermal expansion which is the first order of anharmonicity (section 6.1). In SIFC-TDEP we

FIGURE 9.9: Vibrational Gibbs free energy of $\text{Ti}_{50}\text{Al}_{50}\text{N}$. The effect of thermal expansion can be seen by comparing the harmonic SIFC-TDEP-HA curve with the quasiharmonic SIFC-TDEP-QHA curve. The effect of anharmonicity at high temperatures can be seen by comparing the quasiharmonic SIFC-TDEP-QHA curve with the fully anharmonic SIFC-TDEP curve. Anharmonic effects become considerable at temperatures above 2000 K.

explicitly include all anharmonic terms: thermal expansion and anharmonicity though the temperature dependent potential.

9.3.3 EXPERIMENTAL VERIFICATION

Experimental verification of the theoretical phase diagram (figure 9.8) is a challenging task. Because of the high melting temperature of TiN, its alloys are synthesized by thin-film deposition techniques, often followed by an annealing. Due to the explicit out-of-equilibrium nature of this metastable transformation, direct information from equilibrium experiments is not available, so atom probe tomography experiments were performed on thin films of $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ which were annealed at 1073 K for 2, 4, 12 and 100 hours.

Figure 9.10 shows 2D compositional maps of 2 nm thick slices through the deposited film. The initially homogeneous cubic solid solution decomposes isostructurally, forming cubic Ti- and Al-rich domains during the first 12 hours. After 100 hours, the metastable cubic AlN-rich phase has to a large extent transformed to its stable wurtzite phase.¹²² During the first 12 hours, the evolution of the microstructure and the chemical segregation become gradually more pronounced, which is consistent with the spinodal decomposition.⁴⁰ After 100 hours the microstructure is coarser.

The phase diagram (Figure 9.8) shows a substantial shift in the solubility at 1073 K compared to the predictions excluding vibrational effects, especially for the solubility of Al in TiN. In order to experimentally verify this, we extracted the maximum and minimum local composition in the decomposed microstructure by constructing histograms of the concentrations in 1 nm^3 bins throughout

FIGURE 9.10: 2D contour plots extracted from atom probe tomography data for $\text{Ti}_{1-x}\text{Al}_x\text{N}$ at different annealing times. After two hours of annealing, the film consists of small isostructural cubic domains of AlN and TiN. As time passes, the metastable cubic AlN domains transform to stable wurtzite AlN, resulting in a coarser microstructure.

the sample. These two local compositional extrema are plotted in 9.11 as a function of annealing time, and demonstrate the timescale and decomposition path of the alloy. The solubility of Al in TiN at 1073 K tends to a final solubility of $\sim 2\%$ according to the theoretical phase diagram, while the solubility of cubic AlN asymptotically approaches the theoretical value ($x = 1$).

This is manifested on the extreme left of the computed phase diagram (figure 9.8). The experiment starts in the middle of the miscibility region at 1073 K and $x = 0.5$. In the absence of vibrations, annealing causes it to decompose to pure TiN and AlN, as evidenced by the line labeled “without vibrations”. Including vibrations, there is a narrow solid solution region around the $x = 0$ composition and 1073 K, which agrees with the observation that the TiN solubility asymptotically approaches approximately 2%.

However, this explanation comes with a caveat. We do not consider the possibility of the wurtzite AlN phase forming in the theoretically reconstructed phase diagram, even though this is the experimentally verified ground state. In principle, it is necessary to include the calculations on all $(\text{Ti}_{1-x}\text{Al}_x\text{N})$ alloys and AlN) wurtzite phases on the phase diagram.

FIGURE 9.11: The limits of the concentration of metal sublattices as a function of aging time. The curves converge to 1 on the AlN-rich side, and to approximately 2% on the TiN-rich side. This supports the predicted phase diagram, which suggests that there will be a narrow solid solution region when x is close to zero.

