Molecular Dynamics Simulations of Primary Radiation Damage from Collision Cascades

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Dedicated to my daughter, Emilia.
Abstract

In the face of the world’s increasing demand for energy, and the need to find sustainable and environmentally friendly ways of producing that energy, fusion power offers an attractive possibility. However, while fusion is technically already achievable, the operating conditions of future fusion devices are extremely harsh, posing a significant challenge for materials development and engineering of a commercially viable fusion power plant.

Tungsten (W) and tungsten alloys are current candidate materials for both structural and plasma-facing components, due to favourable properties such as good thermal conductivity, high heat strength and stability, and resistance to erosion. However, fusion reactor components will be subjected to high neutron loads, and little is currently known of the effects of radiation on the mechanical properties of this intrinsically brittle metal.

The extreme conditions in a future fusion reactor cannot be reproduced in existing experimental facilities, rendering simulation an invaluable tool in understanding the radiation damage processes, and predicting the materials response to radiation. Multiscale methods are necessary to span the length and time scales involved in radiation damage, from the picosecond and nanometer scale of displacement cascades giving rise to the primary damage, to the evolution of the radiation induced microstructure over the seconds of typical in-situ ion irradiation experiments, and further to the years of a reactor component’s life time.

In order to implement a multiscale simulation method, information must be distilled and transferred from the smaller scale to the larger. A microstructural evolution model needs as input the primary defects formed from individual impacts. Molecular dynamics (MD) simulations are ideal for studying the primary damage, but individual cascades vary greatly, and simulating high energy impacts in MD requires immense computer capacity. It is therefore not possible to simulate directly the whole variety of cascade outcomes. General laws deduced from the MD data, however, can be used to statistically generate varying cascades in the thousands.

In this thesis we use MD simulations to study the primary damage in metals, with focus on tungsten. We investigate the dependence of the results on various simulation parameters. We find that predic-
tions of cascade damage in the high energy regime are very sensitive to the treatment of electronic energy losses, as well as to the details of the interatomic potential chosen to model the atomic interactions. By directly comparing to experiments we validate results in regard to interatomic potentials as well as to simulation methodology.

Detailed analysis of the primary damage from high-energy cascades shows the formation of novel defects, confirming recent experimental observations. We also show that defect cluster sizes follow a general scaling law, which can be used to generate input for microstructural evolution models such as object kinetic Monte Carlo codes, thus avoiding the need to explicitly simulate thousands of cascades. A scaling law is found both for bulk and thin film, and is in good agreement with results from in-situ transmission electron microscopy experiments performed at 30 K.
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Chapter 1

Introduction

As the global demand for energy increases, new methods of producing electricity are needed. One possible method is from the energy freed by the fusion of light atomic nuclei. Several approaches to producing fusion energy are currently being studied. The most promising one is magnetic confinement fusion, involving a hot plasma confined by strong magnetic fields in a toroidal reactor, called a tokamak [1].

Production of this form of nuclear energy differs dramatically from the currently available fission energy. Fusion powers the sun by a reaction starting from protons (H), but here on earth, the most easily realized and efficient fusion reaction is between deuterium (D) and tritium (T). Hence current tokamak designs focus on this fuel combination [2]. However, even for these nuclei, the conditions required to reach a sustainable fusion reaction are extremely challenging to accomplish, and very sensitive to any disturbance. Thus a malfunction or other incident in a fusion power plant would immediately shut down the fusion process, so the risk for a runaway reaction is non-existent. Also, neither long-lived radioactive waste nor greenhouse gases are produced; the waste product from D-T fusion is helium.

Nevertheless, a certain measure of radioactivity is unavoidable in nuclear applications. Some activation of the tokamak walls could occur as a result of nuclear reactions between atomic nuclei in the material and penetrating energetic neutrons, which are also a product of the fusion reaction. In addition, the fuel component T is itself radioactive. However, methods of in-vessel tritium production [3] would eventually overcome the need to transport radioactive fuel material, and the activated reactor components would be safe to handle within 100 years [4], in stark contrast to the tens of thousands of years of containment required for high-level nuclear waste from fission plants.
Thus, commercial fusion power plants would provide a welcome addition to the world’s energy production. Unfortunately, the reactor environment is extremely harsh, with high heat loads and high radiation doses limiting the choices of viable wall materials. The walls of a future D-T fusion reactor will be subjected to particle bombardment from plasma particles, plasma impurities, and fusion neutrons [5]. Each of these species will impact with different energies, and the total radiation damage will depend on the complicated interplay between many competing processes. Tungsten (W) is a candidate material both for structural and plasma-facing components [6], due to its high temperature stability, good thermal conductivity, and resistance to erosion. However, W is an intrinsically brittle metal, and currently little is known regarding the embrittlement from neutron irradiation [7]. In addition to transmutation reactions, leading to activation of vessel walls and impurities in the material, the neutron irradiation also causes atomic displacements leading to microstructural damage. The long-term effects of radiation damage, such as swelling, blistering, hardening and embrittlement, determine the lifetime of reactor components, and thus crucially impact both practical and economic considerations.

Radiation effects are sensitive to both the irradiating species and the irradiation environment, including such factors as temperature, dose, and dose rate [8]. The conditions in a future fusion reactor cannot be reproduced in current experimental facilities. Thus sophisticated modelling techniques are required to predict material response to radiation [9, 10], and facilitate the development of materials able to meet critical performance criteria.

Long-term radiation damage depends on the thermal evolution of primary defects created from the individual particle impacts. Models simulating the microstructural evolution build on detailed knowledge of the migration and interaction behaviour of defects [11]. Since the evolution is sensitive also to the nature and morphology of the primary damage [12], the parameters describing these traits constitute important input for microstructural evolution models.

Molecular dynamics (MD) [13] simulations are ideally suited to studying the formation of primary damage. With modern computer capacity, MD allows us to follow the interactions of millions of atoms for up to nanosecond time scales, enough to cover the whole cascade process. However, care must be taken when performing MD simulations, since the methods necessarily rely on numerous approximations. Most notably, MD treats atoms as point particles, with no internal structure, and in particular no electrons. Furthermore, collision cascades are highly non-equilibrium processes, which involve interactions over a wide range of energies, and strong temperature and pressure gradients [14]. This puts high demands on the interatomic potentials describing the forces between the atoms. For this reason, validation of simulation methods by comparison to experiment is crucial, but not always easily achievable, since collision cascades take place at length and time scales not directly accessible by experimental methods.
In the work presented in this thesis, we study the formation of primary damage through MD simulations, assessing the sensitivity of results to variables in the applied methodology. We identify and quantitatively characterize aspects of the morphology of the damage in W, in a way which is directly transferable to microstructural evolution codes, and verify our findings by comparison to ion irradiation experiments.
Chapter 2

Purpose and structure of this study

The purpose of this thesis is to develop and deepen the understanding of the formation of primary radiation damage in metals, with focus on tungsten. The methods and results presented here will help to provide essential input for the increasingly sophisticated models of microstructural evolution being developed, with the ultimate goal of accurately predicting material response to radiation in future fusion reactors.

This thesis consists of a brief summary and 4 original articles, which are either published or under review in international peer-reviewed journals. The publications are referred to in bold Roman numerals in the text.

The structure of this thesis is as follows. This section summarises the articles, and details the author’s contributions. Chapter 3 briefly describes the physics of primary damage formation, and in Chapter 4 the key aspects of the simulation methods used in this work are discussed. Chapter 5 describes the primary damage in W, and Chapter 6 summarizes this work.

2.1 Summaries of the original publications

Publication I: High energy collision cascades in tungsten: dislocation loop structures and clustering scaling laws

Primary damage from 150 keV collision cascades in W is studied, showing dislocation loops of both $1/2\langle 111 \rangle$ and $\langle 100 \rangle$ type among the debris, in agreement with recent *in-situ* ion irradiation experiments. This find is unexpected, since energy criteria favour the
formation of 1/2⟨111⟩ type loops. In addition, the distribution of SIA cluster sizes is found to follow a scaling law, enabling statistical predictions of cascade damage without the need for hundreds of MD simulations. Such a scaling law is typical for fractal systems, and the fractal nature of the initial cascade development is highlighted.

