Atomistic simulations of lattice defects

MATTIAS FORSBLOM

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Abstract

Mechanical properties of solids are governed by crystal imperfections. Computational materials science is largely concerned with the modelling of such defects, e.g. their formation, migration, and interaction energies. Atomistic simulations of systems containing lattice defects are inherently difficult because of the generally complicated geometrical structure of the defects, the need for large simulation cells, etc.

In this thesis, the role of lattice defects in the mechanism behind homogeneous melting is demonstrated. Also, a generic calculational scheme for studying atomic vibrations close to extended defects (applied to a dislocation) has been considered. Furthermore, heat capacities in the solid and liquid phases of aluminium have been calculated, as well as various thermophysical defect properties.

The work was carried out using classical atomistic simulations, mainly molecular dynamics, of aluminium and copper. The interatomic forces were modelled with effective interactions of the embedded-atom type.

The main results of this thesis are the following:

- The thermal fluctuation initiating melting is an aggregate typically with 6–7 interstitials and 3–4 vacancies.
- In the initial stage of melting, no signs of a shear modulus melting mechanism, or the presence of line-like defects (dislocations), can be seen.
- The typical time interval from when melting initiates to the time at which the liquid phase is fully developed is of the order of $1000\tau$, where the period $\tau$ corresponds to the maximum vibrational frequency in the solid.
- The solid-liquid boundary advances at a pace comparable to that of thermal transport by vibrating atoms in the crystal at high temperatures.
- The seemingly small anharmonic effect in the heat capacity of aluminium is caused by a partial cancellation of the low-order term linear in the temperature and anharmonic terms of higher-order in the temperature.
- The core region of an edge dislocation in face-centred cubic aluminium has compressed and expanded regions. The excess volume associated with the dislocation core is small, about 6 percent of the atomic volume, as a result of a partial cancellation between the volume changes of the compressed and expanded regions.
- The compressed and expanded regions of the edge dislocation core give negative and positive contributions, respectively, to the excess vibrational entropy. The overall effect is a positive vibrational excess entropy of the dislocation core which is about $2k_B$ per atomic repeat length along the dislocation core.
- The atomic vibrations near the dislocation core are modelled by considering an atomic cluster with about 500–1000 atoms containing the core of dislocation, embedded in a large discrete, but relaxed, lattice of about 23 000 atoms. An atomic region that is four atomic layers thick and about 18 atomic diameters long in the direction parallel to the Burgers vector, accounts for most of the excess entropy.
- The constant-pressure heat capacity of aluminium shows a minimum as a function of temperature in the liquid phase.
Preface

This thesis describes research carried out at the Department of Physics at the Royal Institute of Technology from December 2000 to May 2005. The text is divided in two parts. The first part provides a background to the results of the research. Some original results are also given here, mainly in chapter 7. The second part consists of scientific papers giving the main results of the research:

1. Mattias Forsblom, Nils Sandberg, and Göran Grimvall,
   Vibrational entropy of dislocations in Al,

2. Mattias Forsblom, Nils Sandberg, and Göran Grimvall,
   Anharmonic effects in the heat capacity of Al,

3. Mattias Forsblom and Göran Grimvall,
   How superheated crystals melt,

4. Mattias Forsblom and Göran Grimvall,
   Homogeneous melting of superheated crystals:
   Molecular dynamics simulations,
   under consideration for publication (2005).

5. Mattias Forsblom and Göran Grimvall,
   Heat capacity of liquid Al,
   submitted for publication (2005).
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Part I

Introduction and background
Chapter 1

Introduction

The range of materials studied in computational materials science is vast. Examples are organic polymers, metals, semiconductors, and biologically relevant materials, all of which are studied in computer simulations. The community of materials scientists has traditionally been divided into subcommunities, depending on the length-scales of interest to them. In the macroscopic regime, from millimetres to metres, the modelling has centred around continuum models which are solved by finite-element methods. The mesoscopic regime ranges from micrometres to millimetres. Mesoscopic models should give a coarse-grained description of the dynamics in the system, but also incorporate the essential physics from the microscopic level. In the microscopic regime the modelling is done at the atomic level.

The structure of crystalline materials is made up of periodically repeating a structural building block, the unit cell. The pattern of ions or atoms within the crystal is described by the lattice. A lattice point need not be a particular ion, but may be a set of ions or atoms, which can be repeated to construct the crystal. The group of atoms associated with a given lattice point is known as the basis of the lattice. The lattice and unit cell completely specify the crystal structure. Mechanical properties of crystalline materials used in engineering applications are governed by imperfections which disrupt the ideal lattice structure. Materials science is largely concerned with how such lattice defects are formed, how they interact with each other, and how they affect macroscopic properties. Such problems may extend over many length scales and be characterised by time periods ranging from femtoseconds (e.g. ultrafast melting) to years (e.g. in materials aging problems).

In computational materials science the goal is to emulate the behaviour of the system which is studied, using computer simulations, and gather information about it. A simulation which takes into account the interaction between the constituents of the complete system in greatest possible detail, is an extremely large many-body problem. In just a very small specimen the number of atoms is of the order of $\sim 10^{23}$. This is clearly not manageable. Instead of simulating the complete system a small set of atoms is often repeated periodically in three dimensions. This is a
good approximation in crystals.

There is an ever rapid increase in computational capacities. Both faster computers and the creation of more sophisticated algorithms contribute to this. With increased computer power the complexity of the problems which may be studied grows. Longer time scales, larger systems, and more degrees of freedom can be handled. Simulations are useful as a link between theory and experiments as they are relatively cheap, may be used to help to interpret or devise new experiments, and are not limited to specific cases. For instance, simulations at constant volume, in close to perfect vacuum and at 0 K are routinely carried out. Computer simulations may also give new insights to physical mechanisms which may be hard or impossible to test experimentally. Further, they can give ideas on how different theories can be coupled, or on the influence of some parameter in a theoretical model. One of the aims of computational materials science is to replace costly and lengthy experiments by accurate simulation schemes in the design of new materials and molecules (cf. Eberhart and Clougherty (2004)). This is realistic in some cases. However, many processes in materials occur, e.g. at high temperatures or in complex geometries. In such cases theoretical calculations may be limited to understanding mechanisms and key properties of the material.

The work described in this thesis has been aimed to further the understanding of the influence of lattice defects on macroscopic properties and phenomena. Aluminium, and to some extent copper, has been used as ‘test’ materials in the simulations. Both metals, which have the face-centred cubic structure, are important in industrial applications. They are good test materials because of the large collection of experimental data available for these metals. Also, the face-centred cubic structure is a common crystal structure among crystalline engineering materials. The behaviour of one crystalline material is not expected to differ fundamentally from the behaviour of another material with the same structure.
Chapter 2

Atomistic simulations

There are different approaches to computer simulations in the microscopic regime. Classical simulations use some form of effective interaction between the constituents of the system, and ab-initio methods solve the quantum-mechanical electronic-structure problem through a series of approximations. In terms of calculating the forces between the particles in the system, the first approach is many orders of magnitude faster than the second. However, it uses an effective interaction between the atoms. The effective interactions are assumed forms of the potential energy of the system, fitted to experimental data, ab-initio calculated properties, or a combination of them.

This chapter gives a brief introduction to atomistic simulations in the microscopic regime. The focus is on classical simulations, mainly molecular dynamics simulations. A short account of ab-initio methods is also given. The latter methods have not been used in this work, but some background material is needed in the discussion of the limitations and possibilities of classical simulations found elsewhere in this thesis.

2.1 Ensemble averages

When considering macroscopic quantities, an ensemble is a collection of all possible systems which have common macroscopic properties but differ in their microscopic states. For example, the isobaric-isothermal ensemble is a collection of all systems whose thermodynamic state is characterised by a fixed number of particles, a fixed pressure, and a fixed temperature. The ensemble average of some quantity $A$ is defined as

$$\langle A(q,p) \rangle_{\text{ensemble}} = \int A(q,p)\rho(q,p)dqd\mathbf{p},$$

where $\rho(q,p)$ is the probability density of the ensemble, and $q$ and $p$ are the particle coordinate and momentum, respectively. The set of all $q$ and $p$ is called the phase space (or configuration space). For $N$ particles it is thus $6N$-dimensional.
CHAPTER 2. ATOMIC SIMULATIONS

The integration is carried out over all possible states in the ensemble. This integral is in general inaccessible since \( \rho(q, p) \) may be complicated or unknown. In molecular dynamics simulations (Allen and Tildesley, 1987, Frenkel and Smit, 1996), the states in the ensemble are generated sequentially in time by numerically solving Newton’s equations of motion, see section 2.3. A state here means a given point in configuration space. The time average of the quantity \( A \) is calculated as

\[
\langle A(q, p) \rangle_{\text{time}} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(q(t), p(t)) \, dt \approx \frac{1}{M} \sum_{i=1}^M A(q_i, p_i), \tag{2.2}
\]

where \( t \) is the time, \( M \) is the number of time steps \( \Delta t \) and \( q_i = q(i\Delta t) \), \( p_i = p(i\Delta t) \). The last step in equation 2.2 is of practical importance since the molecular dynamics simulations generate the particle trajectories at discrete time steps. In Monte Carlo simulations (Allen and Tildesley, 1987, Frenkel and Smit, 1996) the dynamics of the system is not simulated as in molecular dynamics. Instead the time average is replaced by a direct sampling of the configuration space, see section 2.2.

An ergodic system is a system in which during a long enough simulation all points in phase space are visited (Plischke and Bergersen, 1994). Under the assumption that the simulation system is ergodic,

\[
\langle A(q, p) \rangle_{\text{ensemble}} = \langle A(q, p) \rangle_{\text{time}}, \tag{2.3}
\]

which is the ergodic hypothesis – a fundamental axiom in statistical mechanics. Thus, in ergodic systems ensemble averages may be evaluated by calculating time averages, for instance using molecular dynamics simulations. Statistical mechanics provides the link that relates the microscopic quantities obtained in atomistic simulations to macroscopic properties (Allen and Tildesley, 1987), e.g. the pressure, energies, and heat capacities.

2.2 Monte Carlo simulations

In Monte Carlo simulations the configuration space is sampled from a sequence of ‘Monte Carlo moves’. The simulation is carried out in successive steps in which new configurations in the ensemble are generated from old ones. The sequence of states is generated according to a Markov process (see, e.g. Plischke and Bergersen (1994)). The sampling is controlled by transition probabilities to ensure the approach to thermal equilibrium through a detailed balance condition (microscopic reversibility). This condition essentially means that the probability per time for going from state \( A \) to state \( B \) is equal to the probability per time for going from state \( B \) to state \( A \). There are many ways in which the condition of detailed balance can be fulfilled. The algorithm of Metropolis et al. (1953) is the standard one and was the first to be proposed. It was used in the Monte Carlo simulations described in paper 2. A Monte Carlo simulation using the Metropolis method consists of three steps:
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1. An initial state is specified.

2. A trial state is generated from the ‘old’ state, and is accepted using a criterion based on detailed balance. If the trial state is accepted the new state in the Markov process is set equal to the trial state. If the trial state is rejected the old state is retained.

3. Step 2 is repeated until a sufficient number of equilibrium states has been generated to form accurate statistical averages.

For particles in a simulation box, each move (step 2) could be an attempt to displace a particle in an arbitrary direction a random fraction of some maximum allowed distance.

The Monte Carlo method outlined above leads to simulations in the microcanonical ensemble. Generalisations to other ensembles are possible. For example, in the canonical ensemble, where the volume is allowed to fluctuate, attempts to randomly change the volume are incorporated. In the grand canonical ensemble, moves that allow the number of particles to change are included.

Monte Carlo simulations are inherently stochastic, in contrast to molecular dynamics simulations which are deterministic in nature – once the position and velocity of each atom are known, the state of the system can be predicted at any time forwards or backwards in time.

2.3 Molecular dynamics simulations

Molecular dynamics simulations (Allen and Tildesley, 1987, Frenkel and Smit, 1996) numerically solve the equations of motion of a system composed of interacting molecules or atoms. The generated information is microscopic – at each moment in the simulation (i.e. at every discrete time step) quantities such as the position and velocity of every particle are known.

