Erosion and modification of metal surfaces by light and heavy ions

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ACADEMIC DISSERTATION

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in the Small Auditorium E204 of the Department of Physical Sciences (Physicum), on August 20th, 2005, at 10 o’clock a.m.

HEL deterministic

UNIVERSITY OF HELSINKI REPORT SERIES IN PHYSICS

HU-P-D123

Classification (INSPEC): A3410
Keywords (INSPEC): molecular dynamics method, Monte Carlo methods, ion-surface impact, ion implantation, sputtering, metal clusters, impurities, bubbles in solids, diffusion in solids

ABSTRACT

Using molecular dynamics and kinetic Monte Carlo simulations erosion and surface modification phenomena of metals subjected to light and heavy ion irradiation have been studied. The phenomena include the formation of craters, the sputtering of clusters, and the formation and rupture of He clusters in W irradiated by non-damaging He ions. The differences in formation of H and He gas-impurity clusters in W have also been examined.

A scaling law suggested in the literature for the size of microscopic craters is shown to be inaccurate. The present results reveal that the melting temperature of the bombarded material is on a equal footing with the cohesive energy, pointing out the importance of local melting of the material.

The investigations of sputtering of Ag and Au by heavy and energetic ions show that a significant fraction of all ejected atoms are bound in clusters. The size distributions of hot, newborn clusters and those remaining after fragmentation are successfully described by an inverse power law, with exponents for newborn and fragmented clusters not differing dramatically.

The present results from the examination of the energetics of H and He clusters in W show that the vastly different experimental depths for these clusters can be successfully explained by a different self-trapping behavior: H atoms do not form stable interstitial pairs in perfect W, but He atoms do.

Finally, it is found that continuous implantation of 50-200 eV He ions into single-crystalline W results in the spontaneous formation of clusters down to depths of a few tens of Ångströms. Two clear mechanisms for the growth of these clusters are obtained. The results also show that the clusters are able to rupture and eject He atoms, but no associated erosion of W atoms is observed.
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1 INTRODUCTION

As early as in 1852 W. R. Grove, studying electric discharges between metal electrodes in various gas atmospheres [1], observed that material was removed from the negative electrode (the cathode) and deposited on the glass walls containing the electrodes and the gas mixture. Since this initial discovery the mechanisms behind this erosion and surface modification process have been investigated quantitatively in experiments and theoretical simulations.

Today it is well known that the simplest erosion process, called sputtering, is the ejection of material from the surface of a solid [2]. This removal of material, either atoms or chunks of these, is caused by the impact of particles like neutrons and electrons, atoms, atomic ions (charged atoms), cluster ions (charged groups of atoms), or energetic photons. In the following the discussion will be limited to ionic particles.

As long as the irradiation does not give rise to sputtering, the development of the affected surface-near region of the target is simply subjected to surface modification. This concept may be defined to encompass processes that alter the first few atomic layers of the surface, or the whole region down to the average depth of the particles that have been incident on the solid.

One application of erosion and surface modification of metals, or solids in general, is the deposition of thin films on various substrates. This process involves sputtering of the material which the film is to be made of, and the subsequent deposition of this material on the intended substrate. These films can be used in areas such as microelectronics (e.g. single-electron transistors based on Al, Ta and Cr [3]), optical coatings (e.g. mirrors and large architectural windows [4; 5]), magnetic recording layers and hard wear resistant coatings [6]. Superconducting thin films [7] as well as conventional low-temperature and ceramic high-temperature superconductors [8] may also be manufactured. Sputtering can also be used for etching, polishing, and cleaning of solid surfaces [9].

Examples of surface modification, which do not rely on erosion, include the production of superinsulating surfaces on insulating mica targets using Xe ion irradiation [10], and the strengthening of deposited Cr films using Ni ion irradiation to reduce the strain in the film [11].

Several techniques to analyze solid surfaces or surface regions rely on erosion of the surface layers. These methods include Elastic Recoil Detection Analysis (ERDA) and Secondary-Ion Mass Spectrometry (SIMS). The overall goal of these techniques is to determine the depth profile of the material under investigation, i.e. the concentration of different elements at different depths.
2 PURPOSE AND STRUCTURE OF THIS STUDY

The purpose of this thesis is to increase the knowledge on erosion and surface modification of metallic surfaces irradiated with light and heavy ions.