Publication II: Radiation damage production in massive cascades initiated by fusion neutrons in tungsten

The morphology of the primary damage in high-energy collision cascades in W is studied in more detail, including analysis of the effect on simulation results of the treatment of electronic energy losses, and the choice of interatomic potential.

Publication III: On the lower energy limit of electronic stopping in simulated collision cascades in Ni, Pd and Pt

The effect of the choice of kinetic energy cut-off for electronic stopping in MD simulations of collision cascades is studied quantitatively. Comparison is made to experiments of mixing in Ni, Pd and Pt. We find that a low cut-off results in too much energy lost to electronic stopping and too rapid quenching of the liquid heat spike area, resulting in an estimation of the atomic mixing efficiency below that of experiment for all metals considered. The impact of the energy losses was largest in high-energy cascades.

Publication IV: Direct observation of size scaling and elastic interaction between nano-scale defects in collision cascades

Results from in-situ transmission electron microscopy experiments at cryogenic temperature are analyzed, both with respect to size and spacial distributions. These are compared to MD simulations of foil irradiation, with a geometry matching that of the experiments. Size distributions of dislocation loops in the experimental micrographs are found to follow a power law which agrees well with predictions from the simulations. Furthermore,
evidence is found of elastic trapping of defects, highlighting the importance of the morphology of the primary damage on microstructural evolution.

2.2 Author’s contribution

In publications I, II and III, the author carried out all the simulations and the analysis, and wrote the text in its entirety.

The calculations demonstrating the predictive power of the scaling law in publication I were suggested by S.L. Dudarev.

In publication IV, the author performed all the simulations and the analysis of the simulations, and wrote the parts of the article pertaining to the simulations.

2.3 Other scientific work

In addition, the author, Andrea Sand (née Meinander), has contributed to various (related and unrelated) scientific fields through the following publications, which, however, are not part of this thesis:


Chapter 3

Radiation damage in metals

3.1 The radiation damage event

Radiation damage refers to the structural changes in a target material subjected to impinging energetic particles. Most structural materials in future fusion reactors will be metals and metal alloys, with ordered crystalline atomic structure. Defects include atoms which are not located at a crystal lattice site, and vacant sites. Particles which are able to generate defects by displacing atoms from their lattice sites include neutrons, ions, electrons and photons.

In fusion reactors, the 14 MeV fusion neutrons constitute a major source of radiation damage. In addition to displacing atoms, neutrons can induce nuclear reactions which may result in the transmutation of target atoms into other species, thus introducing impurities in the material. For example, the reactions forming the bulk of transmutation products in 14 MeV neutron irradiated tungsten (W), \((n, \gamma)\) and \((n, 2n)\), mainly result in rhenium and osmium isotopes [15]. Transmutation reactions may also result in by-products, such as H and He. Irradiation induced impurities affect the mechanical properties of a material, and may also give rise to secondary effects, including changing the material’s response to continued irradiation. In the following, however, we concentrate on the effect of elastic collisions and resulting atomic displacements in pure metals.

When an incident particle enters a target material, it may undergo elastic collisions with atoms in the material, transferring kinetic energy in the process. If the recoil energy imparted to an atom in the target material exceeds a certain threshold displacement energy (TDE), it is removed from its lattice site, leaving behind an empty site, or vacancy. With this, a radiation damage event [8] is initiated. The recoiling atom is called the primary knock-on atom (PKA), and if the PKA is energetic enough, it can in turn set off secondary recoils, and so on, resulting in a displacement collision cascade. In order to
study the immediate effects of individual particle impacts, it is sufficient to follow the collision events between target atoms, starting from the PKAs.

### 3.2 Nuclear stopping

The collisions between target atoms are governed by their interaction potential. The classical interaction arises from the repulsive Coulomb forces between nuclei and the attractive chemical binding between the atoms. The magnitude of the energy $T$ transferred to an atom of mass $M_2$ in a collision can be solved \[8\] using classical hard sphere kinematics, and gives

$$T = 4 \frac{M_1 M_2}{(M_1 + M_2)^2} E_i \cos^2 \theta$$  

(3.1)

where $E_i$ is the initial energy of the recoil of mass $M_1$, and $\theta$ is the scattering angle in the laboratory reference frame. The energy transfer cross section $\sigma(E_i, T)$ gives the probability of a collision occurring with a given energy transfer $T$, and can be used to calculate the magnitude of the nuclear stopping, *i.e.* how effectively a projectile’s velocity is retarded in a material. The energy transfer cross section can be determined from the full trajectories of the colliding particles, which are dictated by the interaction potential. The trajectories can be derived from the energy conservation criterium, requiring that the path of colliding particles must at all times be such that the sum of kinetic and potential energies equals the kinetic energy of the asymptotic trajectories. The nuclear stopping is then given by

$$S_n(E_i) = - \frac{dE_i}{dx} \frac{1}{N} = \int_{T_{\text{min}}}^{T_{\text{max}}} T \sigma(E_i, T) dT,$$

(3.2)

where $N$ is the atomic density.

The classical description of binary collisions is applicable when the quantum mechanical uncertainties in position and momentum of the colliding particles are small \[16\]. The uncertainty in momentum $(\Delta P)_q$ must be small compared to the classical change in momentum $(\Delta P)$, and the uncertainty in position $(\Delta r)_q$ must be small compared to the distance of closest approach $R_{\text{min}}$ during the collision. Heisenberg’s uncertainty relation $(\Delta P)_q(\Delta r)_q \simeq \hbar$ leads to the requirement

$$\Delta P \times R_{\text{min}} \gg \hbar.$$

(3.3)

This restriction means that the classical treatment is not valid for very small scattering angles, and it sets both an upper and lower limit on the collision energy. Collisions with energy transfer from a few eV up to the MeV range, which are relevant in a collision cascade, are well described classically.
3.3 Electronic stopping

Atomic projectiles, or recoils, in a solid also experience retarding forces due to interactions with electrons. The electronic stopping power dominates at higher recoil velocities, while nuclear stopping dominates at lower energies, especially in the case of heavier projectiles. Different models are used to describe the effect of electronic stopping $S_e$ of heavy ions over different energy scales. The phenomenon is best understood for very high energy recoils, with kinetic energies on the order of MeV. In this energy regime, the electronic stopping of charged ions is well described theoretically by the Bethe formula [17], which predicts the electronic stopping to an accuracy of a few percent. The derivation of the Bethe formula is valid for energies so high that the ion carries no atomic electrons, but certain corrections included in modern Bethe-Bloch theory [18] improve the predictions for lower energies (see Fig. 3.1).

Lower energy recoils are not completely ionized, and for them it becomes more difficult to theoretically predict $S_e$ [21]. The charge state of the ion must then be taken into account, for example using Brandt-Kitagawa theory [22]. The popular SRIM/TRIM code [20] determines $S_e$ semi-empirically [23], by combining both theoretical predictions and experimental values, and gives a reasonable partitioning between nuclear and electronic stopping. The stopping for W ions in W given by SRIM is shown in Fig. 3.2. At very low recoil energies, $S_e$ is extrapolated linearly with respect to recoil velocity, down to zero kinetic energy. However, there are several indications that such a linear dependence breaks down at low velocities [24–26].
On a local level, variations in the electron density also affect the magnitude of the electronic stopping. A clear effect of this is seen in the experimentally verified lower stopping power experienced by channelled ions (e.g. in Refs. [27, 28]). However, in collision cascades, the randomness in positions and directions of the multiple recoils justifies the use of an average stopping power, disregarding local effects.

### 3.4 Defect production

Binary collision approximation (BCA) codes such as SRIM/TRIM [20] are based on the assumption that collision cascades can be described as a collection of binary collisions, described by the energy transfer and scattering cross-section outlined in section 3.2. Vacancies are created when a recoil receives an amount of energy exceeding a certain average TDE value $E_d$. In BCA simulations, $E_d$ is considered constant, although in reality it can be highly anisotropic, and furthermore, the probability of defect formation with respect to PKA energy is not a monotonously rising function [29].