The states in the ensemble are generated sequentially through numerical integration of Newton’s equations of motion,

\[
\begin{align*}
\mathbf{v}_i &= \mathbf{\dot{r}}_i, \\
m_i \mathbf{\ddot{r}}_i &= \mathbf{F}(\mathbf{r}_i), \\
\mathbf{F}(\mathbf{r}_i) &= -\frac{\partial V(\mathbf{r})}{\partial \mathbf{r}_i},
\end{align*}
\]

where \(m\) is the particle mass, \(\mathbf{r}\) is the position, \(\mathbf{v}\) is the velocity, \(\mathbf{F}\) is the force, and \(V\) is the potential energy. The label \(i\) is a particle index, and the dots denotes time derivatives. A numerical integration of equation 2.6 leads to a simulation in the microcanonical ensemble if periodic boundary conditions are used.

In many cases it is advantageous to realize other ensembles in the simulations, e.g. the isobaric-isothermal ensemble (fixed pressure, fixed number of particles, and fixed temperature) or the canonical ensemble (fixed volume, fixed number
of particles, and fixed temperature). This can be done by coupling appropriate ‘thermostats’ and ‘barostats’ to the dynamics of the system. Thus, Andersen (1980) introduced a ‘piston’ which varies the volume in order to maintain a fixed pressure during simulations. Parrinello and Rahman (1980) extended this idea to allow for a simulation cell which could not only change in volume but also in shape. The axes of the simulation cell thus are time dependent, and one cell edge vector may evolve in time independently of the others.

Based on a method of Nosé (1984), Hoover (1985) coupled an additional variable \( \eta \) to the dynamics which represents a thermostat with a fictitious ‘mass’ \( Q \). Newton’s equations of motion are extended by a ‘friction’ term

\[
\ddot{\mathbf{r}} = \frac{\mathbf{F}_i}{m_i} - \eta \dot{\mathbf{r}}. \tag{2.7}
\]

The variable \( \eta \) fluctuates in time around zero according to

\[
\dot{\eta} = \frac{1}{Q} \left( \sum_{i=1}^{N} m_i v_i^2 - 3 N k_B T \right), \tag{2.8}
\]

where \( N \) is the number of atoms, \( k_B \) is Boltzmann’s constant and \( T \) is the temperature.

Let \( \mathbf{h} \) be the matrix formed by the column vectors \( \mathbf{a}, \mathbf{b}, \) and \( \mathbf{c} \), with \( \mathbf{a}, \mathbf{b}, \) and \( \mathbf{c} \) being the simulation cell edges. The volume of the simulation cell is \( V = \det(\mathbf{h}) = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) \). Denote the ‘piston’ mass by \( M \). Expressed in reduced coordinates \( \mathbf{s} = \mathbf{h}^{-1} \mathbf{r} \), the equations of motion in the isobaric-isothermal ensemble are

\[
\ddot{s}_i = \frac{1}{m_i} \sum_{j \neq i} \chi(r_{ij})(s_i - s_j) - (\mathbf{G}^{-1} \mathbf{G}) \dot{s}_i, \tag{2.9}
\]

\[
\dot{\mathbf{h}} = \frac{1}{M} (\pi - p_{ext}) \mathbf{\sigma}. \tag{2.10}
\]

Here \( p_{ext} \) is the external pressure, \( \mathbf{G} = \mathbf{h}^T \mathbf{h} \) (with \( T \) denoting transpose), \( \mathbf{\sigma}_{ij} = \delta \Omega / \delta h_{ij} \), and \( \chi(r) = -\partial V(r) / \partial r \). The time evolution of the ‘thermostat’ variable is governed by equation 2.8. The microscopic stress tensor \( \pi \) is given (in dyadic tensor notation) by

\[
\Omega \pi = \sum_{i=1}^{N} m_i v_i v_i + \sum_{i=1}^{N} \sum_{j \neq i} \chi(r_{ij})(r_i - r_j)(r_i - r_j), \tag{2.11}
\]

where \( \mathbf{v} = \mathbf{h} \mathbf{s} \). Note that equations 2.9 and 2.11 apply to potentials that depend on the interatomic distance \( r \) only. However, they can be generalised to include, e.g. angular dependence.

Since the mathematical form of the potential energy \( V(r) \) generally is complicated, the equations of motion must be solved numerically, using some finite difference method. In each iteration the forces are calculated by differentiating \( V(r) \),
which in general is the most time-consuming part of the simulation. The most effective methods for integrating the equations of motion should conserve energy and momentum and permit a large integration time step. Because a considerable fraction of the simulation time must be spent to equilibrate the system, methods which converge rapidly to the desired ensemble are desirable. Various integration methods may be used, e.g. the Verlet, the velocity-Verlet, and the leapfrog algorithm (Allen and Tildesley, 1987). In this work a fifth order Gear predictor-corrector algorithm (Allen and Tildesley, 1987) was used. Predictor-corrector algorithms provide a general way to numerically integrate equations of motion. Those commonly used in molecular dynamics are due to Gear, and consist of three steps. In the first step (the predictor step) the position and its time derivatives are expressed at the the time \( t + \Delta t \) by means of Taylor expansions. \( \Delta t \) is the time step in the simulation. The second step involves the calculation of the forces (or accelerations) on all atoms. Those will in general differ from the ones ‘predicted’ in the first step. In the third and last step, (the corrector step) the positions and its time derivatives which were calculated in the first step are ‘corrected’ using the difference between the calculated and predicted accelerations.

In principle, the force calculation in a molecular dynamics program is constructed using two nested loops\(^1\) over all atoms. This implies that the time required to perform one molecular dynamics step would scale with the number of atoms \( N \) as \( \sim N^2 \). However, a considerable improvement in speed results by assuming a finite range of interaction with a cutoff distance (Allen and Tildesley, 1987, Frenkel and Smit, 1996). This means that for a given atom, only those atoms contained within a fixed cutoff radius are considered as interacting. By using such a truncated interaction the time to perform one molecular dynamics step scales linearly with \( N \). Very large systems may be studied in molecular dynamics simulations. Kadau et al. (2004), using a state of the art parallel supercomputer, demonstrated the possibility of simulating a system containing about \( 1.9 \times 10^{10} \) interacting Lennard-Jones particles.

**Constrained molecular dynamics**

In some simulations it may be desirable to restrict the simulation to a fixed region of the configuration space. Monte Carlo simulations in combination with, e.g. umbrella sampling (Torrice and Valleau, 1977) is one way to achieve this. In molecular dynamics constraint techniques can be used. Following Gillan et al. (1987), a way to restrict a single degree of freedom to a fixed value in molecular dynamics simulations is now described.

The degree of freedom \( \epsilon \) of the system should be restricted to a fixed value during the simulations. \( \epsilon \) is expressed in terms of the atomic positions \( \mathbf{r} \) in some

\(^1\)The two nested loops are constructed from the following steps: (1) Loop over all atoms in the system. (2) For each atom in the loop, loop over all atom-atom pairs.
region $\Gamma$ as

$$\epsilon = \sum_{i \in \Gamma} \alpha_i \cdot r_i,$$

(2.12)

where the summation is over all atoms belonging to the region $\Gamma$. The quantities $\alpha$ are constants, normalised to $\sum_{i \in \Gamma} |\alpha_i|^2 = 1$. The dynamics of the system can be restricted to a fixed value of $\epsilon$ by adding a set of suitable reaction forces $F_i^{\text{react}}$ to equation 2.5. To ensure that the energy is conserved in the dynamics of the atoms in the plane of motion, $F_i^{\text{react}}$ must be taken normal to that plane (i.e. the plane of constant $\epsilon$):

$$F_i^{\text{react}} = f^{\text{react}} \alpha_i,$$

(2.13)

If $\epsilon$ shall remain fixed during the simulations, $\dot{\epsilon} = \ddot{\epsilon} = 0$ must hold at each time step. The latter condition leads to

$$f^{\text{react}} = -\mu \sum_{i \in \Gamma} \frac{\alpha_i \cdot F_i}{m_i},$$

(2.14)

where

$$\frac{1}{\mu} = \sum_{i \in \Gamma} \frac{|\alpha_i|^2}{m_i}.$$  

(2.15)

The former condition is fulfilled by adding a set of corrections $\Delta v_i$ to the atomic velocities $v_i$, perpendicular to the plane of fixed $\epsilon$. This gives

$$\dot{\epsilon} = \sum_{i \in \Gamma} \alpha_i \cdot (\Delta v_i + v_i) = 0.$$  

(2.16)

The normalization of $\alpha$ leads to

$$\Delta v_i = \Delta v \alpha_i,$$

(2.17)

where

$$\Delta v = \sum_{i \in \Gamma} v_i \cdot \alpha_i.$$  

(2.18)

In paper 1 this technique is used. The degree of freedom which is kept fixed during the simulations is the difference between the center of mass of the atomic (111) planes immediately above and below the mutual glide plane of two edge dislocations of opposite sign. This keeps the relative distance between the two edge dislocations constant, and prevents that the two dislocations annihilate each other during the atomic relaxation to zero forces, cf. paper 1.

### 2.4 Ab-initio methods

The basic properties of condensed matter are described by quantum mechanics, but the methods described in section 2.2 and 2.3 are strictly classical. Furthermore,
they rely on effective interatomic potentials, which are empirical in nature. Ab-initio approaches refer to formalisms used to solve the Schrödinger equation for the electrons and nuclei using a number of approximations. The great advantage is that no assumption about the interaction between the atoms is needed. Static properties can be calculated in this way, using density-functional theory (Kohn and Sham, 1965), usually for systems with the number of atoms in the range 100–1000. For a brief review see Segall et al. (2002).

Attempting to solve the time-dependent Schrödinger equation numerically for a large system of nuclei and electrons is at present not feasible even on the fastest of computers. ‘Ab-initio molecular dynamics’ is a term referring to a class of methods for studying the dynamical motion of atoms without relying on effective interactions. This method was introduced by Car and Parrinello (1985) and is based on the density-functional theory of Kohn and Sham (1965). In its usual form, the atomic trajectories evolve in time according to Newton’s equations of motion as in classical molecular dynamics. However, at each time step the forces on the atoms are calculated by solving the quantum-mechanical electronic-structure problem. Ab-initio molecular dynamics is many orders of magnitude slower than classical molecular dynamics (Binder et al., 2004), with the time required to advance one simulation step scaling with the number of atoms \( N \) usually as \( \sim N^3 \). Even with a modern parallel supercomputer one is generally confined to system sizes of the order of 100 atoms and simulation times of a few nanoseconds (Nieminen, 2002).

Path-integral molecular dynamics (Tuckerman et al., 1993, Müser, 2001, Schöffel and Müser, 2001) and Monte Carlo simulations (Pollock and Ceperley, 1984, Ceperley, 1995) are alternative methods to account for quantum-mechanical effects. Both methods rely on the path-integral approach (e.g. Feynman (1998)) to quantum statistical mechanics of Feynman. Such techniques are crucial in the study of solids at low temperatures, in order to ensure that thermal properties are compatible with the third law of thermodynamics.\(^2\)

\(^2\)For example, correct quantum simulations of the thermal expansion converge to zero as \( T = 0 \) K is approached, whereas classical molecular dynamics or Monte Carlo simulations generally do not (Müser, 2001).
Chapter 3

Lattice defects

Every crystal contains lattice defects, or imperfections, which locally disrupt the ideal structure of the crystal. They come in several types and are often classified according to the number of spatial dimensions which is required to geometrically describe them. Their presence affects physical properties and phenomena. In this chapter basic properties and brief historic reviews for some common types of lattice defects are given.

3.1 Point defects

In a perfect lattice all atoms are located at specific lattice sites (ignoring thermal motion). There are two possible point defects: vacancies and interstitials. A vacancy is an unoccupied lattice point, and an interstitial is an atom located at a non-lattice site. At all finite temperatures there is an equilibrium concentration of vacancies in a crystal. In many common metals the fraction of vacant lattice sites just below the melting temperature is of the order of $10^{-4}$ to $10^{-3}$ (Simmons and Bollif, 1960, Schilling, 1978). The equilibrium concentration of interstitials near melting is expected to be orders of magnitude smaller than the equilibrium concentration of vacancies (Schilling, 1978). (However, see Gordon and Granato (2004).) In metals there may be impurities which can also be considered as point defects. There are two types: substitutional (an atom of a kind different from the host atoms occupy a lattice site) and interstitial (an atom of a kind different from the host atoms occupy a non-lattice site).