This thesis consists of the summary below (in this section and those that follow) and five publications — printed, accepted, or being reviewed for publication — in international peer-reviewed journals. These publications (although two of them not finally accepted and printed), will be referred to by bold face Roman numbers, are included at the end of the summary.

The structure of the summary is as follows. In this section a brief overview of all publications is given, as well as a clarification of the author’s contribution to these. The necessary basic concepts and the background of the results reported in this thesis are given in section 3. In section 4 an overview of the methods used to obtain the results, namely molecular dynamics and Monte Carlo simulations, is given. The results of the calculations, pertaining to surface modification by heavy ions, are presented in section 5. In section 6 the results on surface modification by light ions are given. The conclusions are presented in section 7.

2.1 Summaries of the original publications

In publication I the formation of craters on dense metals by heavy, energetic ions was investigated. The initial stages of He cluster formation and the mechanisms responsible for the subsequent surface modification in W were studied in publication II. The evolution of clusters sputtered from dense metals irradiated with energetic ions was the subject of publication III. The difference between H and He cluster formation in W was elucidated in publication IV. In publication V the nucleation and rupture of He clusters in W was investigated.


In this study it was shown that the size of microscopic craters in dense metals subjected to heavy and energetic ion irradiation is inversely proportional to the product of the cohesive energy and the melting temperature of the irradiated target. This is a correction to the previously reported inverse-square dependence on the cohesive energy alone, and gives direct evidence of the role of melting in crater production.

In this study a new potential for the He-W atomic interaction was used to investigate the formation of He clusters (or bubbles) in W. It was found that He ions with lower energy than needed to create lattice damage in W were able to cluster athermally. The main mechanism behind the nucleation of small clusters was observed to be the formation of (111) crowdion interstitials.


The evolution of clusters sputtered from Ag and Au targets under energetic Xe ion irradiation was followed up to 1 microsecond after ejection using molecular dynamics simulations. The size distributions and temperatures of newborn and metastable (at 1 microsecond) clusters were obtained, and was found to agree with experiments.


In this study density functional theory calculations, molecular dynamics simulations, and kinetic Monte Carlo simulations were used to investigate the behavior of H and He atoms in W. The motivation for this was to understand the vastly different clustering depths of H and He atoms implanted into W using non-damaging irradiation. It was observed that the difference is due to different self-trapping behavior of H and He: H can not form stable clusters, but He can.


He cluster nucleation and rupture in W was investigated systematically and in detail for implantation energies of 50 eV, 100 eV, and 200 eV, at 0 and 300 K using molecular dynamics simulations. The main mechanisms for cluster nucleation were found to be the formation of (111) crowdion interstitials and interstitial dislocation loops. Ruptures of surface-near He clusters were observed, but no associated erosion of W atoms.
2.2 Author’s contribution

In publication I the author of this thesis developed the analysis algorithms, ran the simulations, and wrote about half of the final publication.

The author carried out all the calculations, performed the analysis of the results, and wrote most of the text of publications II, III, and V.

In publication IV the author completed the outline suggested by Prof. K. Nordlund, and edited all parts except that dealing with the description of the density functional theory method. All calculations and simulations, except the density functional theory calculations, were performed by the author.

3 ION IRRADIATION EFFECTS ON METAL SURFACES

3.1 Sputtering

The development of the irradiation effects investigated in this thesis is schematically illustrated in Figs. 1 and 2. In the following an introduction into the specific surface modifications investigated in this thesis will be given.

![Schematic diagrams](image)

Figure 1: Schematic description of what happens when a heavy or energetic ion impinges on a dense, metallic target. In (a), the path of the incident ion is shown. (b) When the ion hits the target surface and penetrates through it, a hot, molten and liquid-like region quickly develops. Single atoms or clusters may be sputtered before the molten region is completely formed. (c) When the hot, expanding region flows out on the target surface, a crater is left behind. Simultaneously, atoms and clusters are ejected. The material that remains near the crater on the surface will make up the rim of the crater, a small part of it is dispersed into small islands on the surface.
Figure 2: Schematic description of what happens when the target is subjected to a continuous flow of light and low-energy ions. In (a), the path of the incident ion is shown. (b) After a continued irradiation the ions come together and form bubbles in the target. (c) Bubbles close to the surface may succeed in temporarily forming a channel to the surface, through which atoms in the bubble may escape.

The physical process at work in sputtering events became known about 50 years after Grove’s initial discovery that electric discharges in gas mixtures caused material to be eroded from the cathode (see section 1). Still, it was not until the 1950s that a quantitative description of this erosion process could be established [2].