The BCA picture leads to the prediction of defect numbers as a linear function of energy. The standard experimental radiation exposure measure, dpa (displacements per atom) [30], is based on the formula suggested by Norgett, Robinson and Torrens (NRT) [31]. The NRT formula gives the number of defects as

$$N_{NRT}(T_d) = \begin{cases} 
0 & : T_d < E_d \\
1 & : E_d < T_d < 2E_d/0.8 \\
0.8T_d/2E_d & : 2E_d/0.8 < T_d < \infty.
\end{cases} \quad (3.4)$$

Here, $E_d$ is the threshold displacement energy, and $T_d$ is the damage energy, i.e. the energy available for atomic displacements, defined as the recoil energy minus the energy lost to electronic stopping. The factor 0.8 stems from BCA simulations. In the NRT standard, the damage energy is calculated using an approximation to Lindhard’s theory (LSS) [32].

The dpa quantity is then given by the number of displaced atoms in a volume, divided by the number of atoms in the same volume. The advantage of the dpa measure is that it allows quantitative comparison of radiation exposure between different target materials and projectile species. However, it does not take into account the morphology of the primary damage, and furthermore, it is well established, both experimentally and with MD simulations, that the NRT equation overpredicts defect numbers in metals, and should not be used to directly determine the actual amount of damage [30].
Figure 3.3: The temperature in the core of a spherical 150 keV cascade in W, as a function of distance from the center of the liquid region. The temperature is determined for shells of thickness 3 Å, from the relation $E = \frac{3}{2}kT$, and plotted for different times. The predicted melting point $T_{\text{melt}}$ of the potential is indicated with a dotted line.

### 3.5 Heat spikes

In dense materials such as W, collision cascades develop into heat spikes [14], which are highly disordered areas in the core of cascades (see fig. 3.4). The duration of the heat spike is of the order of picoseconds, depending on the PKA energy and the melting point of the target material, as well as on the ambient temperature. The velocities of the atoms in the heat spike follow a Maxwellian distribution typically corresponding to temperatures on the order of 10000 K (see fig. 3.3 for a plot of the temperature in an MD simulation of a 150 keV cascade in W). The characterization of a “melt” is also supported by the fact that the radial pair distribution in the core region in MD simulations resembles that of a liquid [33], and self-diffusion coefficients in simulated cascades are found to agree with values of self-diffusion in the liquid state [34].

In a heat spike, the number of displaced atoms strongly exceeds that predicted by the NRT equation. However, as the heat spike cools, the defects recombine, so that the final defect count is only a fraction of the NRT prediction. This “self-healing” process is particularly strong in metals, and is called athermal recombination, to differentiate from thermally assisted migration and recombination of defects, which takes place over much longer time scales. Fig. 3.5 shows the evolution of point defects...
during a 150 keV cascade in W. The stable defects remaining after the cascade has cooled constitute the primary damage, and further changes in the damage morphology occurs through thermally activated processes.

The displacement of the atoms within the heat spike results in atomic mixing, which, in the case of energetic heat spikes in metals with high atomic number, can contribute significantly to the total mixing that takes place as a result of ion irradiation [35, 36]. The mixing efficiency depends on the duration and size of the liquid volume [37], and is thus sensitive to the melting point of the material, and the irradiation temperature [34].

3.6 Defects and microstructural evolution

When a vacancy is formed as a result of irradiation, the ejected atom eventually comes to rest somewhere in the lattice, forming a self interstitial atom (SIA). Such vacancy-SIA pairs are called Frenkel pairs (FP). In addition to single vacancies and SIAs, also defect clusters form athermally in cascades. Moreover, the high energies and strong disorder present in the cascade core may enable the creation of defects which are not likely to form thermally due to energy minimization.

Defects can cluster in 3-dimensional configurations, or in the form of small dislocation loops. A perfect dislocation loop is a closed dislocation line, with perfect lattice running through the middle. For a \(\langle 100 \rangle\)-type loop in a body centered cubic (bcc) lattice, such as that of W and Fe, this involves either two extra atomic layers, or alternatively two missing layers within the loop. For a \(1/2\langle 111 \rangle\)-type loop, only one layer is added or missing. The migration of such a defect is dictated by that of dislocations, and is one-dimensional, as opposed to that of single defects or 3-dimensional clusters. Furthermore, dislocation loops interact through long-range elastic forces [38], which significantly affect the evolution of one-dimensionally migrating defects, in contrast to the negligible impact of the elastic interactions between three-dimensionally migrating defects on microstructural evolution [39].

There are marked differences in the migrational behaviour of small dislocation loops seen in transmission electron microscopy (TEM) studies of Fe [39], depending on whether the sample was electron or ion irradiated. Regular “fractal” Brownian motion is exhibited by dislocation loops in electron irradiated samples, while the dislocation loops in ion irradiated material exhibit discrete long distance jumps, between which they are immobile. This behaviour is explained by the elastic interaction of the dislocation loops with small vacancy clusters (invisible in the TEM) in the ion irradiated samples. Similar “pinning” of dislocation loops was seen in ion irradiated W at 500 K [40]. Since vacancies in W are practically immobile at temperatures up to 500 K [41], vacancy clusters will appear in initially
Figure 3.4: Snapshots of the evolution of a heat spike in the core of a 150 keV cascade in W. The picture shows the atoms in a 2 Å thick slice of a 20 nm × 20 nm area through the middle of the cascade. The coloring is according to the kinetic energy of the atoms (in eV), on a logarithmic scale. The simulation time is given in the lower right hand corner of each frame. In the final frame, parts of a surviving vacancy cluster and an interstitial-type dislocation loop are visible.
Figure 3.5: Snapshots of the evolution of defects during a heat spike in the core of a 150 keV cascade in W. The picture shows the interstitials and vacancies determined by a Wigner-Seitz analysis (see section 4.5), from the same time frames, and with the same orientation and scale as in fig. 3.4 but showing all the defects rather than just a slice. Dark spheres indicate vacancies, while light spheres represent interstitials.
pristine material only if they are athermally created. This is possible in the dense heat spikes which occur under heavy ion or energetic neutron irradiation, but not from the near-threshold displacements caused by electron irradiation.

There is thus experimental evidence of the direct impact of the morphology of the primary damage on the microstructural evolution. Since the short term evolution of the damage from a single particle impact depends on the concurrent state of the target, the final radiation damage depends not only on irradiating species and irradiation dose, but also on dose rate and irradiation temperature. Thus comparison of radiation effects under varying circumstances is highly complicated [8]. As a result, predicting the response of materials to the highly aggressive conditions in a future fusion reactor is a challenging task. Since similar conditions are irreproducible in today’s experimental facilities, a sophisticated multi-scale simulation approach is necessary, where the morphology of the primary damage plays a crucial part.
Chapter 4

Simulating collision cascades with MD

Collision cascades take place on length and time scales not currently accessible by experimental means. Molecular dynamics (MD) simulations thus provide a valuable tool for directly studying the cascade processes. With current computer capacity, the interactions of millions of atoms can be simulated with MD for time scales on the order of nanoseconds. As an example, the 150 keV collision cascades simulated in publications I and II involved roughly 10 000 displaced atoms, which found their final positions in approximately 30 ps. In addition, an integral part of the cascade consists of the shock wave which propagates outward from the cascade core, temporarily displacing tens of thousands of atoms, so that the total number of atoms required in the cubic simulation cells was almost 8 million.

Simulating such system sizes necessarily requires simplifying the physics; full quantum mechanical calculations with e.g. density functional theory (DFT) are only possible for systems of around one thousand atoms. On the other hand, MD provides more detailed information than the computationally more efficient BCA method, and unlike the latter, it is able to describe the heat spike and recombination, which is typical for collision cascades in metals.

4.1 MD algorithm

Classical MD involves solving the equations of motion for all atoms in a system. This means that the atoms are seen as point particles, with no internal structure, and in particular no electrons. The total energy of the system and the interactions between the particles are dictated by an interatomic potential. The acceleration, and thus the movement, of the particles is evaluated from the total force acting on each atom, by Newton’s equation $F = ma$. The force is given by the derivative of the interatomic potential, which is thus a key component in MD simulations.
Newton’s equations of motion are solved by numerical integration over finite time steps. There are several possible integration schemes, with different trade-offs between efficiency and precision [42]. For example, the Verlet method is derived from the Taylor expansion of the position vectors with respect to time, and gives an equation for calculating the positions $r$ at time $t + \delta t$ as

$$ r(t + \delta t) = 2r(t) - r(t - \delta t) + \delta t^2 a(t) $$

(4.1)

where $a(t)$ is the acceleration. Several variations of this algorithm exist, with different advantages and drawbacks relating to the efficiency of computation and memory usage. However, while the method is formally energy conserving up to a term of order $O(\delta t^4)$, the discreteness of the computer memory introduces additional numerical errors, further increasing the violation of energy conservation in the simulated system.