Point defects influence many physical properties of metals. For example, the atoms surrounding a vacant lattice site are more loosely bound than those in a perfect lattice. The forces between the atoms thus are weakened (i.e. the vibrational frequencies are lowered) giving an increased vibrational entropy compared to the bulk. Interstitials, on the other hand, give a negative excess entropy because the lattice is more compressed in the vicinity of an interstitial. Point defect mechanisms dominate in self-diffusion processes (Sandberg et al., 2002). Vacancies cause an
increase in the volume of a crystal, and hence contribute to the thermal expansion. The enthalpy and heat capacity increase due to point defects.

The formation of point defects in solids was first predicted by Frenkel in 1926. At high temperatures the thermal vibrations of the atoms may cause an atom to leave its equilibrium lattice site and occupy an interstitial position in the lattice. In this mechanism a vacancy and an interstitial are created simultaneously, and are referred to as a Frenkel defect. In 1930, Wagner and Schottky demonstrated a way for the creation of vacancies: an atom leaves its lattice site and occupies an available position at the surface of the crystal or at internal imperfections in the crystal such as dislocations, grain boundaries, or inclusions. This mechanism dominates in metals with close-packed structure where the formation energy of vacancies generally is much lower than the formation energy of interstitials (Kraftmakher, 1998). Experimental measurements of vacancy concentrations often rely on the influence of vacancies on thermophysical properties, e.g. thermal expansion and electric resistivity (for a review see Kluin (1992)). The problem is to separate the effect of vacancies from other effects, e.g. anharmonicity. Differential dilatometry measures the vacancy concentration directly. In such experiments the linear thermal expansion coefficient and the change in the lattice parameter with temperature are measured simultaneously. From the difference between those quantities the vacancy concentration can be deduced (e.g. Simmons and Balluffi (1960)). The equilibrium concentration of interstitials can be determined using elastic constants measurements (Gordon and Granato, 2004).

Computer simulation studies of point defects are abundant in the literature. Both classical simulations and ab-initio methods have been used. Geometrically, isolated point defects are among the simplest defect configurations, and require relatively small simulation cells. For example, Hatcher et al. (1979) calculated the formation entropy of single vacancies and divacancies for copper using pair potentials. Nordlund and Averback (1998) determined equilibrium concentrations of self-interstitials and divacancies in copper using molecular dynamics simulations. Carling et al. (2000), using density-functional calculations, concluded that divacancies are unstable in aluminium, and dissociate into separate vacancies.

3.2 Dislocations

Imagine that the bonds between the atoms in a simple cubic lattice are represented by flexible springs. If all bonds intersected by a plane which goes through non-atomic sites were instantaneously broken, the lattice would separate along this line if pulled in tension. A screw dislocation is introduced by displacing the two faces of such a cut relative to each other. If instead an extra atomic plane would be placed between the faces, an edge dislocation is created, cf. figure 3.1. In a real crystal, dislocations may have characteristics of both edge and screw type. Dislocations have a high formation energy and are not thermally generated at normal temperatures. However, dislocations are introduced through mechanical deforma-
Figure 3.1: Schematic picture of an edge dislocation in a simple cubic lattice. An extra half plane of atoms has been inserted in the upper part of the lattice.

Dislocation, even at intermediate temperatures. The dislocation density is defined as the total length of dislocations per volume. In a carefully treated metallic crystal this value can be as low as $10^2 \text{ cm}^{-2}$. It increases rapidly with plastic deformation, and a typical value for a heavily deformed metal is $5 \times 10^{11} \text{ cm}^{-2}$. The dislocation density in metallic crystals generally is higher than in non-metallic crystals. Thus, dislocations may become important at high temperatures, and are essential in understanding the deformation of materials. They account for the difference, by many orders of magnitude, between measured critical shear stresses of crystals and theoretical estimations.

The idea of dislocations dates from the end of the 1920s. In 1934 Orowan, Polanyi, and Taylor in simultaneous independent papers laid the foundations of the modern dislocation theory of slip, although the concept of dislocations had been introduced some years earlier (see Nabarro (1967)). The first major review of the dislocation theory of crystals was written by Seitz and Read (1941), and later by Cottrell (1949). At the end of the 1960s, much of the modern theory of dislocations had been completed. The geometrical and elastic properties of dislocations, the theory of plastic deformation, and the role of dislocation theory in explaining crystal growth, were developed. There are many techniques for the detection of dislocations in crystals, e.g. X-ray diffraction, transmission electron microscopy, and field ion microscopy (Hull, 1965).

According to the mathematical theory of dislocations there is an elastic strain field around a dislocation, which diverges at points too close to the centre of the defect (Hirth and Lothe, 1982). The region where elasticity theory fails is called the dislocation core. The geometrical arrangement of atoms in the dislocation core
CHAPTER 3. LATTICE DEFECTS

Figure 3.2: Schematic picture of an intrinsic stacking fault. The atomic planes A, B, and C are close-packed ($\bar{1}$11) planes in the face-centred cubic lattice.

has been studied experimentally with high-resolution electron microscopy (for a recent application see Srinivasan et al. (2005)) and using classical simulations (e.g. Häkkinen et al. (1990), Aslanides and Pontikis (1998), Fang and Wang (2000)). Recently, the core structure of dislocations has also been studied in simulations using the discrete Peierls-Nabarro model (Hirth and Lothe, 1982) combined with ab-initio methods which do not rely on effective interactions between the atoms (Lu et al., 2000, Lu et al., 2001, Shoecck, 2002).

The forces between the atoms near the core are weakened compared to the forces between atoms in the bulk, i.e. the frequencies of the atomic vibrations are lowered. Thus the vibrational entropy of an atom in the core of a dislocation is higher than the entropy of an atom in bulk. Estimations of the vibrational entropy of dislocations were made by, e.g. Kuhlmann-Wilsdorf (1965) and Friedel (1982). Using classical calculations, the vibrational entropy was calculated for an edge dislocation in body-centred cubic iron (Ya-Fang et al., 2001) and for an edge dislocation in face-centred cubic aluminium (paper 1 in this thesis).

3.3 Stacking faults

Perfect lattices can be described as a stacking of identical atom layers arranged in a regular sequence. There may be one or several ways to position one layer on top of another. In a face-centred cubic lattice there are two ways in which close-
3.3. STACKING FAULTS

packed planes (the (111) planes) can be placed on top of each other. The stacking of such planes can schematically be described as the the sequence ABCABC... (cf. the left-hand part of figure 3.2). In the right-hand part of figure 3.2 a C layer has been partially removed in the regular stacking sequence, which creates an 'intrinsic' stacking fault.

Stacking faults play an important role in materials science because of their interaction with dislocations. They can be visualised by electron diffraction (Guy, 1972). Dislocations often split into partial dislocations (in face-centred cubic metals), which are connected by a stacking fault (this is indicated in figure 3.2). The stacking fault energy $\gamma$ is the energy required to introduce a stacking fault in a crystal (cf. section 7.1). It is directly related to, e.g. the dissociation of a dislocation into two partials (Hirth and Lothe, 1982). Calculations of the stacking fault energy have been carried out using classical simulations (e.g. Fang and Wang (2000), Lu et al. (2000), Zimmerman et al. (2000), Szelestey et al. (2002), van Swygenhoven et al. (2004), Srinivasan et al. (2005)) and ab-initio methods (e.g. Lu et al. (2000), Ogata et al. (2002)). Using isotropic elasticity theory, the splitting distance $d_{\text{split}}$ between two partial dislocations can be calculated (Hirth and Lothe, 1982), from which $d_{\text{split}} \sim \gamma^{-1}$. The relation between $\gamma$ and $d_{\text{split}}$ may be used in experimental determinations of the stacking fault energy.
Chapter 4

Interaction models

As described in section 2.4, static properties of systems with 100–1000 atoms may be calculated using density-functional theory, and the dynamics of small systems can be calculated with other ab-initio methods. However, many problems in computational materials science require the study of systems with a very large number of atoms, e.g. systems with extended defects (Zhou et al., 1997) or cascade-damage radiation (Puigvi et al., 2004). Hence approximations are necessary.

4.1 Effective interactions

In early classical simulations using molecular dynamics or Monte Carlo simulations, the interaction between the constituents of the system has been modelled in with pair potentials. Such potentials may give a good description of, e.g. noble gas systems (Allen and Tildesley, 1987). The description of metals using pair potentials has several shortcomings (see e.g. Foiles (1985)). To describe metals, pair potentials must be complemented by a term depending on the total volume of the system (Voter, 1995). However, the treatment of systems with defects, for which the volume is ill-defined (such as systems containing a free surface), is ambiguous. Generally, pure pair-wise interactions work less well for metals when the local atomic environment differs much from the uniform bulk. Daw and Baskes (1984) proposed an interaction based on ideas of density-functional theory, known as the embedded-atom method. One of the fundamentals of the density-functional theory is that the total electronic energy of an arbitrary arrangement of atoms in an external potential can be expressed as a functional of the total electron density (Hohenberg and Kohn, 1964). In the embedded-atom method, the total electron density is approximated by a linear superposition of the contributions from each individual atom. The electron density in the vicinity of an atom is expressed as the sum of the contributions to the electron density from the atom itself and from the atoms surrounding it. The embedding energy of an atom is the energy required to embed the atom in the surrounding electron density. This energy is a function of
the electron density. There is also an electrostatic energy resulting from interaction between the nuclei. The potential energy of a system of $N$ atoms is

$$V = \sum_{i=1}^{N} F\left[ \sum_{j \neq i} \rho(r_{ij}) \right] + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \Phi(r_{ij}).$$ \hspace{1cm} (4.1)$$

Here $r_{ij}$ is the interatomic distance between atoms $i$ and $j$, $\Phi(r_{ij})$ is a pair potential term which models the primarily repulsive interaction between the nuclei $i$ and $j$, $\rho(r_{ij})$ is the electron density of atom $j$ at the site of atom $i$, and $F[\sum_{j \neq i} \rho(r_{ij})]$ is the energy required to embed atom $i$ in the surrounding electron density. $\sum_{j \neq i} \rho(r_{ij})$ corresponds to the density of the host system with atom $i$ removed. The functional form of equation 4.1 has been derived by Manninen (1986) and Jacobsen et al. (1987) using the formalism of density-functional theory (Kohn and Sham, 1965).

Model potentials of the form in equation 4.1 are constructed by fitting the potential functions $\Phi$, $\rho$ and $F$ to a set of experimental data, ab-initio calculated properties, or a combination of them. As a consequence, fitted properties are well described, but maybe not so for other properties. The approach in fitting a potential is to seek the best possible fit of the potential functions to the chosen set of data. The mathematical forms of the potential functions are chosen so as to fit their expected behaviour, based on physical arguments. The data set can be pictured as a certain region of phase space, which the potential should emulate. The desired result of the fitting is a potential, which gives a reasonable description in other parts of configuration space.

There are some alternative empirical interactions to equation 4.1 when modelling metals, e.g. the effective-medium theory (Jacobsen et al., 1987), the potentials of Finnis and Sinclair (1984), and the second-moment approximation to the tight-binding model (Tománek et al., 1985). In the tight-binding method (Sutton et al., 1988) the ion-ion interaction is modelled by an effective band term and a short-range repulsive pair potential. Tight-binding molecular dynamics is a method which is up to three times faster than ab-initio molecular dynamics and at the same time accurately describes the electronic structure of the system (Kirchoff et al., 2001). However, it is slower than molecular dynamics using empirical potentials.

Some potentials with pure pair-wise interactions are still used. An example is the Lennard-Jones interaction (Jones, 1924)\(^1\). It has the functional form $\Phi_{LJ} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$, where $r$ is the interatomic distance, $\epsilon$ is the potential well-depth, and $\sigma$ is the ‘Lennard-Jones diameter’. The first term dominates at short distances and models the repulsion between atoms when brought in close proximity. The second term dominates at large distances and gives an attractive interaction, as well as the cohesion of the system. The Lennard-Jones potential is well known to give a good description of noble gases such as argon or krypton (Allen and Tildesley, 1987). It also constitutes an important model system in simulations. Another example of a pure pair-wise interaction is the Morse potential (Morse, 1929).