The effects of sputtering on a target depend on the properties of the ion as well as the target itself. If the ion is heavy and energetic and the target is dense, which is true for e.g. 20 keV Xe ions impinging on Au, the ion will first cause ejection of single atoms, which may be charged, when it penetrates the target surface. The ion will then collide with the atoms of the target and eventually slow down. When this happens, a fairly localized region of the target will have been heated to the extent that it melts and becomes liquid-like. In most cases the specific volume of metallic target will increase upon melting, making the molten material expand upwards and up on the surface. At the same time hot atoms will be ejected from the target, together with clusters, which separate from the liquid or from the melt that has reached the surface. After cooling, there will be a small hole in the surface, encircled by solidified material protruding from the surface. The hole usually looks like a crater, and the encircling material like a crater rim. Craters will be further discussed and illustrated in section 3.2.

For a long time only the charged fraction of the sputtered clusters was studied [12]. The first observation came in 1958 when Honig found dimers in the mass spectrum of positive ions. Taking Ag as an example, it may be noted that Krohn found clusters with up to five atoms in 1962, Hortig and Müller found negative clusters with up to 60 atoms in 1969, and Katakuse found positive clusters with up to 200 atoms in 1986.
The drawback with investigations of charged clusters is that they may not be representative for the whole spectrum of sputtered particles containing more than one atom. For example, Wahl [13] has noted that nothing conclusive can be said about e.g. the total cluster size distribution from the charged part alone.

Since the 1990s the detection of neutral sputtered clusters has become more efficient. Nowadays, quite large clusters, containing up to 200 atoms [14], can be identified. This is mainly due to the technique of single photon ionization, which utilizes ultra violet (UV) and very ultra violet (VUV) laser light to ionize neutral clusters shortly after ejection [13; 15]. In the ideal case, a cluster is ionized by absorption of a single photon.

Some problems still remain to be solved for the single photon ionization method. These are mainly the cluster fragmentation induced by photons [16], and the inherently lower detection efficiency of large clusters, if post-acceleration or other corrections are not carried out [17].

One of the important properties of sputtered clusters is their size distribution, which is a convenient measure for e.g. the fraction of atoms which are clustered. The size distribution $Y(n)$ is defined as the number $N(n)$ of clusters containing $n$ atoms, divided by the total number $N_{\text{ions}}$ of ions that have been directed onto the target,

$$Y(n) = \frac{N(n)}{N_{\text{ions}}}.$$  

(1)

In several experiments (Refs. in [16; 17]) the dependence

$$Y(n) = Y_1 n^{-\delta},$$

(2)

with $Y_1$ and $\delta$ being constants, has been found. More recent experiments are those by Staudt et al. [14; 17] and Rehn et al. [18]. In these studies the function in Eq. (2) was successfully fitted to the cluster size distributions, and values of the parameter $\delta$ close to 2 and 3 were obtained. The former value $\delta = 2$ is in accordance with analytical models of cluster ejection [19; 20], which predict an inverse power law dependence with an exponent very close to 2.

It must be realized that the analytical models and some simulations of the cluster size distribution are for the so called nascent clusters, i.e. for the hot, ”newborn” clusters right after ejection. In experiments, on the other hand, the distribution of fragmented and cooled-down — or, ”final” — clusters,
is obtained. The power law exponents $\delta$ extracted from (short-time) simulations and experiments therefore do not need to be identical.

### 3.2 Crater formation

In section 3.1 craters were described to be formed when a heavy and energetic ion are incident on a dense target, when molten material flows up on the target surface and leaves behind a surface hole.

Crater formation has been observed to occur on length scales of vastly different magnitudes, from craters produced by meteor impacts [21; 22] to those created by ion impacts on metals, e.g. Au (in experiments [23; 24; 25] and in simulation studies [26; 27]) and Cu (in simulation studies [28]).

An illustration of macro- and microscopic craters is shown in Fig. 3. The linear length scales in this case are meters and nanometers.