Another approach to solving the coupled differential equations is by so called predictor-corrector algorithms. The predictor-corrector method takes a two-step approach. First, based on the Taylor expansion and values of position, velocity, etc. at time $t$, values at time $t + \delta t$ are calculated. Then the error of the prediction is estimated from the force actually obtained at the new position, and using this information the predicted values are corrected. The MD code PARCAS [43], used in the work included in this thesis, employs one such corrector-predictor algorithm, the Gear algorithm [44]. The Gear algorithm is more accurate than the Verlet for small time steps, although the error increases more rapidly for longer time steps [42]. Another advantage of the Gear method is that the particle velocities are available from the integration, and need not be calculated separately.

### 4.1.1 Time step

In order to conserve the energy of the system, the time step must be small enough so that no atom moves too far during one step. For computational efficiency, PARCAS uses a variable time step [45], defined by

$$ \Delta t_{\text{new}} = \min \left( \frac{k_t}{v}, \frac{E_t}{F_v}, 1.1 \Delta t_{\text{old}}, \Delta t_{\text{equi}} \right) $$

(4.2)

where $k_t$ and $E_t$ are proportionality constants, $v$ is the velocity of the recoil, and $F$ is the maximum force of any atom in the system.

The use of a variable time step is especially motivated in cascade simulations, where for a few femtoseconds a number of atoms have very high kinetic energies, but for the rest of the simulation the energies remain low. For example, due to the high velocities and very close approaches in the initial
collisions of 100 – 200 keV cascades in W, the variable time step results in around 90 % of the total CPU time being consumed during the first 0.25 % of the total simulated time.

4.1.2 Temperature and pressure control

The basic (energy conserving) microcanonical simulations can be modified by the use of temperature or pressure control. In cascade simulations at a finite ambient temperature, initial equilibration of the simulation cell is done at constant temperature and pressure, employing a thermostat and barostat. Bulk material is simulated by enforcing periodic boundary conditions on the simulation cell in all three directions. Temperature control can then be used to mimic thermal diffusion from the cascade area into the surrounding bulk. In this case, the atoms in the border layers of the simulation cell are thermostated to the desired temperature. This method also serves to dampen any residual pressure waves emanating from the cascade core, to ensure that cascades don’t self-interact over the periodic boundaries.

In PARCAS, the temperature is controlled by a Berendsen thermostat [46], which constitutes a weak coupling to an external bath. The temperature of the system is corrected towards the desired value $T_0$ by scaling the atomic velocities by a factor $\lambda$, given by

$$\lambda = \left[1 + \frac{dt}{\tau} \left(\frac{T_0}{T} - 1\right)\right]^{1/2}$$

(4.3)

where $\tau$ is a constant, and the temperature $T$ in an MD simulation is determined by

$$T = \frac{1}{3N k_B} \sum_{i=1}^{N} \frac{|p_i^2|}{m_i}$$

(4.4)

This scheme does not conserve the canonical ensemble, but has the advantage that it is computationally very efficient. Thus it is suitable for non-equilibrium simulations such as cascades.

The pressure is controlled in an analogous way, by scaling the dimensions of the system so that the pressure approaches the desired value. The scaling factor $\mu$ is given by

$$\mu = \left[1 - \frac{\beta dt}{\tau} (P_0 - P)\right]^{1/3}$$

(4.5)

where $\tau$ is again a constant, $\beta$ is the isothermal compressibility, and the pressure $P$ is given by

$$P = \frac{1}{V} \left[\frac{1}{3} \sum_{i}^{N} \left(\sum_{i<j}^{N} F_{ij} |r_i - r_j| + \frac{|p_i|}{m_i}\right)\right] .$$

(4.6)
4.2 Interatomic potentials

The predictive power of MD simulations depends critically on the interatomic potential used to describe the interaction between the atoms. Generally, when constructing a potential, a suitable functional form must first be determined. Then, parameters of the function are fitted to a database of values describing physical properties, such as, e.g., lattice parameters, bulk elastic constants and defect energies. Typically, modern potentials are fitted to a wide set of values [47], including both experimental and density functional data, resulting in very accurate predictions under conditions for which the potentials were fitted. However, an extensive fitting procedure does not guarantee the performance of the potential in all situations. Both the functional form and the data used in the fitting procedure affect the transferability of the potential, i.e. how well it performs in situations to which it was not fitted [48].

Since collision cascades involve a wide range of effects, modelling full cascades sets enormous requirements on the potential [49], which in addition to describing reasonably well the equilibrium properties of the material over a wide range of temperatures and pressures, also should describe well properties such as the formation and migration energies of the various defects produced in the cascade. As a result, validating potentials intended for use in cascade simulations is non-trivial.

4.2.1 EAM-like potentials

EAM-like potentials are named after the embedded-atom method potentials [50], which are based on the idea that any atom in a system can be considered as an impurity, embedded in the host of surrounding atoms. The energy of the impurity is then a functional of the electron density of the unperturbed host. Potentials of this type are better capable of describing defects and surfaces in metals than what pair potentials are. The total energy of the system in EAM-type potentials is given by the general functional form

\[ E_{\text{tot}} = \sum_{i,j} \phi_{ij}(r_{ij}) + \sum_i F_i(\sum_j \rho_j(r_{ij})), \]  

(4.7)

where \( \phi_{ij} \) is a pair potential, \( r_{ij} \) is the distance between atoms \( i \) and \( j \), and \( \rho_j(r_{ij}) \) signifies the electron density at position \( i \) resulting from the atom in position \( j \). Various physical motivations have been used which lead to the same general functional form, with different expressions for the embedding term \( F_i \). The pair potential is typically short ranged and repulsive, and often \( \rho_j(r_{ij}) \) is an arbitrary fitted function, not directly related to the actual electron density.
The Finnis-Sinclair (F-S) potentials [51] are EAM-type potentials derived using a second-moment approximation of the tight-binding theory of solids [52], which results in the simple functional form $F_i(x) = -A\sqrt{x}$. Ackland and Thetford [53] introduced a short-range modification to the pair part of these potentials, which improves the behaviour of systems under pressure, where atoms come into closer proximity to each other. The resulting potential for W (hereafter denoted AT) has been widely used, also to model radiation damage [54]. However, the AT potential underestimates the formation energies of interstitial point defects (see table 4.1).

A more recent F-S-type potential for W was fitted by Derlet et al. (DD) [55], using electronic structure data from DFT calculations in the fitting procedure. This potential gives good predictions for bulk properties as well as point defect energies, but has the undesirable property that it predicts negative thermal expansion [56].

Yet another modification of the F-S potential was created by Juslin et al. (JW) [57], which improves upon the predicted defect formation energies while retaining the equilibrium properties of the original potential.

A set of four EAM-type potentials for W were recently developed by Marinica et al. [47], by fitting to an extensive DFT database, including liquid configurations. These potentials give a good description of the core structure of screw dislocations, which has been a longstanding problem with existing potentials, but have not previously been tested in cascade simulations.

### 4.2.2 Tersoff-type potentials

The Tersoff-type potentials [58] give the bond energy between atoms $i$ and $j$ as

$$V_{ij} = f(r_{ij})[V_R(r_{ij}) - b_{ij}V_A(r_{ij})],$$

(4.8)

where $V_R(r)$ and $V_A(r)$ are exponential functions, as in a Morse potential, and $f(r)$ is a cut-off function. The bond-order function $b_{ij}$ includes an explicit angular-dependent term, which stabilizes more open crystal structures, and can describe the deformation of bonds, making these potentials ideally suited to modelling covalently bonded materials.