9.3.4 OTHER GROUP IV ALUMINIUM NITRIDES

Having covered an experimentally well-characterised system, I will now discuss the vibrational contribution to the Gibbs free energy of two more systems with higher mass disorder and phase diagrams that have not been theoretically constructed, cubic $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and cubic $\text{Hf}_{1-x}\text{Al}_x\text{N}$. Using the example of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys I showed that my new method succeeds where the static calculations fail by reducing the maximum temperature of the miscibility gap to a realistic value. However, Ti (atomic mass 47.867) and Al (26.982) are somewhat close in mass, whereas the substitution of different group IV elements, Zr (atomic mass 91.224) and Hf (178.49) results in much greater mass disorder. This will also serve to demonstrate the reliability of the force constant symmetrisation when the mass disorder is higher.

Using the same method as for $\text{Ti}_{1-x}\text{Al}_x\text{N}$, I have constructed theoretical phase diagrams for $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$ in figure 9.12. There are two obvious points to note. Firstly, the solid solution regions for $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$ occur at above 1500 K and over a very narrow, low AlN concentration range. In the absence of the vibrational contribution, the miscibility gap would close at unrealistic temperatures, in excess of 15 000 K. $\text{Hf}_{1-x}\text{Al}_x\text{N}$ is stable over a slightly larger region. Secondly, it can be seen that $\text{Hf}_{1-x}\text{Al}_x\text{N}$ is dynamically unstable at low temperatures and a large concentration range ($0.17 < x < 0.85$).

Regions of spinodal decomposition are defined as the second derivative of the Gibbs free energy and are plotted on the phase diagram. However, this is an isostructural phase diagram that includes only cubic like structures, but not hexagonal. We can claim that there is a potential spinodal decomposition, but it is unlikely to be observed in experiments since the hexagonal phases of $\text{Hf}_{1-x}\text{Al}_x\text{N}$ and $\text{Zr}_{1-x}\text{Al}_x\text{N}$ are thermodynamically favoured. On the other hand, it is possible that the hexagonal phase is kinetically locked due to the experimental temperatures. One possible explanation for the lack of observed

FIGURE 9.12: Phase diagrams of $\text{Ti}_{1-x}\text{Al}_x\text{N}$, $\text{Hf}_{1-x}\text{Al}_x\text{N}$ and $\text{Zr}_{1-x}\text{Al}_x\text{N}$, in order of size of solid solution region. Despite being in between Ti and Hf in group IV of the periodic table, Zr is the most resistant to forming a solid solution. $\text{Hf}_{1-x}\text{Al}_x\text{N}$ is dynamically unstable at low temperatures.

spinodal decomposition is the excessive mismatch between the MN and AlN lattices for Hf and Zr.^{123,124}

The phase diagrams of $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$ are remarkably similar, the main difference being the dynamical instability in the $\text{Hf}_{1-x}\text{Al}_x\text{N}$ phase diagram. This can be explained by examining the contributions to the Gibbs free energy of mixing in figure 9.13. The difference in mixing enthalpies between $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$ is almost identical to the difference between their vibrational free energies, so they cancel each other out to a large extent, resulting in a very similar free energy of mixing.

One might naïvely expect that going down group IV in the periodic table would result in alloys with a lower vibrational free energy, since more massive atoms have lower vibrational frequencies. However, this trend is not observed suggesting that chemical and volume considerations are more important.

The configurational entropy is the same for all three alloys in the mean field approximation, and is of the same order of magnitude as the vibrational entropy. The vibrational contributions of all three alloys are of the same order of magnitude, but $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$ have considerably higher mixing enthalpies, which explains why there is no solid solution region on the phase diagram in the absence of a vibrational contribution. These trends can be explained using a simple Debye model, which relates the Debye frequency, the maximum vibrational frequency of a system, to the bulk modulus. The computed bulk moduli of all three alloys are plotted in figure 9.14, demonstrating the huge deviation from Vegard's law.