![Figure 3: (a) Achelous crater on Ganymede (Courtesy NASA/JPL-Caltech). (b) Crater made by 100 keV Xe impacting on Au [27].](image)

Analysis of the crater size and shapes have shown that several of the scaling laws used for macroscopic craters also hold for microscopic ones. However, one of the central laws, which describes the dependence of the crater size on the cohesive energy $E_{coh}$ of the target, differs in the two regimes [28]. For the macroscopic craters, the crater size $N_{cr}$ (proportional to the volume $V$ of the excavated region) scales as (see reference in [28])

$$N_{cr} \propto \frac{1}{E_{coh}},$$

(3)

whereas for the microscopic craters the behavior
has been reported [29]. Viscosity of molten flow has been proposed to explain the extra $E_{\text{coh}}$ factor, since in studies of crater formation on Au [30; 31] and Cu [32] plastic or viscous flow of molten material has been either proposed or observed. However, Bringa et al. [29] have shown this explanation is insufficient.

### 3.3 Bubble formation

In section 3.1 it was mentioned that the surface of metals can be modified, not only by the formation of craters and sputtering of various-sized groups of atoms, but also by continuous irradiation of light, low-energy ions. In the following the discussion will be limited to H and He. In addition, "surface modification" will be understood to have the second meaning mentioned in section 1, namely changes in the region between the surface and the average depth of the implanted ions.

In order for light ions to give rise to surface modification of e.g. a metallic target, the ions must become trapped in the solid, or at least unable to migrate to the surface and escape on a time scale comparable to the time between successive ion implantations. The surface modification of primary interest is then the formation of clusters or bubbles \(^1\), that is, groups of implanted atoms that do not contain host lattice atoms (atoms making up the target). Under continuous irradiation these bubbles will grow in size, possibly turning so large they become visible on the target surface, as hillocks or mounds, having a diameter which can even be of the order of micrometers. These surface bubbles are called blisters. If the pressure in the blisters becomes large enough, the blisters may rupture, ejecting all or some fraction of the clustered atoms, and possibly also some target material.

Trapping of gas ions in solids was first observed in 1858 in gas discharge experiments carried out by Plücker, who found that the color of the discharge changed over time [33]. Plücker discovered that this phenomenon was caused by loss of gas into the electrodes.

Turning to the specific noble gas He, Barnes et al. [34] were among the first to observe cluster formation in metals (Cu, Al, and Be) irradiated with He. They discovered that clusters grew only in samples that had been annealed. The growth was attributed to thermal vacancies. This conclusion was challenged in 1973 when Sass and Eyre [35] found evidence for growth of He clusters in Mo.

\(^1\)The words "bubbles" and "clusters" are taken to refer to the same thing.
at room temperature, where the contribution from thermal vacancies should be insignificant. Similar findings were obtained by Mazey et al. [36] in 1977.

A solution to the growth mechanism problem was proposed in 1978 by Caspers et al. [37], who investigated He in Mo. The solution was called trap mutation, which was proposed to work as follows. Assuming the He atoms which form the cluster are all contained in a single vacancy, the addition of one extra He atom will cause the vacancy to mutate into a divacancy, resulting in expulsion of a self-interstitial atom (SIA) into the surrounding lattice. Trap mutation has been observed for He in W [38], and it was found that the mutation in W takes place when 10 or more He atoms have been trapped in a vacancy.

It has been observed that He can form clusters in face centered cubic (FCC) metals, such as Ni and Au, even under non-damaging irradiation conditions [39; 40; 41]. This strong tendency for clustering has been attributed to the low solubility of He [42; 43; 44]. In addition, there is no clear evidence for different clustering behaviors of He in FCC and body centered cubic (BCC) metals when using damaging irradiation.

Is the situation similar for hydrogen? One should expect H to be a weaker promoter of clusters than He, since its solubility is larger than that of He, at least in W. As a matter of fact, in several studies (see [42] and references therein) of H/D and He implanted into metals at roughly similar irradiation energies, temperatures, and fluences, it has been found that He has a more severe effect on the target: diameters of bubbles close to the surface are larger and there is more erosion of surface layers taking place when the blisters rupture. Experiments on W show that even at temperatures where the migration rate of He is larger than for H (at 500 K, for example), He will form bubbles right at the surface, at depths \( \sim 100 \, \text{Å} \) [45], while H clusters are formed at micrometer depths [46; 47; 48]. Although much studied, the reason to this huge difference is not well established [46; 48].