It can be shown that the Tersoff-type potentials (without an angular dependence) and the F-S potentials derived with the second moment method are equivalent [59, 60], and thus Tersoff-type potentials can also be used for metallic systems. Due to the angular term, evaluating the potential energy requires an explicit three-body loop, so that they are computationally much slower than the EAM-type potentials.
Table 4.1: Properties of different potentials for W used in this work, compared to experiment and \textit{ab initio} values. The lattice constant $a_0$ (Å), cohesion energy $E_{coh}$ (eV), melting point $T_{melt}$ (K), range of the potential $R_{cut}$ (Å), vacancy formation energy $E^f_v$, and interstitial formation energy for the ⟨111⟩ crowdion and ⟨100⟩ and ⟨110⟩ dumbells, in eV units. In some cases two values from different sources are given, to illustrate the level of uncertainty in the calculated values. \( a \) \cite{62}, \( b \) \cite{61}, \( c \) \cite{63}, \( d \) \cite{64}, \( e \) \cite{65}, \( f \) \cite{66}, \( g \) \cite{67}, \( h \) \cite{57}, \( i \) \cite{68}, \( j \) \cite{69}, \( k \) \cite{70}, \( l \) \cite{71}, \( m \) \cite{72}

They are, however, ideally suited to modelling compounds involving both metals and non-metals \cite{59}. Because of this important application, we have tested the performance of one recent Tersoff-type potential for W \cite{61}, hereafter denoted as AH.

### 4.3 Short-range interactions

The energetic, binary collisions between atoms involve interaction ranges which are not usually included in the fitting of interatomic potentials. In order to model such interactions, the interatomic potential used in the simulations must be modified at short distances, or “hardened”, which is usually done by modifying the repulsive pair-part of the original potential.

At very short distances, the interaction between two atomic nuclei with atomic numbers $Z_1$ and $Z_2$ is well described by pure Coulomb repulsion

$$V(r) = \frac{e^2}{4\pi\epsilon_0} \frac{Z_1Z_2}{r}. \quad (4.9)$$
At slightly greater distances, the atomic electrons screen the nuclei from each other, and the Coulomb repulsion must be modified by multiplication with a screening function $\phi(r)$.

### 4.3.1 The ZBL universal potential

A commonly used repulsive potential, also employed in this work, is the universal ZBL potential developed by Ziegler, Biersack and Littmark [21]. It includes a fitted universal screening function

$$
\phi(x) = 0.1818e^{-3.2x} + 0.5099e^{-0.9423x} + 0.2802e^{-0.4029x} + 0.02817e^{-0.2106x} \quad (4.10)
$$

where $x = r/a_u$, $a_u = 0.8854a_0/(Z_1^{0.23} + Z_2^{0.23})$, and $a_0$ is the Bohr radius.

While it is possible to construct more accurate, material-specific repulsive potentials using DFT or Hartree-Fock methods [73], the $\sim 10\%$ accuracy of the ZBL potential was found to be sufficient for collision cascade simulations [49].

### 4.3.2 Hardening of potentials

When hardening a potential for use in cascade simulations, the short-range repulsive potential must be smoothly joined to the equilibrium range potential. To avoid affecting the interstitial formation energies, the joining should be done at a distance below about $80\%$ of the nearest neighbor separation. However, in some instances it may be possible to improve the SIA energies compared to the original potential [57], by extending the interpolation to slightly longer distances. For EAM-type potentials, care should also be taken to ensure that the embedding function does not interfere with the ZBL at short distances. This can be done, for example, by letting the electron density saturate at short distances.

The mid-energy range, over which the repulsive potential is joined to the equilibrium potential, strongly affects the predicted TDEs. Experimentally determined TDEs can therefore be used to tune the interpolation. However, while it is clearly desirable that a potential used in cascades simulations correctly reproduces the TDEs, there are indications that reasonable TDEs do not necessarily guarantee a well behaved potential [74, 75].

In order to test this hypothesis directly, in Ref. [76], we have joined the EAM4 potential by Marinica et al. [47] to the ZBL repulsive potential in two different ways. The resulting potentials are here denoted by EAM4-s and EAM4-h. Both versions of the hardened EAM4 potential retain the original
<table>
<thead>
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<th></th>
<th>DD</th>
<th>AT</th>
<th>JW</th>
<th>AH</th>
<th>EAM4-h</th>
<th>EAM4-s</th>
<th>exp.</th>
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<tbody>
<tr>
<td>$E_d \langle 100 \rangle$</td>
<td>$41 \pm 1^a$</td>
<td>$57 \pm 1$</td>
<td>$63 \pm 1$</td>
<td>$39 \pm 1$</td>
<td>$43 \pm 1$</td>
<td>$31 \pm 1$</td>
<td>$40 \pm 2^b$</td>
</tr>
<tr>
<td>$E_d \langle 110 \rangle$</td>
<td>$93 \pm 1^a$</td>
<td>$103 \pm 1$</td>
<td>$93 \pm 1$</td>
<td>$69 \pm 1$</td>
<td>$71 \pm 1$</td>
<td>$51 \pm 1$</td>
<td>$&gt; 70^b$</td>
</tr>
<tr>
<td>$E_d \langle 111 \rangle$</td>
<td>$41 \pm 1^a$</td>
<td>$89 \pm 1$</td>
<td>$61 \pm 1$</td>
<td>$59 \pm 1$</td>
<td>$65 \pm 1$</td>
<td>$45 \pm 1$</td>
<td>$44 \pm 1^b$</td>
</tr>
</tbody>
</table>

Table 4.2: Predicted threshold displacement energies $E_d$ (eV) in the three main crystallographic directions, for the different W potentials. $^a$Ref. 62, $^b$Ref. 67

defect formation energies and other equilibrium properties, and both predict reasonable TDEs. Figure 4.1 shows the intermediate range of the potentials used in various parts of this thesis, and the predicted TDEs in the main crystallographic directions are given in table 4.2.

### 4.4 Electronic effects

Although collision cascades involve highly energetic, penetrating atoms, historically they were simulated without including electronic effects. In such simulations, the initial PKA energy is taken to be equal to the damage energy (cf. chapter 3.4), and the corresponding actual recoil energy is calculated using the NRT approximation [31] to Lindhard’s theory [32] of electronic energy losses. This method has been particularly prevalent in simulations in Fe [77, 78], and is still in use today also in W [79].

#### 4.4.1 Electronic stopping in MD

A fairly simple and straightforward method of including electronic effects dynamically, which is used in the simulations in this work, is to incorporate electronic stopping $S_e$ as a frictional force on each atom with kinetic energy above a given cut-off $T_c$. The velocity of the atom is then subtracted with

$$\Delta v = \Delta t \frac{S_e}{m}$$

where $m$ is the mass of the atom, and $S_e$ is the target and projectile dependent electronic stopping as calculated by SRIM [20].

The cut-off parameter $T_c$ is necessary when $S_e$ is included in simulations as a frictional force, else all thermal modes are quickly quenched. However, the parameter lacks a physical motivation, and the value has been rather arbitrarily chosen in the literature. Options include using a general value of $T_c = 10$ eV [80, 81], or, alternatively, a value corresponding to twice the cohesive energy of the material [82]. On the other hand, in a comparison of energy losses in cascades from 1 keV PKAs,
Figure 4.1: Mid-range part of the interaction energy with different W potentials, calculated for a W dimer from the whole potential, i.e. including both the pair part and the embedding term for the EAM-type potentials.

simulated with an $S_e$ frictional term, to the energy transfer between electronic and ionic subsystems determined using quantum mechanical Ehrenfest dynamics in a hypothetical one-free-electron metal, a value of $T_c = 1$ eV was found to give the best agreement [83]. However, cascades with such low PKA energies do not develop a full heat spike, so energy transfer in the heat spike regime was not included in this study.

Although the NRT damage energy calculation, and the $S_e$ given by SRIM, are both based on Lindhard’s theory, the resulting energy losses from simulations with $S_e$ do not necessarily agree with the LSS calculated value. The disagreement arises from the fact that the energy losses to electronic stopping from atoms with kinetic energies between 1 and 10 eV is not negligible in high energy cascades, where the number of such atoms is significant for a long period of time in the liquid core of the cascade. Different values of $T_c$ thus result in different magnitudes of losses, which do not correspond exactly to the Lindhard predictions. As discussed in publication III, this introduces an element of ambiguity when comparing simulation results, obtained with different methods, to experiments, where the recoil energy may be known, but the damage energy must be calculated.