If the bulk modulus obeyed Vegard's law, the vibration free energy of mixing would be minuscule, while a positive deviation would give a positive free energy of mixing, and as is the case here, a negative deviation would give a negative free energy of mixing. Simply put, the softer the material, the weaker the chemical bonds are, and the larger the phase space for the vibrations; the net result is a larger the vibrational entropy. This is why the mixing enthalpy and vibrational free energy cancel each other out to a large extent, resulting in a small Gibbs free energy of mixing. This interpretation is borne out by the peak in the mixing enthalpy, at $x = 0.7$, for which the concentration coincides with the minimum in the bulk modulus. The sum of the enthalpic and vibrational contributions is shown in figure 9.15. $\text{Zr}_{1-x}\text{Al}_x\text{N}$ has the highest mixing free energy as a result of its high enthalpy, and the trend in stability does not follow the trend in atomic mass.

FIGURE 9.13: Mixing enthalpy (positive), vibrational entropy (negative) and configurational entropy (negative) contributions to the Gibbs free energy of $\text{Ti}_{1-x}\text{Al}_x\text{N}$, $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$. These are summed to compute the Gibbs free energy of mixing. The configurational entropy is the same for all three alloys.

FIGURE 9.14: Bulk moduli of $\text{Ti}_{1-x}\text{Al}_x\text{N}$, $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$ as a function of concentration at 1500 K. The straight lines are present to show the deviation from Vegard's law.

It seems intuitive that the $M_{1-x}Al_xN$ system would be a good test system for the effect of mass disorder, since Zr has approximately twice the mass of Ti, and Hf has approximately twice the mass of Zr. However, in spite of its lower vibrational entropy $Hf_{1-x}Al_xN$ is less stable than $Ti_{1-x}Al_xN$. The same line of reasoning would suggest that higher concentrations of Hf atoms in $Hf_{1-x}Al_xN$ would result in a lower vibrational entropy and therefore a skew in the vibrational free energy plot (figure 9.13) towards the MN-rich side of the plot. This is the case for both Hf and Zr, but despite the fact that Hf is so much more massive, the curves have their minima at roughly the same concentration. Moreover, the curve for $Ti_{1-x}Al_xN$ is skewed in the opposite directions. The strongest conclusion that can be drawn from these observations is that mass disorder does not have a noticeable effect in $M_{1-x}Al_xN$ systems, and that it is dwarfed by chemical and thermal expansion effects. It could be argued that as a pseudobinary system, $M_{1-x}Al_xN$ is not a good test of the effect of mass disorder, since chemical bonding has such a decisive influence, and the situation is complicated by the presence of nitrogen atoms. A better test of the SIFC-TDEP method would be a simple binary system.

Finally, I show the phonon density of states of $Hf_{0.75}Al_{0.25}N$ at 0 K and 700 K in figure 9.16. This composition is dynamically unstable at 0 K, as evidenced by the imaginary frequencies, but is stabilised at 700 K by the vibrational entropy. This demonstrates that in contrast with the common tangent construction, dynamical instability is not a problem in computing phase diagrams when using SIFC-TDEP. Together with the high mixing enthalpies of $Zr_{1-x}Al_xN$ and $Hf_{1-x}Al_xN$, this dynamical instability explains why it is so difficult to synthesise the metastable cubic phase of these two alloys.

FIGURE 9.15: Total Gibbs free energy of $\text{Ti}_{1-x}\text{Al}_x\text{N}$, $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$ at 0 K and 1500 K. Note that $\text{Hf}_{1-x}\text{Al}_x\text{N}$ is dynamically unstable at 0 K, and therefore does not have a well-defined Gibbs free energy, so its enthalpy is plotted for comparison.

FIGURE 9.16: Phonon density of states of $\text{Hf}_{0.75}\text{Al}_{0.25}\text{N}$ at 0 K and 700 K. The imaginary frequencies at 0 K, which vanish at 700 K, demonstrating that $\text{Hf}_{1-x}\text{Al}_x\text{N}$ is stabilised by temperature.

9.4 Temperature dependent mechanical properties

Temperature also affects mechanical properties, but is rarely considered in calculations of elastic constants. Elastic properties can easily be calculated from first principles at zero temperature, resulting in temperature-independent elastic constants, which are unreliable at high temperatures.