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\(^1\)Later J. E. Lennard-Jones.
4.2 Model potentials

In the following, the potential models which were used in this work are described in some detail. All interactions have the functional form of equation 4.1.

Ercolessi and Adams interaction

The potential of Ercolessi and Adams (1994) describing aluminium has been constructed using a numerical scheme to extract interatomic potentials from large amounts of data produced by ab-initio calculations. The potential functions $\Phi$, $\rho$, and $F$ were represented by piece-wise cubic spline polynomials, and have been fitted to a large number of ab-initio-calculated atomic forces at different temperatures and in various configurations, e.g. solids, liquids, systems undergoing melting, and a bulk system containing a vacancy, in order to achieve a good structural transferability. The fitting of the interaction model was further subjected to 32 additional constraints, among them the cohesive energy, the vacancy formation energy, the equilibrium lattice spacing, and the bulk modulus and the shear moduli $c_{11} - c_{12}$ and $c_{44}$ at $T = 0$ K. The potential has been used in many instances to study a varying range of phenomena and does well in reproducing thermal and surface properties. The authors of the potential have recently developed an improved version of their potential, by using a slightly larger cutoff radius for the potential functions $\Phi$ and $\rho$, which more closely reproduces the stacking fault energy (Liu et al., 2004).

Mishin et al. interaction

In the interaction model of Mishin et al. (1999) describing aluminium, the potential functions $\rho$, $\Phi$ and $F$ are represented by piece-wise cubic spline functions, similar to the model of Ercolessi and Adams (1994). Mishin et al. constructed their potential from a large set of experimental data and ab-initio calculated properties. The experimental part of the fitting database included the equilibrium lattice spacing, the vacancy formation energy, the cohesive energy, the elastic constants $c_{11}, c_{12}$, and $c_{44}$, the vacancy migration energy, the intrinsic stacking fault energy, phonon-dispersion relations, and others. Ab-initio energies of structures other than the face-centred cubic structure were included in the fit to enhance the structural transferability.

Mei and Davenport and Sabochick and Lam interactions

The aluminium interaction of Mei and Davenport (1992) was fitted to the experimental values of the cohesive energy, the lattice spacing, the vacancy formation energy, and elastic constants of a static face-centred cubic aluminium crystal. The
potential functions were represented by analytical functions. The potential functions of the copper potential of Sabochick and Lam (1991) also have analytic forms. The experimental properties fitted were the atomic volume, the bulk and shear moduli, the anisotropy ratio $2c_{44}/(c_{11} - c_{12})$, and the vacancy formation and migration energies.
Chapter 5

Vibrations in crystals

Given a potential $\Phi = \Phi(r_1, r_2, \ldots)$ for the interaction between the atoms at positions $r_1, r_2, \ldots$, the total lattice energy $U$ can be expressed in terms of atomic displacements from their equilibrium sites. With $i$ and $j$ denoting atoms and $\alpha$ and $\beta$ denoting Cartesian components,

$$U = \frac{1}{2} \sum_i \frac{p_i^2}{m_i} + \Phi_0 + \frac{1}{2} \sum_{i,j,\alpha,\beta} \Phi''_{ij}(i,j)u_{i\alpha}u_{j\beta} + \Phi_{\text{anh}},$$  \hspace{1cm} (5.1)

where $u_i$ is the displacement of atom $i$ from its equilibrium site and $p_i$ is its momentum. The first term in equation 5.1 is the kinetic energy, and the second is an arbitrary reference energy. The third term is the harmonic contribution to the total lattice energy, and the last term represents the anharmonic terms of $\Phi$, i.e. terms with powers of $u$ of higher order than two. The primes denote derivatives. The derivatives in equation 5.1 are evaluated at the atomic equilibrium sites.

5.1 Harmonic approximation

In the harmonic approximation only terms in $\Phi$ quadratic in the displacements $u$ are retained. The quantity $\Phi_{ij}(i,j)$ in equation 5.1 is an atomic force constant, whose physical meaning is the force per unit distance on atom $i$ in the $\alpha$ direction, resulting from atom $j$ being displaced a unit distance in the $\beta$ direction. The dynamical matrix $D$ is defined by

$$D_{i\alpha j\beta} = \frac{1}{(m_im_j)^{1/2}} \frac{\partial^2 \Phi}{\partial u_{i\alpha} \partial u_{j\beta}}.$$ \hspace{1cm} (5.2)

The normal vibrational frequencies are given by $\omega_n = \lambda_n^{1/2}$, where the index $n$ enumerates the eigenvalues $\lambda_n$ of the matrix $D$. For a system with $N$ atoms, the dynamical matrix has $3N \times 3N$ elements. Paper 1 and chapter 7 describe calculations of the eigenvalues of different dynamical matrices $D$. The calculations were

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CHAPTER 5. VIBRATIONS IN CRYSTALS

carried out using standard eigenvalue-problem routines for unsymmetric, real
matrices (see Wilkinson and Reinsch (1971) and Press et al. (1992) for details). The
matrix $D$ was first reduced to an upper Heisenberg matrix,$^1$ and the eigenvalues
were then obtained using an iterative ‘QR’ algorithm.$^2$

The vibrational Helmholtz free energy in the harmonic approximation is (Grimvall,
1999)

$$F_{\nu b} = \sum_{n=1}^{3N} \left[ \frac{\hbar \omega_n}{2} + k_B T \ln(1 - e^{-\hbar \omega_n / k_B T}) \right],$$

(5.3)

where $\hbar = h/(2\pi)$, with $h$ being Planck’s constant. From $F_{\nu b}$, the vibrational
entropy of the system is

$$S_{\nu b} = -\frac{\partial F_{\nu b}}{\partial T} = -k_B \sum_{n=1}^{3N} \left[ \ln(1 - e^{-\hbar \omega_n / k_B T}) - \frac{\hbar \omega_n / k_B T}{e^{\hbar \omega_n / k_B T} - 1} \right].$$

(5.4)

In the high-temperature limit (i.e. well above the Debye temperature, where $k_B T \gg \hbar \omega$),

$$S_{\nu b} = 3N k_B \left[ 1 + \ln \left( \frac{k_B T}{\hbar \omega(0)} \right) + \frac{1}{24} \left( \frac{\hbar \omega(2)}{k_B T} \right)^2 - \frac{1}{960} \left( \frac{\hbar \omega(4)}{k_B T} \right)^4 + \cdots \right].$$

(5.5)

Here $\omega(0)$, $\omega(2)$, etc. are frequency moments, defined from the phonon density of
state (Grimvall, 1999). The leading term of $S_{\nu b}$ is

$$S_{\nu b} \approx k_B \sum_{n=1}^{3N} \left[ 1 + \ln \left( \frac{k_B T}{\hbar \omega_n} \right) \right].$$

(5.6)

5.2 Anharmonicity

In the harmonic approximation $\Phi_{an}$ is left out of equation 5.1. This is a good
approximation in some cases. However, in a strictly harmonic crystal the equi-
librium volume would not depend on temperature (because the pressure in the
harmonic model depends only on volume but not on temperature (Ashcroft and
Mermin, 1976)), thus giving zero thermal expansion. Further, elastic constants
would not depend on temperature and volume, there would be no difference be-
 tween adiabatic and isothermal elastic constants, and the thermal conductivity
would be infinite in a harmonic crystal (Ashcroft and Mermin, 1976). Anharmonic
terms play essential roles in most processes by which the vibrating lattice transmits
energy.

---

$^1$An upper Heisenberg matrix $A$ has zeros in every element below the diagonal except for the
first lower-diagonal row, i.e. $A_{ij} = 0$, $i > j + 1$.

$^2$The QR algorithm is essentially an orthogonal transformation, which leaves the eigenvalues
of a matrix unchanged.
5.3. EXCESS PROPERTIES OF DEFECT CRYSTALS

If the lattice parameters change due to thermal expansion, the derivatives in the harmonic part of equation 5.1 may be evaluated at the equilibrium sites corresponding to the new temperature. This approach is called quasiharmonic, which thus accounts for volume changes but neglects the anharmonic effects which explicitly depend on the increasing magnitude of atomic vibrational displacements with temperature.

Analytical calculations of anharmonic effects rely on different approximation schemes (Cowley and Shukla, 1974). Few such calculations include higher-order terms of $u$, cf. equation 5.1. Molecular dynamics and Monte Carlo simulations account for anharmonicity of all orders (Shukla and Cowley, 1998), given the interaction potential. In paper 2 the vibrational heat capacity at fixed volume, deduced from constant-pressure experiments (Ditmars et al., 1985), is compared with molecular dynamics and Monte Carlo calculations. It is found that the seemingly small anharmonic effect in aluminium (Leadbetter, 1968, Rosén and Grimvall, 1983) is caused by a partial cancellation between a large low-order linear term in the temperature and higher-order terms.

5.3 Excess properties of defect crystals

Let $X$ be some thermodynamic quantity. An excess property $\Delta X$ is defined by

$$\Delta X = X_{\text{defect}} - \frac{N_{\text{defect}}}{N_{\text{bulk}}} X_{\text{bulk}},$$

(5.7)

where $N_{\text{defect}}$ and $N_{\text{bulk}}$ are the numbers of atoms in the systems, and $X_{\text{defect}}$ and $X_{\text{bulk}}$ are the quantities calculated in a defect and a perfect system, respectively. The quantity $\Delta X$ is small, compared to $X_{\text{bulk}}$ and $X_{\text{defect}}$, because $N$ generally is large in defect systems.

As an example, consider the high-temperature limit of the vibrational entropy, as given in equation 5.6. Three eigenvalues of the dynamical matrix are zero due to the translational invariance of the total energy. Taking this into account,

$$\Delta S = S_{\text{defect}} - \frac{N_{\text{defect}} - 1}{N_{\text{bulk}} - 1} S_{\text{bulk}},$$

(5.8)

and

$$S_{\text{vib}} \approx k_B \sum_{n=1}^{3N-3} \left[ 1 + \ln \left( \frac{k_B T}{\hbar \omega_n} \right) \right].$$

(5.9)

A combination of equations 5.8 and 5.9 gives

$$\Delta S_{\text{vib}} = k_B \ln \left( \frac{\prod_{n=1}^{3N_{\text{bulk}}-3} \omega_n^{\text{bulk}} (N_{\text{defect}} - 1)/(N_{\text{bulk}} - 1)}{\prod_{n=1}^{3N_{\text{defect}}-3} \omega_n^{\text{defect}}} \right).$$

(5.10)

Here $\omega_n^{\text{bulk}}$ and $\omega_n^{\text{defect}}$ are the vibrational frequencies of the $n$-th vibrational mode, for the bulk lattice and the defect lattice, respectively. The vibrational frequencies
are obtained from a diagonalisation of the dynamical matrix, defined in equation 5.2.

5.4 Defect entropy calculations

While the formation energies of defects may be calculated almost routinely, defect formation entropies require a more elaborate analysis. Different problems associated with these calculations were reviewed by, e.g., Foiles (1994). The vibrational entropy of point defects in metals has previously been studied in computer simulations by, e.g., Hatcher et al. (1979), Fernández et al. (2000), and Mishin, Sorensen and Voter (2001). Atomistic calculations of vacancy entropies in metals have traditionally been done following two different approaches. In the first approach (the ‘supercell method’), the defect formation entropy is determined by calculating the total entropy change of the whole simulation cell. The entropy is calculated in the harmonic approximation by constructing the dynamical matrix for the simulation cell (cf. section 5.1). The equilibrium configuration of the simulation cell is found by a static relaxation to zero atomic motion.

In the second approach (the ‘embedded cluster’ method) only the entropy change of a region appropriately sized for the inclusion of the distorted lattice around the defect is considered. This region is surrounded by material with a bulk-like structure. As before, the whole simulation cell is relaxed to zero atomic motion before determining the defect formation entropy in the harmonic approximation. The atoms in the embedded cluster are treated as dynamic while all atoms outside the cluster are treated as static (note that the static atoms interact with the atoms in the cluster, thus providing a ‘boundary condition’ for the cluster). In situations where this method is meaningful the cluster typically is much smaller than the simulation cell in which it is embedded.