The findings mentioned above indicate He atoms implanted into FCC metals are able to form clusters also in the absence of radiation damage. One may ask if this can occur also in less dense lattices, e.g. the BCC lattice. Tungsten is an appropriate example of a BCC metal, partly because it is among the ten elastically hardest (measuring by the bulk modulus) elements in the periodic system [49], and partly because it has been included as a candidate material for the plasma-facing wall in the International Thermonuclear Experimental Reactor (ITER) [50; 51; 52]. Specifically, W is to be used in the divertor, which is the part designed to take the largest loads of heat and particles (including H and He ions) exiting the plasma. If He atoms are able to cluster in defect-free W, they can grow under prolonged irradiation until they may form blisters. If they rupture, then divertor material may be eroded into the fusion plasma. This gives rise to energy losses, such that the higher the nuclear charge state (the \( Z \) value) of the plasma impurity, the greater the cooling effect [53]. Therefore the possible
degrading effects of W are worse than for example Be and C, which are also candidate materials for parts of the first wall (the plasma-facing wall) and divertor, respectively [51].

4 METHODS

4.1 Molecular dynamics simulations

The molecular dynamics (MD) methods are essentially numerical techniques for studying the temporal evolution of a system of particles, for which an interaction (or force) model describing the forces between the particles has been specified [54]. The first molecular dynamics simulation was carried out as early as 1957, by Alder and Wainwright [55]. In all the following ”particles” will be understood to mean ”atoms”.

The molecular dynamics methods can be separated into two classes, based on the interaction model they employ: classical and quantum-mechanical. In this thesis only the classical version has been used, so the quantum-mechanical one will not be described.

In MD simulations (MDS) of atomic interactions using a classical force model, the forces between the particles in the system are derived from a potential energy function, whose functional form is often based on a quantum mechanical (QM) treatment of the system. The more fundamental QM interaction is simplified and various parameters are taken into use. The values of these parameters are taken from first principles calculations or from fits of the model to experimental data. In the latter case the force model is called semiempirical.

The potential energy of an atom A naturally depends on the surrounding atoms. If the energy can be calculated by summing up terms, which only depend on the pair A-B, where B is any surrounding atom, then the potential is called a pair potential. Potentials, for which the energy cannot be calculated in this way, but depend on the environment in a more complicated way, are called many-body potentials.

One routinely uses the Born-Oppenheimer approximation to separate the dynamics of the electrons from that of the atomic nuclei [54]: when an event in the system of atoms occur, the electrons will reach a new equilibrium state much faster than the nuclei, therefore the electronic contribution to the dynamics may be ignored when calculating the forces between the atoms.

Using the classical force model, the Newtonian equations of motion are solved for each atom and integrated over a small time step. The time step is kept small enough to conserve the total energy.
Often a variable time step is used, to speed up the calculations [56]. By using additional computational tricks and optimizing the code to run on several processors in parallel, one can achieve a linear dependence of the computational time on the number of atoms in the system.

The advantages of MDS over experiments are that systems can be studied on short time and length scales, down to femtoseconds and Ångströms, making detailed knowledge of "nanoscopic" events possible. However, these properties of MDS are at the same time the main disadvantages of MDS: millisecond or longer events, and events at e.g. micrometer length scales are not tractable. Nowadays, systems containing up to 3.3 million atoms can be routinely simulated up to at least 4 ps using the EAM potential [57]. In addition, shock waves in systems containing 60.8 million atoms interacting via the Lennard-Jones potential have been simulated for a total of 2000 time steps on 68 computational nodes, requiring a total of 44 hours [58].

It is also important to realize that the force models limit the properties that can be investigated: a semiempirical potential cannot be used to investigate phenomena which are sensitive to e.g. interactions between electrons, since the electronic degrees of freedom are not explicitly present in the potential.

The MDS results presented in this thesis have been obtained using a computer code called PARCAS [59].

### 4.2 Interatomic potentials

In this thesis semiempirical potentials based on the Embedded Atom Method (EAM) by Daw, Baskes and Foiles [60; 61; 62], and the EAM-like model by Finnis and Sinclair [63; 64], were used to calculate the forces exerted by metal atoms on other metal atoms. Pair-potentials were employed for calculations involving interactions between rare gas atoms, and between these and metal atoms.

The EAM potential is an example of a many-body potential, which is mainly suited for metals. In this model the metal can be thought of as consisting of positive "ionic cores" (the atoms with their valence electrons removed) embedded in a "sea" of electrons.