Elastic constants are important for optimizing the performance of materials used in high temperature applications. I consider the specific example of TiN and TiN-based alloys, which are important hard-coating materials. Elasticity, and more specifically, elastic anisotropy,^{39,125} affects their microstructure and therefore hardness as a result of spinodal decomposition in $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys.^{126,127,36} Moreover, the elastic constants are important in the design of new materials with specific properties, but can be difficult and tedious to measure, especially in the case of thin films. My interest in this topic is to elucidate the atomistic origins of high temperature elastic anisotropy, and in the context of Earth science, where elastic constants are important in understanding seismological observations such as sound wave velocities.

In the first instance, I discuss the zero-temperature elastic constants of iron carbide. I also consider two method of computing finite temperature elastic constants; the first of these is stress-strain relationships, or Hooke's law, and the second is solving the equations of motion for the crystal using interatomic force constants in the long wavelength limit. I use the former to calculate the elastic constants and anisotropy of crystalline TiN, and the latter for the case of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys.

9.4.1 STATIC ELASTIC CONSTANTS OF IRON CARBIDE

Sound velocities are are measured seismologically to determine the composition of the Earth, so it is useful to be able to calculate them theoretically in order to determine the viability of materials that may be important in the Earth's core.

FIGURE 9.17: Longitudinal velocity (v_p) and transverse sound velocity (v_{s1} , v_{s2}) in km s^{-1} for orthorhombic Fe_7C_3 at experimental (150 GPa) and Earth's core (360 GPa) pressure. Note the anisotropy in the sound velocities.

I computed the sound velocities of the new orthorhombic Fe_7C_3 phase by solving the Christoffel equation (chapter 7.1) using static elastic constants. The calculated sound velocities ranges of $v_p = 9.30\text{--}10.1 \text{ kms}^{-1}$ and $v_s = 3.94\text{--}4.84$ at 150 GPa, which compare well with the experimental values of $v_s = 4.6 \text{ kms}^{-1}$ and $v_p = 10.7 \text{ kms}^{-1}$ at 158 GPa and 300 K,²⁷ despite the fact that we only consider single-crystal elastic constants computed at zero Kelvin. Here, the v_s components are averaged since only one component is experimentally reported. I have also computed the anisotropy of the sound velocities in figure 9.17. The next step would be to calculate the temperature dependent elastic constants.

9.4.2 FINITE TEMPERATURE ELASTIC CONSTANTS FROM STRESS-STRAIN RELATIONS

For TiN, elastic constants were calculated by applying the stress-strain relationships to distorted cells. The temperature dependence was captured by running NVT molecular dynamics simulations and computing the stresses of uncorrelated snapshots. For every equilibrium volume and temperature, it was necessary to use at least five cell distortions, so to reduce the computational expense, a parallel molecular dynamics scheme was employed. Thermally excited initial states were generated as in section 6.6 to minimise equilibration time, and used to start independent molecular dynamics simulations.

The temperature dependent elastic constants of TiN are presented in figure 9.18, demonstrating the decrease in the three symmetry-unique elastic constants with temperature. In particular, c_{11} is very strongly temperature dependent, resulting in an increase in elastic isotropy as the temperature increases. This increase in isotropy may explain the softening of TiN at high temperatures.

FIGURE 9.18: Temperature dependent single crystal elastic constants of TiN. Note the different scales: there is only a strong temperature dependence in the C_{11} component, which decreases by almost 30% over the temperature range.

9.4.3 FINITE TEMPERATURE ELASTIC CONSTANTS FROM FORCE CONSTANTS

Using TDEP, or SIFC-TDEP for alloys, one can calculate finite temperature phonon spectra which implicitly include renormalization to all orders of anharmonicity, and thus derive the force constants. From there we can obtain the elastic constants, as in equation (7.3). Using this method results in the correct trend, but the absolute values are incorrect due to finite size effects, and the expression must be scaled by a constant factor ($C_{ij,kl}^{\text{stat}}(V, 0)$ in equation (9.5)) to retrieve the correct temperature dependence.

$$C_{ij,kl}(V, T) = C_{ij,kl}^{\text{stat}}(V, 0) \frac{C_{ij,kl}^{\text{ph}}(V, T)}{C_{ij,kl}^{\text{ph}}(V, 0)}. \quad (9.5)$$

I applied this method to $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys by way of example, decomposing the contributions of thermal expansion and intrinsic anharmonicity to determine their relative effects.