The first approach is by far the most accurate (Mishin, Sorensen and Voter, 2001), but prohibits calculations on systems with extended defects due to the problem of handling large dynamical matrices.\footnote{The time required to diagonalise a matrix with $N \times N$ elements scales as $\sim N^3$ (Wilkinson and Reinsch, 1971, Press et al., 1992).} In the second approach, the defect entropy obviously depends on the size of the dynamic cluster. Thus a series of simulations for varying sizes of the cluster must be done in order to extrapolate the results to an infinite crystal. However, for all defects but the geometrically simplest one (an isolated point defect) it is not clear how such an extrapolation should be done. Even in the simplest case, extrapolation on spherical symmetry and other approximations (Mishin, Sorensen and Voter, 2001). According to Hatcher et al. (1979), the vacancy formation entropy, as a function of the inverse number $N^{-1}$ of atoms in the cluster, must be linearly extrapolated to $N^{-1} \to 0$.

Mishin, Sorensen and Voter (2001) proposed, as an extension of the embedded-cluster method, that an entropic correction due to the strain field outside the the cluster should be added to the cluster entropy. The density of entropy associated
with the elastic strain is \( S = \beta K \Delta \) (Landau and Lifschitz, 1986), where \( K \) is the bulk modulus, \( \Delta \) is the local hydrostatic stress, and \( \beta \) is the cubic thermal expansion factor. The idea of Mishin, Sorensen and Voter (2001) was to apply this continuum expression to the discrete lattice region surrounding the cluster. It was approximated by

\[
S_q = \beta \sum_{\alpha} \Omega_\alpha p_\alpha,
\]

for all lattice sites \( \alpha \) lying outside the cluster. Here \( \Omega_\alpha \) and \( p_\alpha \) are the local atomic volume and local hydrostatic stress assigned to the lattice site \( \alpha \), respectively. When the interaction between the atoms is described by an expression of the type in equation 4.1, each term in the sum is uniquely determined. The quasicontinuum correction to the entropy is in this case given by (Mishin, Sorensen and Voter, 2001)

\[
S_q = \frac{\beta}{3} \sum_{i=1}^{N} \sum_{j \neq i} \left[ \frac{1}{2} \Phi'(r_{ij}) + F'(\sum_{k \neq i} \rho'(r_{ik}) \rho'(r_{ij})) \right] r_{ij}.
\]

(5.11)

A prime denotes differentiation with respect to the function argument. \( r_{ij} \) is the distance between atoms \( i \) and \( j \). The total vibrational entropy in this model thus is \( S = S_c + S_q \), where \( S_c \) is the entropy of the cluster.

This approach has the advantages that the problem associated with the extrapolation of the formation entropy to larger cell sizes is avoided and that in principle only one simulation needs to be carried out. In the case of point defects, the results may be further refined by a linear extrapolation to \( N_s^{-1} \rightarrow 0 \) for a fixed number of atoms \( N \) in the simulation cell (Mishin, Sorensen and Voter, 2001). The method does not require any special symmetry of the strain field surrounding the defect, and the simulation cell and cluster region may have any shape, e.g. cubic. For example, a cluster region with a parallelepipedic shape is suitable to model a dislocation (cf. paper 1). The method assumes that the strained lattice regions outside the cluster follow linear elasticity, and that the gradients of the hydrostatic stress outside the core region are small enough so that the continuum approximation is justified (Mishin, Sorensen and Voter, 2001). This method can be applied to large simulation cells since the time required to calculate \( S_q \) scales linearly with the number of atoms.

The vacancy excess vibrational entropy was calculated using effective interactions describing copper and aluminium. The results are given in section 7.3. Paper 1 describes the calculation of the excess vibrational entropy associated with the presence of an edge dislocation core in a face-centred cubic lattice, using the method described above. To obtain the vibrational entropy, the vibrational frequencies of the atoms in a region containing about 1000 atoms, in which the dislocation core was embedded, were determined. The starting point for the calculation was to relax the atoms in the lattice to their equilibrium sites. Outside the cluster, the dislocation gives rise to a strain field of ‘infinite’ range (Hirth and Lothe, 1982). In practice the range is not infinite but depends on the crystal grain size, the presence of other lattice defects, etc. Thus a significant part of the vibrational entropy associated with a dislocation is stored in the region of the lattice outside the core of the dislocation, cf. paper 1.
Chapter 6

Solid-to-liquid phase transition

Melting occurs when the Gibbs free energy of the liquid and solid phases are equal, at the ‘equilibrium’ melting temperature, which is discussed in section 6.1. But this does not say anything on how the atoms move as the solid phase transforms into the liquid phase. In ‘normal’ melting, the liquid nucleates from the crystal’s surface. Such heterogeneous melting is the most common way by which a solid melts. If the material is rapidly heated to temperatures above the equilibrium melting temperature, the atomic configuration of the entire crystal can be modified on an ultrafast time scale. In such a case nucleation at the surfaces is suppressed, and melting occurs homogeneously from ‘within’ at a temperature above the equilibrium melting temperature. This is discussed in section 6.2.

There exist many microscopic theories for melting, some of which are discussed in section 6.4. Homogeneous melting has been studied in this thesis, with the main results being described in papers 3 and 4. Some specific details about that work are found in the last sections of this chapter.

6.1 Thermodynamics

Classical equilibrium thermodynamics provides a framework for describing the solid-to-liquid phase transition in terms of the Gibbs free energy $G$ (or the Helmholtz free energy). The phase transition occurs at the temperature where the Gibbs energy of the solid and liquid phases are equal, i.e. $G_{\text{liq}}(T) = G_{\text{sol}}(T)$. The Gibbs energies of the solid and liquid phases are continuous in the temperature or pressure at the melting temperature, in contrast to energies, heat capacities etc. which are discontinuous. The variation of $G_{\text{liq}}$ and $G_{\text{sol}}$ in the vicinity of the melting temperature $T_m$ for a simple substance is schematically shown in figure 6.1. Almost all substances expand on melting. For metals, the volume of the liquid typically is a few percent larger than the volume of the solid (Poirier, 1991). The melting process represents a transition from an ordered state to a less ordered state, and thus the liquid phase has a higher entropy than the solid phase. In conclusion, thermody-
namic relations can give information on the melting temperature, volume change on melting etc. However, they cannot describe the detailed melting mechanism, which depends on the microscopic structural state of the material.

6.2 Heterogeneous and homogeneous melting

The first idea that the melting of a crystal nucleates at a surface and then propagates inwards (Dash, 2002, Johnson, 2002) dates back over a century, when Faraday (1860) advanced a theory in which he assumed that ice is coated by a film of water even below the freezing temperature. The atoms at the crystal’s surface are more loosely bound than the atoms in the interior of the crystal. At high enough temperatures, but well below the melting temperature, the atomic bonds are broken and eventually a liquid film is formed on the surface of the crystal (Wettlaufer, 1999). It is the precursor of surface melting (Wettlaufer, 1999), and typically begins as a few atomic layers thick film which gradually thickens as melting occurs. Because of the presence of such liquid films, there is no energy barrier for the heterogeneous nucleation of the liquid phase at the solid-vapor interface.

The first direct microscopic observation of a surface-initiated melting phenomena was made by Frenken and van der Veen (1985) in a study of (100) planes in lead. Recently, Brihuega et al. (2005) monitored a specific set of atoms continuously in time during a surface structural transition using a specially built scanning-tunneling
microscope. Such techniques may lead to further understanding of the details in the surface-melting mechanism. For reviews of surface melting see, e.g. Dash et al. (1995) and Dash (1999).

If heterogeneous nucleation can be suppressed, a solid may be superheated well above the equilibrium melting temperature. In recent experiments (Luo and Ahrens, 2003, Siwick et al., 2003, Sokolowski-Tinten et al., 2003, Rethfeld et al., 2004), ultrafast solid-liquid phase transitions induced by laser pulses were studied. In order to directly monitor the changes in atomic configuration caused by the breaking or formation of atomic bonds a time resolution of $10^{-14}$ s to $10^{-12}$ s is needed (von der Linde, 2003). This was achieved in the experiments by electron diffraction. When the intense radiation penetrates into the bulk of the solid the material is heated very quickly ($\sim 100$ K ps$^{-1}$). The experiments show that under such conditions the atomic configuration of the entire material can be modified on the ultrafast time scale, and melting occurs in a superheated state at a temperature above the equilibrium melting temperature. The melting time of the surface layer of the material is of the order of several picoseconds, which is too short to be explained by the heterogeneous melting mechanism (Zhigilei et al., 2004). The melting process can therefore be attributed to homogeneous nucleation of the liquid phase (Ivanov and Zhigilei, 2003). This makes the detailed melting mechanism a matter of great current interest. Superheating a metallic crystal can also be achieved by embedding it in a solid matrix with a melting temperature higher than that of the encapsulated crystal (e.g. Bahnhart et al. (2003)).

6.3 Two-dimensional systems

The solid-to-liquid transition in two-dimensional systems is a subfield of melting. Such melting has not been considered in this thesis but is briefly mentioned here to point out the differences between melting in two and three dimensions. A short review of this field can be found in, e.g. Dash (1999). According to theories of two-dimensional melting (Kosterlitz and Thouless, 1973, Halperin and Nelson, 1978, Nelson and Halperin, 1979, Young, 1979) a hexatic phase\(^1\) exists between the solid and the liquid. Melting occurs by the generation of two types of topological defects. First, a few tightly bound dislocations in the solid phase are thermally activated and dissociate. The translational long-range order of the crystal is lost at this stage. In the resulting hexatic phase some orientational order still remains, but it is destroyed when the free dislocations dissociate into a different kind of defect (disclinations). Several computer simulations (e.g. Bagchi et al. (1996), Zahn and Maret (2000)) and experiments (e.g. von Grünberg et al. (2004)) have been carried out to test this theory but consensus is yet to be reached.

\(^1\)An ordered intermediate phase between the solid and liquid phases which exhibits hybrid solid and liquid properties.
6.4 Previous melting theories

Many different models of melting have been proposed, see reviews by Boyer (1985), Poirier (1991), and Dash (1999). A few of them are mentioned here.

Assuming a harmonic solid, Lindemann (1910) calculated the Einstein vibrational frequency. As a step in his calculations he assumed that at the melting temperature the thermal displacements are so large that neighbouring atomic spheres collide, which led him to a relation between the melting temperature and the vibrational frequency of the Einstein solid. Gilvary (1956) connected the Lindemann relation with melting when he asserted that melting occurs when the thermal displacements of the atoms exceed a certain fraction of the nearest-neighbour distance. This is often referred to as the ‘Lindemann law’, despite the role Gilvary had in it. Brillouin (1938) and Born (1939) proposed shear instability models of melting, that set the loss of shear resistance as a criterion for melting (since liquids have very low shear strength).

Defect-mediated theories of melting are abundant in the literature. Lennard-Jones and Devonshire (1939), Gorecki (1974), and others developed point defect theories. A model of melting involving interstitials coupled to shear strains was introduced by Granato (1992), Mizushima (1960), Kuhlmann-Wilsdorf (1965), and others, proposed theories involving dislocations in which the melting transition is attributed to the generation of dislocation cores that fill the crystal. Recently Burakovsky et al. (2000) in their theory of melting modelled the dislocations as non-interacting closed loops on a lattice, close to the melting temperature. Reviews of dislocation-mediated theories of melting have been made by Ubbelohde (1978) and Cotterill (1980), the former also discussing the role of point defects in melting.

Tallon (1989) considered the instability limits of a superheated solid at which the material cannot sustain crystalline order. Tallon found that the upper limiting temperature for a rigidity catastrophe (i.e. the temperature at which the shear modulus falls to zero) is below the limits defined by the isochoric and entropic catastrophes (the temperatures at which the volume and entropy of the liquid and solid are equal, respectively). Lu and Li (1998) and Rethfeld et al. (2002) analyzed the melting of superheated crystals by homogeneous nucleation. Lu and Li found that a homogeneous nucleation catastrophe occurs before any of the catastrophes mentioned above. Rethfeld et al. concluded that for high superheating, at temperatures about 50 % above the equilibrium melting temperature, a solid can melt typically within a few picoseconds. Several metals, e.g. aluminium and copper, were considered in their study.