As shown in publication I for the case of W, while simulations with $T_c = 1$ eV result in very high energy losses, simulations with different values of $T_c$ between 5 and 100 eV result in only minor
Figure 4.2: Cumulative electronic energy losses using \( S_e \) with different \( T_c \) in 150 keV cascades in W. From publication II.

Differences in energy losses, and very similar damage predictions. Thus cascade outcomes appear to be insensitive to minor changes in the lower threshold for \( S_e \), so long as the energy losses do not extend past the ballistic phase of the cascade. Although there is no decisive theoretical reason for a lower energy limit on \( S_e \), LSS theory does not consider ions with very low kinetic energy. Furthermore, the treatment pertains to energetic ions penetrating undisturbed lattice, and is not necessarily valid in the highly disordered, underdense region in the core of cascades, which is where the atoms with kinetic energies between 1 and 5 eV reside. In fact, few atoms with kinetic energies in that range exist during the ballistic phase of energetic cascades. This is illustrated by the electronic energy losses in 150 keV cascade simulations in W with different values of \( T_c \), which all show agreement during the the ballistic phase, which lasts \( 200 - 300 \) fs (see fig. 4.2).

### 4.4.2 Electron-phonon coupling

A further uncertainty in the treatment of electronic losses in simulations of energetic collision cascades arises from the interaction between heated electrons and phonons. If the temperature of the electron gas in the cascade core rises significantly, this may result in a feed-back of energy to the ions through electron-phonon (EP) coupling [82]. The possibility of energy transfer from the electronic
subsystem to the ionic subsystem in the liquid-like heat spike of a cascade is the result of a complicated interplay of effects, involving not only the coupling strength between the two systems, but also properties such as the electron heat capacity, mean free path and thermal conductivity [84, 85]. These material properties depend on temperature in a nontrivial way, influenced by the form of the density of states of a given metal [86]. However, momentum transfer in electron-ion collisions is negligible due to the large mass difference, so ionic trajectories would hardly be perturbed by interactions with electrons. Therefore, the coupling between the two subsystems mainly affects the rate of cooling of the heat spike, and thus the duration of the thermal phase.

Including EP-coupling in MD simulations can be done using a two-temperature model (2TM) [84], but is computationally more involved than the $S_e$ frictional term, and requires treating the electronic subsystem in addition to the ionic one. Initial work on cascades with MD+2TM in Fe [82, 87] and W [88] shows indications of possible effects, mainly on defect clustering, which is also sensitive to both the interatomic potential and the $S_e$ energy losses (cf. chapter 5). In the work in this thesis, the effects of EP-coupling are not included.

4.4.3 Determination of energy losses through ion beam mixing

Since the magnitude of electronic energy losses affects the duration of the heat spike, one way to assess the correctness of the over-all energy loss is by investigating the atomic mixing occurring in simulations, since this quantity is directly dependent on the duration of the heat spike. Mixing efficiencies can be determined through ion beam mixing (IBM) experiments [89], but interpretation of the results is complicated by the many processes which affect the mixing, including chemical driving forces such as heat of mixing between marker layers or bilayers. In publication III, we compare the mixing in Ni, Pd and Pt to results of IBM experiments where such chemical effects have been minimized. We find that $T_c = 1$ eV is too low for all the metals considered, while $T_c = 10$ eV gives mixing efficiencies in better agreement with IBM experiments. Furthermore, since results of cascades simulations in W show little difference for $T_c$ values between 5 and 100 eV, as we showed in publication II, we conclude that a general value of $T_c = 10$ eV is a reasonable choice.

4.5 Defect analysis

Interstitial and vacancy type defects were analyzed from the simulation output using two methods. In an automated procedure using the Wigner-Seitz (W-S) cell method [90], the simulation cell is divided into Wigner-Seitz cells [91], centered on the initial position of each atom. These are compared to the
final position of each atom, and empty cells are considered to be vacancies, while multiply occupied
cells are identified as interstitials. This analysis can also be performed on intermediate positions dur-
ing a cascade, but while it gives a measure of the lattice disorder, the interpretation as vacancies and
interstitials must be made with reservations, since most of the defects are not stable at that point. This
method is ideally suited for determining the total number and positions of interstitials and vacancies
in the final damage.

A complementary method of defect analysis is provided by the potential energy of the atoms. When
the ambient temperature of the simulation cell is sufficiently low that thermal fluctuations do not
interfere, filtering out atoms with potential energy higher than the energy of atoms in a perfect lattice
brings out the defects. While this shows more of the defect structure than the W-S analysis, it does
not give an actual defect count, since the numbers depend strongly on the energy value used to filter
the atoms, and furthermore each single vacancy and interstitial gives rise to several higher energy
atoms. Also, the position of atoms with respect to the perfect lattice is not apparent, for example
dislocation loops of both vacancy and interstitial type will show up as a ring of atoms and be practically
indistinguishable. Combining the two analysis methods shows clearly both the defect structure and the
vacancy/interstitial nature. Figures 4.3a and 4.3b show the same defects analysed by energy filtering
and W-S analysis, respectively.

Cluster sizes were also analyzed with an automated procedure, which counts an atom as belonging
to a cluster if it lies within a certain cut-off distance to an atom in the cluster. This cut-off was taken
between the second (2NN) and third (3NN) nearest neighbor distances for vacancies, and between
the 3NN and 4NN distances for interstitials. The clustered fraction of SIA was very insensitive to the
choice of cut-off, since SIA clusters in W tend to be densely packed and well separated form each
other. Vacancies, on the other hand, often clustered loosely in the core of cascades, and as a result the
calculated clustered fraction was more sensitive to the cut-off, but the difference was well within the
bounds of the statistical uncertainties.

Dislocation loops were identified visually from the energy filtered atoms. Burgers vectors for the rel-
atively few perfect dislocation loops were determined manually, by extracting planes of atoms through
the relaxed center of the loops, in two perpendicular orientations, and counting out the Burgers circuit
[92].

Atoms belonging to the liquid core of the heat spike were determined dynamically during simulations,
by a kinetic energy criterion [80]. An atom was considered "liquid" if the average kinetic energy
of it and its nearest neighbors exceeded that corresponding to the melting point predicted by the
interatomic potential, determined through the classical relation $E = \frac{3}{2} kT$. The liquid area corresponds
closely to the disordered area in the heat spike.
(a) Atoms with potential energy more than 0.2 eV above the negative of the cohesive energy are shown. Coloring is according to potential energy, with lighter color signifying higher energy.

(b) Results of a Wigner-Seitz analysis. Pink spheres represent multiply occupied W-S cells, while blue spheres indicate empty cells.

Figure 4.3: Defects from a 150 keV cascade in W, visualized with different methods. Both pictures represent the same defects, with identical scale and orientation.
Chapter 5

Primary damage production in tungsten

Elastic collisions with the 14.1 MeV fusion neutrons [5] will result in recoils in W with a maximum kinetic energy of $E_{\text{max}} = 4\frac{mM}{(m+M)^2} E_n = 300$ keV. A full understanding of cascade damage requires a comprehensive picture of the damage from recoils over the whole energy range. Low energy events result in the displacement of only a few atoms, and are fairly well described by the binary collision picture, when a recombination radius is used in the interpretation of results [93]. As the PKA energy increases, however, the collision cascade develops into a heat spike. Compared to the well studied Fe, W is very dense, resulting in massive heat spikes with compact regions of high energy density, where the liquid region is fully connected even in cascades with very high PKA energies. As a result, novel defects may form in-cascade, which BCA simulation methods cannot describe.

Recent in-situ TEM experiments of 150 keV W ions in single crystal W [40] provide new information on the defects produced from such high-energy cascades, and are the reason why much of the work in this thesis focuses on 150 keV cascades.