In figure 9.19, the elastic constants are plotted as a function of temperature. Here, they were calculated using two methods: statically (but including thermal expansion), and using SIFC-TDEP. The thermal expansion from SIFC-TDEP is in a good agreement with experiments (figure 9.20), giving us confidence that our free energies and phonon spectra are accurate. The static elastic constants deviate greatly (up to 50 GPa at 2000 K) from the TDEP and SIFC-TDEP values at high temperature. Moreover, the high-temperature trends are different for different elastic constants and different compositions, so we can conclude that attempting to decouple thermal expansion and vibrations is an incorrect approach.

FIGURE 9.19: Temperature dependent elastic constants of different compositions of $\text{Ti}_{1-x}\text{Al}_x\text{N}$. Dotted lines represent static elastic constants including thermal expansion, and solid lines are elastic constants computed using force constants. In the case of the disordered alloys, $\bar{C}$ are symmetry-averaged elastic constants. Note that the difference between elastic constants also changes with temperature.

FIGURE 9.20: Temperature dependence of the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ lattice parameter a , expressed as the ratio $(a - a_0)/a_0$ for different compositions. The theoretical thermal expansion is compared with experimental *in situ* high temperature X-ray diffraction results.

FIGURE 9.21: Elastic anisotropy of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ as a function of temperature and concentration, as computed with SIFC-TDEP. The dashed line illustrates the effect of considering only thermal expansion in a static calculation.

Since the force constants are interpolated over the entire temperature and concentration range in the SIFC-TDEP framework, it is possible to construct a map of the elastic anisotropy (figure 9.21). The dashed line depicts the effect of including thermal expansion without vibrations. The errors for the elastic constant calculations propagate, resulting in a grossly inaccurate temperature dependence.

The relationships between atomic structure and microstructure and hardness are complicated and closely linked to lattice dynamics. Isotropic elastic constants result in domains that are notionally spherical, whereas a high anisotropy will generate elongated domains with irregular shapes and thus more shear stress in the boundaries, and a higher hardness. Building on this notion, we can identify two strategies for improving the hardness of TiAlN alloys. The first is to use Al-rich alloys, which naturally have a higher anisotropy, as shown in figure 9.21. The second is to anneal the alloy at higher temperatures, which similarly increases the anisotropy; the problem with this is avoiding the phase change from cubic to hexagonal at approximately 1300 K.¹²²

9.5 Thermal conductivity of aluminium nitride

In order to describe thermal conductivity, it is necessary to include phonon scattering processes. The lowest order perturbation to the Hamiltonian that includes such phonon-phonon interactions is second order, which describe three-phonon processes.

I have used TDEP to compute the third order force constants and thermal conductivity for the case of AlN. The rocksalt phase can only be grown as a metastable thin film, for which it is difficult to measure the thermal conductivity, but wurtzite AlN is used as a heatsink substrate and there may be a high temperature phase transition from the wurtzite phase, as described in section 9.2.1. Thus a change in the thermal conductivity at high temperature due to a phase transition could have severe consequences.

The effect of third order anharmonicity can be seen in the phonon lineshapes at 2400 K (the temperature at which the phase diagram starts deviating from the QHA) in figure 9.23. The extreme broadening observed for the rocksalt phase indicates that it is subject to far more intrinsic anharmonicity than the wurtzite phase. This is evident when calculating thermal conductivities (as described in chapter 6.4), which are plotted for both phases in figure 9.22. Note that I have only computed the thermal conductivity up to 1000 K, since above this temperature it is approximately constant. It should be noted that the anharmonicity is weak between 0 and 1000 K, and quasiharmonic third order force constants would give approximately the same result.