During the last ten or so years, computer simulations of the homogeneous melting process have been carried out by many authors, mainly focusing on arguments for or against different melting theories. The setup for a computer ‘experiment’ of homogeneous melting is straight-forward since periodic boundary conditions can be used to remove the effects of free surfaces. There exists such a wealth of reported work on melting that only a few will be mentioned here. For example, the classical homogeneous nucleation-and-growth mechanism of melting has been advocated re-

6.5 Local disorder

In molecular dynamics simulations at very high temperatures, the thermal fluctuations of the atoms can be large and rapidly fluctuating, making it difficult to determine if the lattice is locally intact. As a measure of local disorder the following definition was used in papers 3 and 4 (cf. Nordlund and Averback (1998)). The lattice is considered as perfect at a given instant if the Wigner-Seitz cell centred at an equilibrium lattice site contains exactly one atom. The Wigner-Seitz cell is formally defined as the region about a lattice point which is closer to that lattice point than to any other (Ashcroft and Mermin, 1976). At high temperatures some cells may be unoccupied, and an equal number doubly occupied. This is taken as a set of vacancies and interstitials. It is important to establish that this definition describes well-defined point defects even at very high temperatures. This was checked in detail, see paper 3 and appendix A in paper 4.

6.6 Point defect concentrations

Experimental measurements yield an equilibrium vacancy concentration in aluminium at the melting temperature of about $10^{-3}$ (Hehenkamp, 1994). The equilibrium interstitial concentration just below the melting temperature is about one order of magnitude less (Gordon and Granato, 2004).

In simulations using periodic boundary conditions no sources or sinks for point defects are present, and there is an oversaturation of interstitials (Nordlund and Averback, 1998). The equilibrium concentrations of point defects are generated from the creation of Frenkel defects (i.e. vacancy-interstitial pairs), which make the concentrations of vacancies and interstitials in the simulations equal. In simulations of the solid-to-liquid transition we observed point defect concentrations of about $5 \times 10^{-4}$ at the melting temperature in the superheated state (immediately before melting, cf. paper 3 and 4). The melting temperature was about $1.3T_m$, where $T_m$ is the equilibrium melting temperature. After melting had occurred we continued to log the number of ‘point defects’, using the same definition of point defects as in the solid phase, cf. section 6.5. The fraction of unoccupied or doubly occupied lattice sites in the liquid was about 30 %. This ratio must be considered with caution because the concept of point defects is ambiguous in the liquid phase. The fraction
was found independent of the system size (observed in systems with the number of atoms \( N = 2058 \), \( N = 20160 \), and \( N = 196560 \)).

### 6.7 Nucleation and growth of the liquid phase

The mechanism behind the initial steps of the homogeneous melting of superheated crystals is discussed in papers 3 and 4. We found from a step-by-step heating of the simulation cell in molecular dynamics simulations that point defects aggregate to form a ‘nucleus’ from which the liquid phase evolves. This result is in spirit with the classical nucleation-and-growth theory (Lu and Li, 1998, Rethfeld et al., 2002). The spatial distributions of the point defects in the lattice can be represented by forming all distances between the lattice-point centra of the Wigner-Seitz cells corresponding to the point defects. Thus at each time step in the simulation all distances between interstitials and vacancies \( (d_{iv}) \), between vacancies \( (d_{vv}) \), and between interstitials \( (d_{ii}) \) are formed. These distances are normalised as \( x = d_{iv}/a_0 \) etc., where \( a_0 \) is the face-centred cubic lattice parameter at \( T = 0 \) K.

The distributions \( n_{iv} \), \( n_{vv} \), and \( n_{ii} \) of such distances are shown in figure 6.2 at two different times in a simulation at constant temperature \( T = 1189 \) K. At time \( t_a \), there is a bound aggregate of four interstitials and no vacancies, represented by the six interstitial-interstitial distances at small \( x \). The upper cell (a) shows the geometrical distribution of point defects in the simulation cell at the time \( t_a \). The spheres indicate the positions of the lattice-point centra corresponding to the point defects. Blue spheres represent vacancies and red spheres represent interstitials. The bound aggregate with four interstitials and no vacancies is seen in the lower right part of the cell. At the time \( t_b \), 5000 time steps (equal to about 500 typical vibrational periods of atoms in the solid) after time \( t_a \), the defect aggregate has grown in size, and can at this stage be viewed as a liquid drop embedded in the solid matrix. In the liquid state the concept of point defects is ambiguous (cf. section 6.6) and nothing certain can be said about the internal structure of the liquid drop in terms of point defects. With this in mind, the liquid structure contains 15 ‘interstitials’ and seven ‘vacancies’ according to the definition given in section 6.5. The liquid drop is seen in the right-hand side of the lower cell (b). This illustrates how the aggregate of point defects acts as a nucleation site for the growth of the liquid phase.
Figure 6.2: The growth of the liquid phase in the homogeneous melting of a superheated aluminium crystal. The histograms show the distributions of the distances between the point defects (see the text). At time $t_a$, there is a bound aggregate of four interstitials, represented by the six interstitial-interstitial distances at small $x$. This aggregate can be seen in the cell to the upper right. At time $t_b$, the aggregate has grown in size so that it now contains seven vacancies and 15 interstitials.
Chapter 7

Thermophysical defect properties

In this chapter the calculations of some thermophysical defect properties are discussed. Also, a few checks of some of the numerical procedures used in the calculations are described.

Defect energies give the energy associated with the formation of the defect relative to the perfect crystal. The Helmholtz free energy is \( F = U - TS \), where \( U \) is the total energy, \( T \) is the temperature, and \( S \) is the entropy. At high temperatures, the \(-TS\) term may become significant. For example, the vibrational entropy of atoms close to defects becomes important in the high-temperature regime. The vibrational entropy is also relevant in, e.g. the formation and migration free energies of lattice defects, and it may have important effects on phase diagrams (e.g. Ozoliņš et al. (2005)).

7.1 Stacking fault energies of aluminium and copper

There is an energy associated with the introduction of a stacking fault. In section 3.3 the stacking fault was illustrated as the removal of one atomic plane in the regular stacking sequence. An alternative picture is given by considering two blocks of atoms in the crystal, whose common boundary lies between two atomic planes in the stacking sequence. The stacking fault can be seen as one of the blocks being rigidly sheared over the other. For example, an intrinsic stacking fault in the face-centred cubic lattice is introduced by shearing one block of atoms a distance \( a_0/6^{1/2} \) rigidly in the [112] direction from the ideal position, with the other block kept fixed (Lu et al., 2000). The excess energy associated with such a defect relative to a perfect crystal is called the intrinsic stacking fault energy \( \gamma_{sf} \). The excess energy may also be calculated for a fault associated with an arbitrary displacement along the [112] direction. The set of all such excess energies versus the displacement is usually referred to as the generalised stacking fault energy curve. The position corresponding to the intrinsic fault is the only stable configuration along this curve (disregarding the position of zero displacement), although the crystal is not in
its equilibrium structure at that position. A schematic figure of the generalised stacking fault energy curve is shown in figure 7.1, where $\gamma$ is the stacking fault energy plotted as a function of the slip distance $d$. The points C, C', and A correspond to the $\{111\}$ planar stacking of the lattice structures shown in the upper part of figure 7.1. In the curve $\gamma_{if}$ is a local minimum, and the ‘unstable’ stacking fault energy $\gamma_{uf}$ is a maximum. Following Rice (1992), $\gamma_{uf}$ represents the energy barrier that a partial dislocation has to overcome in order to nucleate. Knowing the mechanisms behind dislocation nucleation may lead to a theory that is capable of predicting when a dislocation will be created (Zimmerman et al., 2000).

The generalised stacking fault energy curves were calculated starting from a
7.1. STACKING FAULT ENERGIES OF ALUMINIUM AND COPPER

![Graph](image)

Figure 7.2: Generalised stacking fault energy curves (unrelaxed) for aluminium and copper. $d$ is the slip distance in the [112] direction (see text). The curve with filled triangles was calculated here with the interaction of Sabochick and Lam (1991) for copper. The other curves are for aluminium, calculated with the interactions of Ercolessi and Adams (1994) (filled squares), Mei and Davenport (1992) (filled circles), and Mishin et al. (1999) (filled diamonds).

A system with 672 atoms arranged in a face-centred cubic lattice. The simulation cell consisted of 12 (111) atom planes, each containing 56 atoms, with the cell axes in the [110], [112], and [111] crystallographic directions. Half the cell, i.e. a block of six (111) atom planes, was displaced in small increments in the [112] direction relative to the other half. At each position the excess energy of the faulted crystal relative to the ideal lattice was calculated. In the direction of the close-packed planes the simulation cell was terminated by free surfaces, and periodic boundary conditions were used in the [110] and [112] directions (i.e. the simulation system had the shape of a slab).

Figure 7.2 shows the unrelaxed generalised stacking fault energy curves for alu-
uminium and copper, calculated here using equation 5.7 and with the interactions of Ercolessi and Adams (1994), Mei and Davenport (1992), and Mishin et al. (1999) for aluminium and with the interaction of Sabochick and Lam (1991) for copper. \( d \) is the slip distance in the [112] direction. The symbols on the curves in figure 7.2 are for identification purposes and do not represent the full set of data points. Note that the curves with filled triangles (Sabochick and Lam) and filled circles (Mei and Davenport) have maxima approximately at the displacement \( d/(a_0/6^{1/2}) = 0.5 \), a value expected from geometrical considerations (Zimmerman et al., 2000). The small ‘kink’ in the curve with filled squares (Ercolessi and Adams) near \( d = 0.4a_0/6^{1/2} \) results from details in the potential model rather than being a physical feature of the generalised stacking fault energy curve (cf. appendix A). The potential of Mishin et al. (1999) has been fitted to the stacking fault energy and thus reproduces this value well (cf. the curve with filled diamonds in figure 7.2). None of the other interactions considered here was fitted to \( \gamma_{sf} \). The interaction of Ercolessi and Adams (1994) gives a reasonable value of \( \gamma_{sf} \) compared to the experimental value, but the interaction of Mei and Davenport (1992) fails to accurately describe \( \gamma_{sf} \). Identical calculations were also carried out to examine a possible effect of the free surfaces, using systems containing 120 and 240 (111) atom planes, respectively, each with 56 atoms. The difference in the results between the calculations using different system sizes was negligible for our purposes.

Table 7.1 gives selected values of the calculated \( \gamma_{sf} \) and \( \gamma_{ef} \) for aluminium and copper, deduced from figure 7.2. Experimental data and results of other calculations using effective interactions are listed for comparison. All values reported in table 7.1 correspond to unrelaxed stacking fault energies. In the case of aluminium, \( \gamma_{sf} \) is consistently underestimated compared with the experimental value. The same is true for copper with one exception, cf. table 7.1. In table 7.1 and figure 7.2 there is a considerable scatter in the values of the stacking fault energy. This illustrates the sensitivity of the stacking fault energy to details in the effective interaction. Some checks of this issue are described in appendix A.

### 7.2 Atomic force constants in aluminium

The lattice around a dislocation core has compressed and expanded regions, as discussed in paper 1. The net volume change associated with the core of an edge dislocation is small, as a result of a partial cancellation between the volume changes of the compressed and expanded regions. In the expanded region, the force constants are lowered, leading to a decrease in the vibrational frequencies, whereas the force constants are larger in the compressed region, leading to an increase in the vibrational frequencies. The result is a net increase in the vibrational entropy (cf. paper 1). The vibrational frequencies were calculated from the eigenvalues of the dynamical matrix \( \mathbf{D} \) (cf. section 5.1). The matrix element \( D_{\alpha ij}^{\beta} \) was calculated by displacing atom \( i \) a distance \( \Delta r \) in the direction \( \alpha \), after which the restoring force on atom \( j \) in the \( \beta \) direction was calculated. The choice of the most suitable \( \Delta r \)
7.3. VACANCY EXCESS ENTROPY IN ALUMINIUM AND COPPER

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<th>Copper</th>
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<td>Szelestey et al. (2002)</td>
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<td></td>
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Table 7.1: Intrinsic (γ_{if}) and extrinsic (γ_{af}) stacking fault energies for aluminium and copper (unrelaxed). All energies are in units of mJ m$^{-2}$. Our reported values of γ_{if} and γ_{af} were calculated using the interactions of Ercolessi and Adams (1994) (aluminium) and Sabochick and Lam (1991) (copper).