The EAM can be derived from density-functional theory (DFT) using various approximations [60; 65]. The starting points are theorems by Hohenberg and Kohn, and Stott and Zaremba. Hohenberg and Kohn [66] proved that the ground-state energy of a system of electrons moving in an external potential is a unique functional of the electron density. The external potential can be e.g. due to the ionic cores. On the other hand, Stott and Zaremba [67] showed that the energy of a host (the ionic cores and the electrons) with an impurity atom is a functional of the electron density $\rho_h$ of the unperturbed host, i.e. the host without the impurity.
\[ E = \mathcal{F}_{Z, R}[\rho_h], \quad (5) \]

where \( Z \) is the type of the impurity and \( R \) its position. Since every atom in a solid may be regarded as an impurity embedded in the host of all the other atoms, the total energy can be written as a sum [60]

\[ E = \sum_i F_i(\rho_{h,i}), \quad (6) \]

where \( F_i \) is the so-called embedding energy and \( \rho_{h,i} \) is the electron density at the position \( R_i \) of the "impurity atom" when this atom is absent. In going from the functional \( \mathcal{F} \) to the function \( F \) it is assumed that the electron density is uniform, since e.g. first order derivatives have been dropped. However, corrections that are functions of the electron density can be incorporated. Also, the interaction between the impurity and the positive background, i.e. the ionic cores, needs to be included. This can be done by adding a pair-potential \( V_2 \). The final expression for the total energy is then

\[ E = \sum_i F_i(\rho_{h,i}) + \frac{1}{2} \sum_{i,j,i\neq j} V_2(R_{ij}), \quad (7) \]

where \( R_{ij} \) is the distance between atoms \( i \) and \( j \). This expression can be further simplified by approximating the host density \( \rho_{h,i} \) by a sum of atomic densities \( \rho^{(a)} \):

\[ \rho_{h,i} = \sum_{j,j\neq i} \rho^{(a)}_j(R_{ij}). \quad (8) \]

Here \( \rho^{(a)}_j(R_{ij}) \) is the electron density of atom \( j \), which is at a distance of \( R_{ij} \) from atom \( i \). The EAM potential is a many-body potential since the simultaneous configuration of several atoms, not just two, is included via the embedding function.

There are basically two ways to determine the forms of the functions \( F \) and \( V_2 \). The methods have been described by Daw and Baskes [60], and by Foiles, Baskes, and Daw [62], respectively. In the Daw-Baskes scheme, Eq. (7) is used to derive expressions for the lattice constant, the elastic constants, the sublimation energy, and the vacancy-formation energy. The pair potential is written as
and first-principles calculations are used to impose restrictions on the form of $Z(r)$ and the embedding energy $F(\rho)$, e.g. $F$ should have a single minimum. Experimentally obtained bulk properties are then used to obtain the functions $Z(r)$ and $F(\rho)$ at various points. Continuous numerical curves are then obtained by splining.

In the Foiles scheme the equation of state for the metal, i.e. the potential energy of the solid as a function of the distance between nearest neighbors, is equated to Eq. (7). Rose et al. [68] have obtained an analytical form of the equation of state, involving the sublimation energy, bulk modulus, and the lattice constants of the equilibrium state as well as compressed and strained states. Using analytical functions for the electron density $\rho(r)$ and the function $Z(r)$ in the pair potential $V_2(r) = Z^2(r)/r$, the embedding energy can be obtained. The parameters in $\rho(r), Z(r)$ can be obtained from the elastic constants and the vacancy-formation energy.

EAM potentials can also be used for non-metallic, covalent materials, after some modifications. These potentials, originally developed by Baskes et al. [69; 70], are called Modified Embedded Atom Method (MEAM) potentials. The most important modification in the MEAM, as compared to the EAM, is that the electron density depends on the angles between the atoms. MEAM potentials have been developed for at least ten FCC, ten BCC, three diamond cubic, and three diatomic gaseous elements, and their combinations [71], making it possible to simulate e.g. Au atoms on a Si substrate [72].

In the EAM-like model by Finnis and Sinclair the total energy is given by Eq. (7), but the embedding function is $F_i(\rho_i) = -A\sqrt{\rho_i}$, where $A$ is a constant. The square-root dependence follows from the so called second moment approximation of the tight-binding model [73].

The electron densities and embedding functions for Ag (FCC) and W (BCC), using the EAM potential by Foiles et al. , and the EAM-like potential by Finnis and Sinclair, respectively, are shown in Fig. 4 for comparison.

At small interatomic distances all the potentials (for interactions between metal and metal atoms, and between metal and rare gas atoms) were smoothly joined to the universal, repulsive Ziegler-Biersack-Littmark (ZBL) potential [74] to realistically describe high-energy collisions and interaction of atoms at small separations.