5.1 Displacement cascades

High energy cascades in W occur in three distinct phases; the initial, or ballistic phase, the thermal phase, and the relaxation phase. The initial phase of the cascade involves mainly high energy recoils, which interact through energetic binary collisions. Very little energy is transferred in longer range low energy interactions, due to the high velocities of the recoils at this stage. The ballistic recoils penetrate undisturbed areas of the lattice, increasing the disordered volume. Hence, the interactions of ions with electrons during this phase are well described by theories of electronic stopping. The ballistic phase lasts for roughly 200 fs in 150 keV cascades in W, during which the cascade exhibits a clear fractal nature [94], illustrated in publication I.
5.1.1 Subcascade break-up

As PKA energies increase, the probability of the cascade breaking up into separate subcascades also increases. The subcascade structure is determined already during the ballistic phase. An energy threshold can be determined where isolated subcascades begin to appear, but the threshold is not absolute, in that even at higher energies the cascade may occasionally remain intact, or consist of overlapping subcascades. For Fe, subcascade break-up begins at around 10-20 keV, and this signifies the point at which the energy dependence of defect production and clustering diminishes, and even partly reverses [95].

In publications I and II, results from a large number of 150 keV cascades are reported, and it was found that cascades do not completely break up in W even at such a high energy. The size of the unbroken liquid area affects the size of defect clusters, since the maximum spatial extent of a cluster is bounded by the size of the uninterrupted disordered area during the cascade. In publication IV, this effect on defect sizes is evident in the dislocation loop frequency-size distributions in ion-irradiated W foils. The distributions follow a power law up to a certain size, at which point the data deviates significantly from linearity on a log-log plot. This deviation occurs at the same loop size for both 150 keV and 400 keV W⁺ energies, indicating the occurrence of sub-cascade formation at energies slightly above 150 keV.

This observation of subcascade splitting is supported by our simulations in Ref. [76], where a number of 200 keV cascades in W split into subcascades, while a roughly equal number remained intact. Figure 5.1 shows the liquid area at its maximum extent at roughly 2 ps, in a 200 keV cascade in W.

5.1.2 Thermal phase and relaxation

At the end of the ballistic phase, the fractal collision cascade transitions into the thermal spike, where collective effects become important. Simulations in Fe show that during this phase the number of displaced atoms increases further, although at a slower rate, due to the emanating pressure wave as the hot liquid core expands [96]. This same effect is also observed in W, but is dependent on the interatomic potential [76]. Interestingly, the DD potential, which exhibits negative thermal expansion [56], nevertheless results in the most pronounced expansion of the disordered area during the thermal phase. The peak of the expansion occurs at around 2 ps for the highest energy cascades in W studied in this work. The increase in disorder can be seen from the increase in potential energy, or alternatively by a Wigner-Seitz analysis of the simulation cell from snapshots of the cascade development.
Figure 5.1: The W-S defects during the development of a 200 keV cascade in W. The defects are pictured here at their maximum extent, showing clearly that the cascade has broken up into subcascades. The time is 2 ps after PKA initialization.

Also the electronic energy losses affect the behaviour during this phase, with larger energy losses inhibiting the expansion. The expansion during the thermal phase clearly affects also the clustering of the final defects. Figure 5.2 shows the number of empty W-S cells, and the portion of defects in clusters, as a function of time in 200 keV cascades in W, from simulations with three different treatments of energy losses using the DD potential. In particular, one can see that the disorder, measured by the number of empty W-S cells, decreases between 1 and 2 ps if $S_e$ is included with $T_c = 1$ ev, but grows otherwise, and only in the cases where it grows do vacancy clusters form, and SIA clustering is also enhanced.

The final phase, or relaxation phase, involves the recrystallization of the liquid area. The residual heat in the lattice allows migration of SIAs during the relaxation, resulting in some annihilation of single SIAs in the vacancy-rich core, thus slightly increasing the clustered fraction (see fig. 5.2), but vacancies are immobile. The simulations in this work were run for 40 - 60 ps, at which point the lattice had cooled to an average of a few Kelvin above the ambient temperature. The simulation time was sufficiently long that all defect clusters were purely of either interstitial or vacancy type, with no mixed clusters. In this sense the final defects were internally stable, requiring thermal migration for any further recombination to occur.
Figure 5.2: The number of empty W-S cells, the clustered fraction of SIAs, and the clustered fraction of vacancies, as a function of time in 200 keV cascade simulations in W, using the DD potential. Electronic energy losses were included in the simulations in three ways: with electronic stopping and $T_c = 10$ eV, with electronic stopping and $T_c = 1$ eV, and no electronic stopping but $E_{MD} = E_{dam}$. 
5.2 Point defect numbers and defect clustering

The predictions of different potentials regarding the number of defects and clustered fractions from cascades in W have been studied previously up to cascade energies of 50 keV [56, 97]. The different potentials were found to predict similar numbers of defects, although interstitial clustering behaviour differed.

Since the heat spike effects in W are even more dramatic at higher energies, due to the very high threshold for subcascade splitting, it is of interest to study the effect of potentials also in higher energy cascades. We have investigated the dependence on the interatomic potential of defect numbers and clustering properties in cascades with energies up to 200 keV in Ref. [76]. This study also includes the two versions (cf. section 4.3.2) of the very recent, extensively fitted EAM4 potential [47].

Most potentials predict very similar defect numbers in cascades up to 50 keV, as can be seen in fig. 5.3. In particular, the two potentials AT and JW yield almost identical predictions over the whole energy range. These potentials are both modifications of the same F-S potential, and differ mainly at distances of about 2.5 Å, but this leads to a significant difference in the predicted formation energies of point defects (see table 4.1). Thus, rather surprisingly, formation energies affect defect production
in collision cascades only insignificantly. In contrast, the (very small) differences in defect numbers over the energy interval from 100 eV to 50 keV in general correlate fairly well with predicted TDEs.

The most interesting result of the comparison in Ref. [76] is between the two potential versions EAM4-s and EAM4-h, which are identical at distances larger than 2 Å, and smaller than 0.8 Å. In other words, all equilibrium bulk properties and defect formation energies are identical, as well as the high-energy interactions. Furthermore, both versions predict reasonable TDEs, which differ only slightly between the two. Yet defect numbers from cascades differ by a factor of ~ 2 over the whole energy range from 70 eV to 200 keV. This provides direct evidence of the sensitivity of cascade simulations to the mid-range of the potential, and shows that reasonable TDEs provide no absolute guarantee for cascade behaviour.

Clear heat spike effects, in the form of increased defect clustering, begin to appear in cascades with PKA energies between 20 and 50 keV, and are very dependent on the interatomic potential [76]. For PKA energies above 50 keV, some potentials predict high levels of clustering of both SIAs and vacancies, while especially the EAM4 potentials predict very little clustering of either type of defect. However, vacancy migration energies predicted by the potentials do not correlate with the degree of vacancy clustering in cascades. Rather, the tendency is that potentials with too high melting point, which are also the longer ranged potentials, predict little or no increase in vacancy clustering with increasing PKA energy, and only minimal increase in SIA clustering.

The tendency for defects to cluster also affects the absolute numbers of defects, and thus the predicted NRT efficiency for higher energy cascades. The total defect count is higher when more SIAs are trapped in clusters, and thus cannot recombine during the recrystallization phase. The correspondence between the SIA clustered fractions and defect numbers can also be seen within the predictions of a single potential, since all potentials predicted a certain number of cascades with very little clustering, and correspondingly low defect numbers. The different potentials show surprising agreement concerning the correspondence between defect numbers and the SIA clustered fraction, except for the EAM4-s potential, which predicts large numbers of defects yet very little clustering. This is illustrated in figure 5.4 for 150 keV cascades.

The effects on defect clustering of the choice of cut-off $T_c$ for the electronic stopping in 150 keV cascades were investigated in publication II. No vacancy clusters and only few and small SIA clusters form if $T_c = 1$ eV, while very large clusters of both type form when $T_c = 10$ eV. This also slightly affects the average defect numbers, due to the above mentioned correspondence between the clustered fraction of SIA and defect numbers.
36

Figure 5.4: The total number of SIAs vs. the fraction of SIAs in clusters of more than 3, in 150 keV cascades in W with different potentials.