$^a$Using the interaction of Ercolessi and Adams (1994).
$^b$Using the interaction of Oh and Johnson (1988).
$^c$Using a modified version of the interaction of Chantasiriwan and Milstein (1998).
$^d$Using the interaction of Jacobsen et al. (1996).
$^e$See Hirth and Lothe (1982).

depends on the model potential which is used. It is important to determine the appropriate Δr for each potential model. An example of this is given in appendix B.

Figure 7.3 illustrates the softening and stiffening of the force constants mentioned above. The filled circles show force constants k acting in the [110] direction, for a number of atoms along a line in the [110] direction in the (111) plane in the dislocation core immediately above the glide plane of the dislocation, where the lattice is compressed. x is a coordinate along the line of atoms, normalised to the face-centred cubic lattice parameter at T = 0 K. The filled squares show such force constants in the (111) plane immediately below the glide plane, where the lattice is expanded. For comparison, k ≈ 72 N m$^{-1}$ in bulk aluminium. The force constants were calculated from the restoring forces on the atoms in the [110] direction due to a small displacement of these atoms in the same direction.

7.3 Vacancy excess entropy in aluminium and copper

The vacancy excess entropy ΔS for aluminium and copper was here calculated using the effective interactions of Ercolessi and Adams (1994) and Sabochick and Lam (1991), respectively, using the ‘supercell’ method and the method of Mishin, Sørensen and Voter (2001), both of which are described in section 5.4.

First, ΔS was calculated using the supercell method. A cubic simulation cell containing 1372 atoms arranged in a face-centred cubic lattice was relaxed under zero pressure from a low temperature to the atomic equilibrium sites. The dynam-
CHAPTER 7. THERMOPHYSICAL DEFECT PROPERTIES

![Graph showing force constants $k$ acting in the [110] direction, on atoms in the compressed region of the core of an edge dislocation in aluminium (circles) and in the expanded region of the core (squares). $x$ is a coordinate along a line of atoms in the [110] direction, normalised to the face-centred cubic lattice parameter $a_0$ at $T = 0$ K.](image)

Figure 7.3: Force constants $k$ acting in the [110] direction, on atoms in the compressed region of the core of an edge dislocation in aluminium (circles) and in the expanded region of the core (squares). $x$ is a coordinate along a line of atoms in the [110] direction, normalised to the face-centred cubic lattice parameter $a_0$ at $T = 0$ K.

The dynamical matrix for the cell was constructed by giving one atom a static displacement $\Delta r$ of about 0.025 % of the $T = 0$ K lattice parameter (cf. section 7.2) in each of three orthogonal directions, after which the components of the restoring forces on all atoms were calculated. This was repeated for all atoms in the simulation cell. After that one atom was removed from the simulation cell, thus creating a vacancy. The atomic positions were again relaxed to their equilibrium sites under zero pressure, and the dynamical matrix was calculated in the same way as before. A diagonalisation of these matrices yielded the vibrational frequencies of the defect and the perfect system (cf. section 5.1) from which the vibrational excess entropy was calculated using equation 5.10. The results were $\Delta S = 1.09k_B$ for aluminium and $\Delta S = 1.50k_B$ for copper. The sensitivity of these values to the choice of $\Delta r$ was examined. When varying $\Delta r$ by roughly an order of magnitude the results for $\Delta S$ differed by less than 1 %. $\Delta S$ was also determined for simulation cells containing 500, 864 and 2048 atoms. The relative change in $\Delta S$ for aluminium and copper}
was less than 0.5 % compared to the calculation using the cell with 1372 atoms (cf. figure 7.5). Mishin, Sørensen and Voter (2001) calculated $\Delta S$ for copper obtaining $\Delta S = 1.231 k_B$, using the embedded-atom potential model of Voter (1995) with potential parameters appropriate for copper (Voter, 1998). A measurement by Neumann et al. (1999) on copper yielded $1.08 k_B$. The value for aluminium compares well with the ab-initio calculation of Carling et al. (2000) (about $1.1k_B$) and the experimental result of Heikenkamp (1994) ($1.1k_B$).

Second, as an application of the method of Mishin, Sørensen and Voter (2001), $\Delta S$ was calculated considering two separate regions of the simulation system, containing $N_I$ and $N_{II}$ atoms, respectively. A cubic simulation cell with $N = N_I + N_{II} = 5324$ atoms arranged in a face-centred cubic lattice was used, with periodic boundary conditions in each of the three orthogonal directions. Figure 7.4 shows a schematic picture of the simulation cell, viewed along a line perpendicular to one of its faces. The two regions of the lattice are indicated in the figure. In region I, shaped as a sphere approximately centred on the vacancy, all atoms were considered dynamic. Their vibrational frequencies were calculated from the dynamical matrix for the $N_I$ atoms contained in the region (cf. figure 7.4), and the entropy of region I was calculated from equation 5.9. Region I is well embedded in the surrounding lattice, which acts as a boundary condition for the embedded region. In the remaining region II, the entropy contribution of the $N_{II}$ atoms was calculated from the quasicontinuum model of Mishin, Sørensen and Voter (2001) using equation 5.11. Similar calculations were also carried out for a bulk system, using the same partitioning of the simulation cell as for the defect system. The excess entropy was then calculated according to equation 5.7. The cubic expansion factor $\beta$ in equation 5.11 was obtained from the thermodynamic relation $\beta K_T = (\partial S/\partial V)_T$ (Grimvall, 1999), where $K_T$ is the isothermal bulk modulus. The partial derivative of $S$ was approximated by calculating the difference between $S$ for an undisturbed system and one in which the lattice parameter had been expanded by 0.1 %, corresponding to a volume expansion of about 0.3 %. $K_T$ was taken from the 0 K value from the calculation of Ercolessi and Adams (1994) (aluminium) and Sabochick and Lam (1991) (copper), respectively. The computational method outlined above was also applied to a system containing two edge dislocations (cf. paper 1). The choice of the shape and the appropriate size of the embedded cluster region in this case are discussed in paper 1.

Figure 7.5 shows the vacancy excess vibrational entropy $\Delta S$ for aluminium and copper. The open squares and circles give $\Delta S$ of region I as functions of the inverse number $N_I^{-1}$ of dynamic atoms, for aluminium and copper, respectively. Filled squares and circles give the ‘elastically corrected’ excess entropies, i.e. the sum of the contributions to $\Delta S$ from region I and II, as functions of $N_I^{-1}$. In the limit of $N_I^{-1} \to 0$, the filled squares and circles should approach the values which were obtained by using the supercell method (Mishin, Sørensen and Voter, 2001), described above. Those values are indicated in figure 7.5 by the diamond (aluminium) and the cross (copper) symbols. In that case $N_I$ corresponds to the number of atoms in the simulation cell. Figure 7.5 demonstrates the use of the method of Mishin,
Sørensen and Voter (2001). For a given number of dynamic atoms \( N_1 \gtrsim 500 \), this method provides an accuracy comparable to the supercell method but with less computational effort. On the other hand, the entropies obtained from region I only (open squares and circles) do not approach the values calculated using the supercell method (at least not within the limits of available cluster sizes). In fact, figure 7.5 indicates that the open squares and circles diverge when extrapolated to \( N_1^{-1} \rightarrow 0 \), which is in agreement with the analysis of Fernández et al. (2000).

### 7.4 Interstitial energetics in aluminium and copper

The interaction energy between two lattice defects ‘A’ and ‘B’ is defined as (cf. Klemradt et al. (1990))

\[
\delta E = \Delta E_{AB} - \Delta E_A - \Delta E_B,
\]

where \( \Delta E_{AB} \) is the excess energy (see section 5.3) of the AB defect complex relative to the bulk, and \( \Delta E_A \) and \( \Delta E_B \) are the excess energies of the isolated A and B defects. The interaction energy depends on the relative geometrical arrangement of the defects and the distance between them. Point defect interaction energies are important in the understanding of diffusion, short-range order etc. In paper 4 the interaction energy between two self-interstitials in aluminium was calculated, as a function of the distance between the interstitials, and for two different geometrical
Figure 7.5: Vacancy excess entropies $\Delta S$ for aluminium and copper calculated using the method described in section 5.4 by partitioning the simulation system as indicated in figure 7.4. The open squares and circles give $\Delta S$ for region I (see text), for aluminium and copper, respectively, as functions of the inverse number $N_1^{-1}$ of dynamic atoms. Filled squares and circles give the sum of the contributions to $\Delta S$ from region I and II, also as functions of $N_1^{-1}$. The diamonds and the crosses give the values of $\Delta S$ obtained by using the supercell method (see text), for aluminium and copper, respectively.

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<th>$l/a_0$</th>
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Table 7.2: Interaction energy $\delta E$ of two interstitials in copper in parallel and perpendicular configurations (cf. paper 4). $l/a_0$ is the normalised distance separating the interstitials, where $a_0$ is the copper fcc lattice parameter at $T = 0$ K. All energies are expressed in eV.
arrangements (cf. paper 4). In the following, our results for copper are presented and compared with the results of Kogure et al. (2004).

An isolated interstitial in copper with face-centred cubic structure has an extended dumbbell configuration, i.e., two atoms trying to occupy the same lattice point (Ehrhart, 1978). The excess energy for a single interstitial was calculated as $\Delta E_i = 3.2$ eV using the potential of Sabochick and Lam (1991), which compares well with an earlier calculation (Suzuki and Mishin, 2003) using a model potential of Mishin, Mehl, Papaconstantopoulos, Voter and Kress (2001) (3.1 eV) and the result of Kogure et al. (2004) (3.24 eV). An experiment gave $\Delta E_i = 2.2 \pm 0.7$ eV (Schilling, 1978). The interaction energy of two self-interstitials is calculated as $\delta E = \Delta E_{ii} - 2\Delta E_i$, where $\Delta E_{ii}$ is the excess energy with respect to an ideal crystal for the double interstitial configuration. The two interstitials were either in parallel or perpendicular configurations, cf. figure 7.6. Table 7.2 gives our results in comparison with the results of Kogure et al. (2004).
Chapter 8

Introduction to the scientific papers

Here follow short introductions to the scientific papers, and also comments on my contribution to them.

8.1 Introductions

Paper 1: Vibrational entropy of dislocations in Al

Close to a lattice defect, there is severe distortion compared to an ideal lattice, while the strain in the surrounding bulk to a good approximation obeys Hooke’s law, i.e. the stress-strain relation is linear. Using this fact, we treat the vibrations of the atoms in a system with an extended defect (an edge dislocation) in two different ways. In the region closest to the defect (the ‘cluster’), the full dynamical matrix for the atoms is diagonalised, yielding the vibrational frequencies. In the surrounding region, the vibrations are treated with a quasicontinuum method used in an earlier study of the vibrations of the atoms around point defects. These two approaches are then joined in calculating vibrational properties of the system. The great advantage of this method is that for a given size of the cluster, it gives an accuracy comparable to the larger computational problem of calculating the vibrational frequencies for all atoms in the simulation cell. The main result of the work is an estimation of the excess vibrational entropy of the atoms caused by the edge dislocation. The excess entropy of the dislocation core has positive and negative contributions, depending on the sign of the local strain. Typically, the excess entropy is $2k_B$ per atomic repeat length along the dislocation core in face-centred cubic aluminium. The method is of generic nature and can be used to study the vibrations of other systems with extended defects.
CHAPTER 8. INTRODUCTION TO THE SCIENTIFIC PAPERS

Paper 2: Anharmonic effects in the heat capacity of Al

Previous works (e.g. Leadbetter (1968), Rosén and Grinyvall (1983)) have shown a seemingly small anharmonic contribution to the heat capacity. In the present work, the vibrational heat capacity (i.e. the contribution from the phonons to the heat capacity) at fixed volume is calculated using molecular dynamics and Monte Carlo methods, which account for anharmonicity to all orders, for a given effective interaction between the atoms (Shukla and Cowley, 1998). From experimental data at constant pressure (Ditmars et al., 1985) the vibrational part of the heat capacity at fixed volume is deduced, and compared with our simulation results. At low temperatures the low-order anharmonic terms are dominant. By a linear extrapolation of the heat capacities at low temperatures we show that anharmonic effects are indeed very important in aluminium. The small (total) anharmonic effect in aluminium is caused by a partial cancellation between the low-order term linear in the temperature and higher-order terms with a more rapid temperature dependence.