There is an excellent agreement between the calculated thermal conductivity of the wurtzite phase at ambient temperature and pressure ($320 \text{ W m}^{-1} \text{ K}^{-1}$) and experiments ($319 \text{ W m}^{-1} \text{ K}^{-1}$), so the thermal conductivity of the wurtzite phase can be treated with confidence. The thermal conductivity of the rocksalt phase was found to be $96 \text{ W m}^{-1} \text{ K}^{-1}$, a factor of almost four lower. Setting the third order force constants to 1 (the Peierls approximation) for both phases resulted in thermal conductivities that differed by less than 1%, so the relative conductivities can be attributed to the difference in strength of anharmonic

FIGURE 9.22: Thermal conductivity of wurtzite and cubic AlN as a function of temperature at ambient pressure. In experiments, grain boundaries and defects have a more significant effect on phonon scattering at low temperatures, hence the divergence below 200 K.

FIGURE 9.23: Phonon lineshapes for rocksalt and wurtzite AlN at 300 K and 2400 K at the equilibrium volume for the corresponding temperature. The broadening is much more severe for the rocksalt phase at high temperature, implying a higher degree of anharmonicity. Also note the broadening in the acoustic branches for the rocksalt phase, particularly between 2 and 7 THz.

FIGURE 9.24: Electronic band structure average over a molecular dynamics trajectories for rocksalt and wurtzite AlN at 300 K and 2400 K and ambient pressure. The band structure calculated at the equilibrium volume for the corresponding temperature. Note the change from a direct band gap to an indirect band gap at high temperature for the rocksalt phase.

three-body interactions. On average, the third order force constants are twice as large in the rocksalt phase, compared with the wurtzite.

9.6 Temperature dependent electronic structure of aluminium nitride

Temperature has also been suggested as a means of controlling the electronic band gap in AlN.¹²⁸ At finite temperatures, lattice vibrations and thermal expansion shift and broaden the electronic band structure. To quantify this, I computed the electronic band structure of uncorrelated snapshots from molecular dynamics simulations, and calculated the ensemble average of the bands. Band unfolding^{129,130} was employed to reduce the band structures and average the spectral function. Note that electronic band gaps are consistently underestimated in the GGA formalism, but here I am only interested in the temperature dependence trend. This addition of thermal disorder is not true electron-phonon coupling since in the Born-Oppenheimer approximation electrons and phonons are decoupled by definition, but provides a first approximation for a temperature dependent band structure. The spectral functions for both AlN phases are plotted in figure 9.24.

There is minimal thermal broadening at 300 K, but at 2400 K there is considerable broadening and distortion, which both narrows the band gap and changes it from indirect to direct in the case of rocksalt. The variation of the band gap as a function of temperature is plotted in figure 9.25. These calculations are consistent with cathodoluminescence measurements, which show a band gap decrease of 0.1 eV between 0 and 300 K.¹²⁸ The large change in band gap can be attributed to the atoms occupying different equilibrium positions as the temperature changes, i.e. a different subset of the Born-Oppenheimer potential energy surface, with different electronic structure. The narrowing of the band gap with temperature suggests that temperature may be a method of band gap control and an alternative to doping.

FIGURE 9.25: Band gap as a function of temperature for rocksalt and wurtzite AlN.