The possibility of a directional effect due to the highly anisotropic $E_d$ in W [67] was also studied in publication II. Neither in 30 keV nor 150 keV cascades were directional effects evident, due to the randomization of secondary, and higher, recoil directions in energetic cascades.

The fact that trends in defect numbers and clustering correspond neither to defect formation energies nor migration energies, nor even ultimately to the predicted TDEs, means that other methods of validation must be used to assess the reliability of cascade damage simulations.

5.3 Morphology of the primary damage

The most direct experimental observations of primary damage in W includes field ion microscopy (FIM) measurements of vacancy clusters [98, 99]. Near-surface depleted zones, i.e. vacancy clusters, were observed in 30 keV W$^+$ ion irradiated samples. These findings were well reproduced by MD simulations [54] using the Finnis-Sinclair potential [51].
5.3.1 Dislocation loops

Recent *in situ* transmission electron microscopy (TEM) experiments of 150 keV W ions in W \[40\] show the formation of both vacancy and interstitial type dislocation loops from single ion impacts. Loops with Burgers vector $\mathbf{b}$ equal to both $\langle 100 \rangle$ and $1/2\langle 111 \rangle$ were identified, in contradiction to previous understanding that only $1/2\langle 111 \rangle$-type loops form in W \[100\]. In publication I, simulations of such high-energy cascades in W were studied in detail for the first time. Dislocation loops with $\mathbf{b} = \langle 100 \rangle$ of both interstitial and vacancy type were found in the simulations. However, vacancy type dislocation loops are very rare in MD simulations of both Fe \[101\] and W. Only one cascade, simulated with the AT potential, resulted in the formation of a vacancy-type dislocation loop, out of a total of over one hundred 150 keV cascades simulated over the course of the work included in this thesis. Thus, the fact that vacancy-type dislocation loops dominated the damage in the low dose limit in the experiments in Ref. \[40\] cannot currently be explained by these simulations.

In publication IV, the TEM experiments were repeated at 30 K, and results confirm that visible dislocation loops (1-10 nm in diameter) form athermally. This supports the simulation method using $T_c = 10$ eV cut-off for electronic stopping, since simulations with $T_c = 1$ eV resulted in no clusters of sizes which would be experimentally visible. It also indicates that the AT and DD potentials may predict the high-energy heat spike behaviour better than the AH and EAM4 potentials, since the latter two do not show the formation of any large defect clusters. This potential dependence may be due to the high melting point predicted by the latter two potentials, and the resulting shorter duration of the heat spike.

5.3.2 Cluster size scaling laws

The configuration and size of defects constituting the primary damage affects the predictions of object kinetic Monte Carlo (OKMC) models of microstructural evolution \[38, 102, 103\]. Since thermal ageing of radiation damage occurs during and after countless particle impacts, ideally debris from countless cascades should be used for the primary damage input. However, the computer resources needed for MD simulations of high-energy impacts makes simulating thousands of cascades highly impractical. On the other hand, the computationally efficient BCA method cannot correctly predict the morphology of the primary damage, since all effects of the heat spike and recombination are missing. In Fe, for example, BCA based methods tend to predict relatively high vacancy clustering but too little SIA clustering \[104\].
In publication **I**, the frequency distribution of SIA cluster sizes from cascades performed in bulk was shown to follow a power law, suggested already by the fractal nature of the cascade. Such a scaling law, together with information of the total number of defects, enables statistical generation of cascade damage suitable for OKMC input, without the need for explicit simulation of thousands of cascades.

Cluster size scaling laws were further studied both experimentally and by simulations in publication **IV**. Both 150 keV and 400 keV W\(^+\) ion irradiation of W foils was carried out at cryogenic temperatures, and an analysis of visible dislocation loops shows that the frequency-size distribution follows a power law \( F(N) = A/N^S \) in both cases. The results were compared to MD simulations of foil irradiation, which also predict that the frequency distribution of cluster sizes from ions incident on a surface follows a power law, very similar to that found for cascades in bulk. The frequency-size distribution found from 150 keV W\(^+\) ion irradiation, with \( A = 2.7 \pm 1.4 \) and \( S = 1.8 \pm 0.1 \), shows remarkable agreement with the predictions of the foil simulations of \( A = 3.6 \pm 0.5 \) and \( S = 1.85 \pm 0.09 \), while the 400 keV results are fitted to an exponent \( S = 1.6 \pm 0.2 \), which agrees with the value of \( S = 1.63 \pm 0.07 \) found previously in publication **I**. This difference between the irradiation energies is attributed to surface effects [105], which are more dominant for lower ion energies.

Although different interatomic potentials predict different numbers of defects and different clustered fractions in the high-energy cascades, the DD and AT potentials nevertheless show good mutual agreement regarding the scaling law [106]. The excellent agreement between experiment and simulation found in publication **IV** lends confidence that the employed simulation methods yield reasonable predictions of clustering behaviour in high-energy collision cascades.
Chapter 6

Conclusions

In dense materials such as W, high-energy collision cascades produce massive heat spikes, with the onset of subcascade break-up occurring at energies above 150 keV. The resulting in-cascade formation of nano-scale dislocation loops, in addition to individual point defects, has major implications for the subsequent thermal evolution of radiation damage, and constitutes an important input for micro-structural evolution models.

Simulated high energy cascade behaviour in W is very dependent on the interatomic potential, and shows no clear correlation with basic properties of the potential which are usually included, or tested, in the fitting process. Potentials thus need validation by comparison to experiments which pertain as closely as possible to the direct effects of the cascade process. Furthermore, damage production from cascades is also sensitive to electronic energy losses during the heat spike phase.

Direct comparison to ion beam mixing experiments in Ni, Pd and Pt allows calibrating the electronic energy losses based on the atomic mixing which takes place in the heat spike. Such a comparison shows that electronic stopping, applied as a frictional term to all atoms with kinetic energies above 10 eV, results in a reasonable cooling rate of the heat spike for the whole range of metals, irrespective of the different densities. A lower cut-off at 1 eV, however, results in excessive quenching in all cases. This inhibits defect cluster formation, and thus strongly affects the morphology of the predicted primary damage.

We have also shown that the intermediate energy range of the interatomic potential is an important factor in cascade behaviour, and that simply calibrating the threshold displacement energies is not sufficient to guarantee reasonable behaviour.

We have further studied the nature of dislocation loops in the final damage in W, and found agreement with the surprising result of recent in-situ transmission electron microscopy observations, which
showed the existence of $(100)$-type dislocation loops in ion irradiated W, though previously it was expected that only $1/2(111)$-type dislocation loops should form.

The defect cluster frequency-size distribution was shown to follow a scaling law, which was confirmed by in-situ transmission electron microscopy experiments performed at cryogenic temperatures. Such a scaling law can be used to generate input for microstructural evolution models, circumventing the need to explicitly simulate thousands of cascades with MD. The TEM experiments further showed that sub-cascade break-up occurs in W at energies slightly above 150 keV, which agrees well with simulations.

These investigations have highlighted multiple issues affecting higher energy cascades simulations, which were previously thought to have insignificant impact on damage predictions, and were therefore treated in a somewhat arbitrary fashion. The result of this work is an increased understanding of the requirements for simulations of fusion-relevant cascades. Furthermore, we have demonstrated the feasibility of extracting statistical information from MD simulations, other than just point defect numbers and clustered fractions, for use as input in microstructural evolution models. The statistical laws derived from these simulations were in addition directly verified by experiments, lending credibility to the simulation methodology and confidence in the reliability of the results thereof.

Work on primary cascade damage is far from complete, however. A pressing question concerns vacancy type dislocation loops, which form only rarely in MD simulations in W, yet experimentally they were found to dominate the microstructure in the low dose limit in ion irradiated W foils at room temperature. The mechanism, and time scale, of cascade collapse resulting in vacancy-type dislocation loops needs further investigation, to determine whether the scarcity of such defects in MD simulations is an effect of the potentials, or whether collapse happens on time scales longer than those covered by MD. Further, the source of the discrepancy between predictions of different interatomic potentials regarding the high-energy heat spike behaviour is not clear. This issue begs investigation, now that modern computer capacity makes simulating numerous high-energy cascades in multi-million atom systems feasible, so that gathering high quality statistical data from them is a genuine possibility.
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Andrea
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