Electronic stopping [74] was applied to all atoms having a kinetic energy larger than or equal to 5 eV, but sometimes a limit of 10 eV was used. In detail, the electronic stopping was calculated as a continuous loss of energy, directly proportional to the distance traveled by the atom from one time step to the next. The coefficient of proportionality is not constant, but depends on the energy of the atom.
In order to reduce the computational cost (measured in units of time) the interatomic potentials are often cut off in a soft manner at some interatomic separation. "Soft" cut-off means that the force goes smoothly to zero when the cut-off distance is approached from smaller values. If the potentials were not cut off, then all other atoms in the system would have to be included when calculating the force on any particular atom. This would make the simulations extremely slow, and also necessitate calculations of different-sized systems in order to achieve convergence of desired properties.

The cut-off distances for the potentials are usually determined the first time they are created. In the studies included in this thesis the cut-off distances of the potentials were not modified. However, in publication II when the pair potential for He-W atom interaction was established, the cut-off was explicitly set. The value was set equal to the cut-off of the W-W potential.

In this context it should be noted that it is not a given fact that the EAM potentials give a good
description of atomic clusters, since they have been mostly fitted to bulk properties [75]. Although the binding energies of small clusters (containing less than about ten atoms) predicted by the EAM potential are not exactly the same as those obtained from experiments and \textit{ab initio} calculations [76], the EAM potential still gives a fairly accurate description of at least the melting and freezing of clusters [77; 78], and the ground state atomic configuration of clusters [76].

One particular drawback of the EAM potential is that it tends to predict too large sputtering yields as compared to experiments. A potential similar to that based on the EAM, but which gives sputtering yields closer to experimental ones [57], is the Molecular Dynamics/Monte Carlo - Corrected Effective Medium (MD/MC-CEM) potential [79]. It has been found that the yield of sputtered clusters containing over ten atoms, when predicted by the EAM potential, is larger than the MD/MC-CEM value by a factor of about ten [57], but it is not clear which value is in better agreement with experiments. In summary, this result indicates that the EAM potential might not give a good quantitative description of sputtering yields. The same conclusion need not necessarily hold for the fragmentation of hot clusters, as will be argued in section 5.2.

4.3 Modeling of ion irradiation

When surface irradiation events are investigated using molecular dynamics simulations free surfaces are obtained by using non-periodic boundary conditions in all three Cartesian directions $x$, $y$ and $z$. For a rectangular simulation cell this gives rise to six free surfaces. To remove five of them and turn them into surfaces which are supposed to model the surrounding fictitious bulk region, the techniques of atom fixing and temperature scaling are employed. Fixing an atom means that its velocity is kept at zero at all times. Temperature scaling of a certain region, if implemented using Berendsen’s method [80], forces the temperature (basically the velocities of the atoms) in that region to approach some predefined value at a certain rate. Any heat or pressure wave incident on the temperature-scaled and fixed regions will be damped similarly to what would happen in a real irradiated target bounded by a large bulk region.

In this thesis, atoms usually in a 4-5 Å thick layer at the walls and the bottom of the cell are fixed. This corresponds to three atomic planes in the \{001\} directions. Also, Berendsen temperature scaling is applied to four atomic planes (in publication I: three planes) between the fixed region and the interior of the simulation cell. In publications I, II, and V the substrate was made periodic in $x$ and $y$, so no atom fixing was carried out at these walls. Temperature scaling was performed.

The impinging ion — single atom or an atomic cluster — in any irradiation simulation in this thesis is started from outside the target, so that the distance between the ion and the nearest target atom
slightly exceeds the cut-off distance of the interatomic potential. The angles at which the ion is shot
sufficiently exceed the cut-off distance of the interatomic potential. The angles at which the ion is shot
towards the surface are in all cases chosen so that the range of the ion is minimized and channeling of
the single-atom ion is avoided.

In publications I and III the initial $x$ and $y$ coordinates of the incident ion are selected according
to a uniform distribution in the interval $[0,a]$, where $a$ is the lattice parameter of the target. This
corresponds to a random point in one of the six side planes of the conventional unit cell for the face
centered cubic (FCC) and body centered cubic (BCC) lattices. It should be noted that in these cases
each ion was impinging on a pristine target.