CONCLUSIONS

The unifying theme in this thesis is that the effect of temperature is extremely important when modelling the solid state, and that at high enough temperatures, anharmonic effects cannot be ignored. This is manifested in the level of approximation used in the literature. “Static” zero temperature first principles calculations are cheap and easy to perform in the framework of DFT, and are therefore common, but they neglect the first order of anharmonicity, namely thermal expansion. Although they are useful, they fail when the effects of temperature are important, for example, when considering the phase stability of alloys, as in the case of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloys. Static calculations have been performed on this material, but when only the configurational entropy and internal energy are considered, the temperature of the miscibility gap is grossly overestimated as 9000 K. The inclusion of the vibrational entropy brings this down to 2860 K. In other words, if vibrations are neglected, $\text{Ti}_{1-x}\text{Al}_x\text{N}$ would only form a solid solution at inaccessible temperatures. This is supported by my atom probe tomography experiments. I go further by constructing theoretical phase diagrams for $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Hf}_{1-x}\text{Al}_x\text{N}$ alloys, showing that they only form solid solutions at high temperatures and low AlN concentrations. Moreover, I have calculated the limits of the dynamically unstable region of $\text{Hf}_{1-x}\text{Al}_x\text{N}$, below 1000 K. These findings explain why these alloys are so difficult to synthesise — because the mixing enthalpies are so large, and including vibrations results in a very narrow region of solubility.

I also use the examples of CrN and AlN to discuss the problem of determining phase stability. AlN crystallises in the wurtzite phase under ambient conditions, and in the rocksalt phase at high pressure. However, the transition pressure can be reduced by increasing the temperature, i.e. including the vibrational contribution to the free energy. In the case of CrN, the orthorhombic phase is always more stable than the cubic phase at zero temperature, but at high temperatures, the cubic phase becomes stable. This is an example of a case where zero temperature calculations will never tell the full story. Moreover, I show that a combination of magnetic and vibrational contributions to the free energy brings the phase boundary between the cubic and orthorhombic phases into better agreement with experiment.

Even when temperature is included in first principles calculations, it is often in the form of the quasiharmonic approximation. Although under many circumstances it is appropriate, it fails under conditions discussed in section 6.1; in this thesis, I concentrate on its failure at high temperatures, and how to correct it. Continuing on the topic of phase stability, the quasiharmonic approximation is incapable of describing systems that are dynamically unstable at zero temperature, but are stabilised at finite temperature. An example of this effect is rocksalt AlN, modeled with the quasiharmonic approximation at large volumes at 0 K. In principle, the rocksalt phase becomes stable at ambient pressure and high temperature due to anharmonicity (assuming it is below its melting point). This change in stability is a direct result of the much higher degree of anharmonicity present in the rocksalt structure compared with the wurtzite. Another example is $\text{Hf}_{1-x}\text{Al}_x\text{N}$, which has negative frequencies in its phonon density of states at zero kelvin, but is dynamically stable at high temperature. These examples highlight one of the advantages of the TDEP method,

which can cope with dynamic instability at zero kelvin, unlike some perturbation theory-based approaches.

The final example of temperature dependent phase stability I use is that of iron carbide. The recently discovered orthorhombic Fe_7C_3 could be a relevant phase at the Earth's core, assuming it is stable at such high pressures and temperatures. Quasiharmonic calculations suggest that this phase is stable compared to the well known hexagonal phase at experimental conditions, but also suggest that it is considerably less stable than hexagonal at Earth's core conditions.²⁸ Preliminary anharmonic calculations using TDEP suggest that the orthorhombic phase is, in fact, stabilised at high temperatures at the pressure of the Earth's core.

In addition to affecting phase stability, I also demonstrate that temperature and anharmonicity can have a tremendous effect on the mechanical properties of a material. TiN , for example, has elastic constants that are strongly temperature dependent, and the isotropy of the elastic constants increases with temperature.⁶ Using my newly developed SIFC-TDEP methodology for alloys, I also show that the elastic constants for $\text{Ti}_{1-x}\text{Al}_x\text{N}$ are strongly temperature dependent, and that the anisotropy *increases* with temperature. This is particularly interesting, because at low anisotropies, nanocrystals will grow in a notionally spherical way, whereas high anisotropies result in elongated and irregular nanocrystalline domains through which it is harder to propagate internal stresses. As a result, a potential strategy for producing harder $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings is to anneal them at higher temperatures. In practice, however, it is not possible to go to higher temperatures than are currently used, since this would result in a phase change to the wurtzite structure, so a better option might be to use compositions that are richer in AlN .