Paper 3: How superheated crystals melt

Molecular dynamics simulations at constant pressure and temperature have been carried out, in a step-by-step heating procedure of face-centred cubic aluminium. At each time step in the simulations the position of each atom is logged in order to follow the microscopic path to melting. The periodic boundary conditions which are used remove the effect of free surfaces and thus inhibit melting. Melting takes place in a superheated state at a temperature considerably above the equilibrium melting temperature. Point defects are identified in simulations by calculating the number of atoms in Wigner-Seitz cells centred at each equilibrium lattice point. An empty cell is interpreted as a vacancy, and a doubly occupied cell is interpreted as an interstitial. From a large number of independent simulations we find that the thermal fluctuation which initiates melting is an aggregate typically with 6–7 interstitials and 3–4 vacancies.

Paper 4: Homogeneous melting of superheated crystals: Molecular dynamics simulations

The results of this paper rests on simulations of the same kind that was briefly described in paper 3. A more detailed picture is given of the melting mechanism reported in in paper 3, and further results on the dynamics of the melting process are discussed. The occurrence of ‘large’ thermal fluctuations which lead to melting is quantified through a large number of simulations, showing that once a thermal fluctuation represented by an aggregate of 6–7 interstitials and 3–4 vacancies occurs, the crystal melts irreversibly in the majority of cases. The typical time from which a thermal fluctuation occurs (which leads to melting) until the long-range order in the crystal is destroyed, is calculated. A comparison with the time scale related
to thermal conductivity shows that the solid-liquid boundary of the liquid nucleus advances by a pace comparable to that of thermal transport by vibrating atoms at high temperatures.

Paper 5: Heat capacity of liquid Al

Tables of recommended data often give the heat capacity at constant pressure, in the liquid phase up to the boiling temperature, as independent of temperature, or in case where accurate experimental data is available, with a shallow minimum. This can be qualitatively understood as the result of two opposing effects – a gradual loss of shear resistance and thermal expansion. (Grimvall, 1975) In this paper a detailed analysis of a liquid metal, in this case aluminium, is carried out using molecular dynamics modelling. The constant pressure heat capacity, calculated with an interaction which gives a good account of anharmonicity (cf. paper 2), has a minimum in the liquid phase. A formal theoretical argument (Wallace et al., 1982) has shown that the constant volume heat capacity should asymptotically approach $2k_B$ per atom with increasing temperature. Such a behaviour is seen in our calculations. However, the fixed volume heat capacity, which has been determined in simulations for temperatures up to 50 000 K, falls below $2k_B$ per atom. The simulated liquid then tends to behave like a system of hard spheres, approximately modelled in our simulations with the repulsive part of the effective interaction.

8.2 Comments

In all papers I contributed to the scientific idea and methods, and to the discussion and analysis of the results. I did all the simulations and other calculations described in the papers. The molecular dynamics simulations were carried out using a program written by Nils Sandberg, and extensively modified by me. Furthermore, a Monte Carlo program by Nils Sandberg, and modified by me, was used for some simulations as described in paper 2. All other computer code was written by me. Paper 1 and paper 3-5 were written jointly by the authors. Paper 2 was written by me and Göran Grimvall. I made the figures in all papers.
Chapter 9

Conclusions and outlook

Melting is one of the examples of a phase transition that may be readily observed in nature. When a crystal melts it loses its long-range crystalline order. The liquid still has short-range order – a given atom will have some mean number of nearest neighbours with no preferred orientations, at an average neighbour distance. The absence of long-range order is characteristic of liquids, while gases additionally have no short-range order. The melting process and the mechanism behind it have been studied for a very long time. In spite of that, melting is still poorly understood on the atomic level. Molecular dynamics simulations allow the positions of all atoms to be traced at every instant, as the system evolves in time. We have used such simulations, relevant for face-centred cubic aluminium, to track the microscopic path to melting. By slowly heating the simulation system we were able to determine the smallest thermal fluctuation responsible for initiating melting, in terms of lattice point defects. This result is important in itself, but may also prove important in the understanding and interpretation of recent high-energy experiments of femtosecond heating where the atomic configuration of the entire material is modified on the ultrafast time scale.

Future work resting on this result could be aimed at examining the melting mechanism for materials with other crystal structures than the face-centred cubic structure, perhaps starting with an interatomic potential suitable to describe a body-centred cubic crystal. Another topic for future simulations would be to study the reverse process of melting - freezing. In analogy to a superheated crystal, a liquid may be undercooled, i.e. remain in the liquid phase even below the freezing temperature. It has been well established since the work of Turnbull (1950) that metallic liquids can be deeply undercooled. Experimentally, it is easier to undercool a liquid than to superheat a crystal. In an undercooled melt there is evidence of icosahedral\(^1\) short-range order (Schenk et al., 2002, Di Cicco et al., 2003). The process of freezing could in principle be studied at the atomic level by slowly cooling the liquid and tracing the positions of all atoms at each instant with the methods

\(^1\)An icosahedral cluster is an arrangement of 13 densely packed atoms.
which have been used in this thesis. Crystallisation from a melt of hard colloidal spheres (Auer and Frenkel, 2001), and the nucleation from a solution of sodium chloride (Zahn, 2004) were studied recently in computer simulations. The time scales of crystallisation processes are presumably very much larger than the time scales accessible through simulations (Zahn, 2004). However, when nucleation starts the process may occur at a very fast time scale. The path sampling method (Dellago et al., 1998) allows for a strategy in which the waiting time for nucleation may be ignored and the simulation can be focused on the nucleation process.

This thesis also has demonstrated the use of a generic computational method which can be used to model the atomic vibrations near extended lattice defects. It was originally developed for the study of vibrational properties of point defects by Mishin, Sorensen and Voter (2001). Here it was applied to an edge dislocation in face-centred cubic aluminium. In such a crystal structure an edge dislocation splits into two partial dislocations (Shockley partials). It is a good example of a crystal imperfection with a complicated geometry. There are expanded and compressed regions in the core of such a dislocation giving lower and higher vibrational frequencies, respectively, compared to the bulk. The overall effect is a positive excess entropy associated with the edge dislocation core. It was quantified in this thesis. The method which was used is generic in nature and can be applied to study the vibrations near other extended defects, e.g. grain boundaries.

In some areas of computational materials science, there is need for large-scale atomistic simulations. Available computer capacities limit the size of the systems that can be treated in ab-initio quantum-mechanical calculations. Thus the need for accurate effective interactions will remain in the future.
Appendix A

Sensitivity of the stacking fault energy to details in the assumed interaction

Splines polynomials are commonly used to represent the potential functions \( \Phi \), \( \rho \), and \( F \), cf. section 4.1. Particular attention was paid to the choice of the number of spline knots and its influence on the stacking fault energy. Many effective interactions use analytical expressions for the potential functions (cf. section 4.2). However, in practice they are fitted to low-order piece-wise polynomials to enhance speed in the simulations. In the implementation of such effective interactions, cubic spline fits with several hundreds of spline knots were used.

Using a varying number of spline knots, the potential functions of the interaction of Cleri and Rosato (1993) were fitted to piece-wise cubic splines. Generalised stacking fault energy curves were then calculated using these ‘modified’ potentials. With too few nodes (below about 25 in this specific case) the generalised stacking fault energy curve showed increasingly larger deviations from the curve corresponding to the case with hundreds of nodes. However, the magnitude of the curve at the position corresponding to the intrinsic stacking fault was negligibly changed. A geometrical consideration shows that \( \gamma_{ff} \) depends only on third-neighbour and more distant atomic interactions (Vitek, 2004). On the other hand, \( \gamma_{ff} \) depends on nearest-neighbour atomic interactions and beyond (cf. figure 7.1). The region of small \( r \) must be well ‘covered’ with spline nodes in the mathematical representation of \( \Phi \) and \( \rho \) to avoid large derivatives at the nodal points, i.e. to avoid large energy contributions to the stacking fault energy at the nodal points. This explains the large sensitivity of \( \gamma_{ff} \), and the insensitivity of \( \gamma_{ff} \), to changes in the number of spline knots in the mathematical representation of the potential functions.

The effect of using quadratic polynomials instead of cubic ones in the spline fit of the Ercolessi and Adams (1994) interaction was also examined. This resulted in large and unphysical changes in the generalised stacking fault energy curve, despite
the fact that it only induced minor changes in the potential functions \( \rho, \Phi, \) and \( F. \)

When calculating, e.g., the potential energy using equation 4.1, the summation over all interatomic pairs is truncated so as to include only the neighbours of a given atom inside a sphere within a fixed cutoff radius (cf. section 2.3). The stacking fault energy, computed by means of effective interactions with a mathematical form such as equation 4.1, depends on the cutoff radius (Heino et al., 1999). The sensitivity of the stacking fault energy to changes in the characteristic length parameter of the potential was examined by varying the lattice parameter \( a_0. \) Minor changes of the lattice parameter, from 0.997\( a_0 \) to 1.001\( a_0 \), gave changes in the generalised stacking fault curve for Ercolessi and Adams aluminium of the order \( \sim 10^{-3} \text{ mJ m}^{-2}. \)

Larger changes, e.g., a 1\% lowering of \( a_0, \) resulted in a slight rise (about 1\%) of the generalised stacking fault energy curve above large displacements \( d \) (above about \( d > 0.7a_0/6^{1/2}, \) cf. the curve with filled squares in figure 7.2).

Finally, the derivatives of the generalised stacking fault energy curves with respect to the slip distance \( d \) were calculated in two cases; the first for a potential fitted to piece-wise cubic polynomials with a small number of spline knots (a few tens), and the second for a spline-fitted potential with a large number of spline knots (a few hundreds). In the first case the generalised stacking fault energy curve showed several irregularities, but not in the second case using the smoother interaction.

In conclusion, the stacking fault energies may depend much on the details in the mathematical representation of the potential functions of the effective interaction. For example, the small ‘kink’ in the curve with filled squares in figure 7.2 caused by the use of low-order spline polynomials rather than being a physical feature.
Appendix B

Elements of the dynamical matrix

The procedure that have been used in this work to calculate the dynamical matrix is to displace an atom a small distance $\Delta r$ in each of the three orthogonal directions, and calculate the restoring forces on the displaced atom and on all other atoms. This is repeated for all atoms in the system. For the Ercolessi and Adams (1994) interaction, the elements of $\mathbf{D}$ are only weakly dependent on the displacement $\Delta r$ for small $\Delta r$. This was found from an examination of different matrix elements for varying $\Delta r$. The elements of $\mathbf{D}$ were calculated for a cubic simulation cell with 500 atoms arranged in a face-centred cubic lattice. In figure B.1 the values of some elements are plotted, in units of N m$^{-2}$, as functions of $\Delta r$. This shows the typical behaviour of $D_{\alpha\beta\gamma}$ for varying $\Delta r$. $a_0$ is the face-centred cubic lattice parameter at $T = 0$ K. It is clear from figure B.1 that for $\Delta r \lesssim 10^{-3}a_0$ the variation with $\Delta r$ is small. For displacements $\Delta r \gtrsim 10^{-3}a_0$, figure B.1 suggests a considerable increase in the absolute value of the force constants, thus indicating a strong anharmonic effect. This was checked in detail and was found to be a spurious effect caused by the low-order polynomial fit of the potential functions (cf. paper 1). For the Ercolessi and Adams interaction the potential functions were represented by piece-wise cubic spline polynomials. The second derivative of such functions are linear in the argument, giving too crude a description of the force constants for large $\Delta r$. 
Figure B.1: Values of some elements of the dynamical matrix calculated for a 500 lattice point system of face-centred cubic aluminium, using varying choices of the atomic displacement $\Delta r$ (see the text). $a_0$ is the face-centred cubic lattice parameter at $T = 0$ K. The values of the matrix elements are given in units of N m$^{-2}$. 
Bibliography