Finally, I examine the effects of temperature and anharmonicity on both thermal and electronic transport with the example of AlN . Wurtzite AlN , which is the stable phase at ambient conditions, is believed to be the best non-metallic thermal conductor, and as a semiconductor, its thermal transport is dominated by phonons. The high pressure/temperature rocksalt phase is metastable under ambient conditions and can only be deposited as a thin film, for which it is difficult to measure the thermal conductivity experimentally. By solving the Boltzmann transport equation, I calculate the thermal conductivities of both phases, finding good agreement with experiment for wurtzite, and showing that the thermal conductivity of the rocksalt phase is lower by a factor of almost four. Since AlN is used as a heatsink substrate, this may be important at temperatures at which there is a phase transition to rocksalt, at which point the thermal transport efficiency would drop massively.

In summary, I have computed phase diagrams, elastic constants and transport properties for a variety of technologically relevant thin film-type systems, demonstrating that temperature and anharmonicity are crucial in describing them correctly. I have also developed a method to perform fully anharmonic phonon calculations on alloys. I have confirmed the accuracy and efficiency of this method with tests on $\text{M}_{1-x}\text{Al}_x\text{N}$ thin film alloys as proof of concept. In the future, I hope that the predictive power of my method will be used to design new materials with an accurate description of their temperature dependent properties.

FUTURE WORK

There are many directions in which my work on alloys can be extended. In the case of $\text{Ti}_{1-x}\text{Al}_x\text{N}$, short range disorder had very little influence judging from the free energy. However it is likely to be important in other systems. For this reason, I would like to implement force constant disorder by the expansion of second order pairwise force constants in the SIFC-TDEP method. It was difficult to see any trend resulting from mass disorder in the free energies of the $\text{M}_{1-x}\text{Al}_x\text{N}$ alloys, probably because the effect of mass disorder was swamped by the effect of enthalpy. It would therefore be instructive to evaluate the effect of mass disorder using a simpler true binary system which is not subject to the complex chemical effects observed in $\text{M}_{1-x}\text{Al}_x\text{N}$. Moreover, in its current form, the force constants between unlike atomic species are treated with the symmetry of the parent lattice, but it is necessary to include the difference in force constants between unlike pairs of atomic species.

Due to their low symmetry, phonons are scattered more in random alloys than in crystals, so alloys have lower thermal conductivities than crystals. This gives them great potential as thermoelectric materials, which must have low thermal conductivities to maximise the thermoelectric figure of merit. However, SIFC-TDEP currently lacks the ability to compute third order force constants. This is an extremely difficult task, and will require great progress.

The work on iron carbide demonstrated that the quasiharmonic approximation is insufficient when discussing the extreme temperatures at the Earth's core, and that it is necessary to include intrinsic anharmonicity. I have made progress in constructing the phase diagram of Fe_7C_3 , including its decomposition to Fe_2C and Fe_3C , but it is important to determine the stability of the phases with respect to decomposition to pure iron and carbon.

Finally, in my work on AlN , I computed the phonon lineshapes and thermally disordered electronic band structures at finite temperatures. However, due to the Born-Oppenheimer approximation, these do not arise from true electron-phonon coupling. Implementing electron-phonon coupling into TDEP would be useful in computing superconductivity critical temperatures as well as Seebeck coefficients for thermoelectrics.

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Papers

LIST OF PUBLICATIONS AND MY CONTRIBUTION

- Paper I I performed some calculations, helped to analyse the data and jointly wrote the manuscript.
- Paper II I did the TDEP calculations, additional convergence tests for the phonon dispersions, and wrote the paper jointly.
- Paper III I analysed the data and jointly wrote the manuscript.
- Paper IV I performed all calculations and wrote the paper jointly.
- Paper V I developed the new method, implemented thermodynamic integration into VASP, performed all calculations, ran the experiments, analysed the experimental data and wrote the paper jointly.
- Paper VI I developed the methodology to compute temperature dependent elastic constants, performed all calculations and wrote the paper jointly.
- Paper VII I performed all calculations and wrote the paper jointly.

Papers

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

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