In publications II and V the initial $x$ and $y$ coordinates are fixed from one irradiation event to the next,
but the target is shifted by a random amount first in the $x$ direction and then in the $y$ direction. If this
is not done, there will be a continuous buildup of ions at the same point in the target, which does not
occur in experiments.

### 4.4 Kinetic Monte Carlo simulations

Monte Carlo (MC) is a collective name for any numerical method which relies heavily on random
numbers [54]. The original Monte Carlo method was created by von Neumann, Ulam, and Metropolis
around 1945, for the study of neutron diffusion in materials that can undergo fission. The name
'Monte Carlo' was coined in 1947 by Metropolis.

A main area of application of Monte Carlo simulations (MCS) is the study of events having a specified
rate, i.e. occurring with a specified probability during some interval of time. Usually there is no direct
correspondence between the number of steps carried out in a MC simulation of some rate-dependent
phenomenon, and the physical time. However, if certain conditions are fulfilled, then the imaginary
time in the MCS can be made to correspond to physical time [81; 82]. In this case the simulation is
called a kinetic Monte Carlo simulation (KMCS).

A collection $\{E_i\}$ of possible events (e.g. a certain impurity atom jumping to a neighboring interstitial
site), each having a specific rate $r(E_i)$, can be simulated using kinetic Monte Carlo (KMC) as follows.
First, the list of all possible rates is established, and the cumulative sums

$$R(j) = \sum_{i=1}^{j} r(E_i)$$  \hspace{1cm} (9)
are calculated. Here the largest possible value of $j$ is $N$. Next, a random number $u$ uniformly distributed between 0 and 1 is chosen, and the index $k$, satisfying

$$R(k-1) < uR(N) \leq R(k),$$

is determined. The object $p$ affected by the event $E_k$ also needs to be determined. If all events are equal, then $R(N) = Nr(E)$ and the index $k$ equals the index $p$ of the affected object.

The event $E_k$ having the rate $r(E_k)$, associated with object $p$, is now carried out, e.g. an interstitial atom migrates to a neighboring site.

Next all possible events and rates are re-evaluated, as well as the set of objects, since e.g. if an interstitial atom has become trapped in a cluster, then the number of interstitials has to be reduced.

After this a new random number $v$ uniformly distributed between 0 and 1 is selected, and the time is updated by an amount $-\ln(v)/R(N)$.

Now the sums $R(j)$, and the cumulative sum $R(N)$, are re-calculated and the process goes on as described above.

### 4.5 Modeling of bubble formation

In publication IV kinetic Monte Carlo simulations are used to study migration of the impurity atoms H and He and to obtain depths of clusters formed by these impurities. The computer code performing the calculations was written by Prof. Kai Nordlund. The atoms are inserted according to a Gaussian distribution centered on the projected range of the atoms. The target is semi-infinite, having the surface at $z = 0$ and extending to $z = \infty$. Empirically determined migration rates for H and He, together with temperature and flux values from experimental setups, are used. In order to obtain clusters, the ions are allowed to bind to one another, when the separation between them, or between an ion and a cluster, is less than a certain distance, called the clustering radius. Clustering distances predicted by molecular dynamics simulations and density functional theory calculations are used.
5 SURFACE MODIFICATION BY HEAVY IONS

5.1 Dependence of crater size on melting temperature

It has been established (see section 3.2) that the size of macroscopic craters, measured by the number \( N_{cr} \) of excavated atoms, follows the law

\[
N_{cr} \propto \frac{1}{E_{coh}^n},
\]

(11)

with \( n = 1 \). The dependence \( n = 2 \) has been found for microscopic craters.

A property which is directly related to the essential observation of liquid flow in association with microscopic crater formation is the melting temperature \( T_{melt} \). It is then possible that one factor \( E_{coh} \) in Eq. (11), with \( n = 2 \), could be replaced with the melting temperature to give

\[
N_{cr} \propto \frac{1}{E_{coh}T_{melt}}.
\]

(12)

The melting temperature of a material described by classical potentials can be artificially modified without any effect on the cohesive energy or the other equilibrium properties, as shown by Nordlund et al. [83] for Pt and Pd. The original potentials, denoted by Pt-A and Pd-A, have melting temperatures of 1530 ± 20 K and 1415 ± 5 K, respectively. The modified potentials, denoted by Pt-B and Pd-B, have melting temperatures of 2130 ± 10 K and 1910 ± 20 K, respectively, which are closer to the experimental values than the former ones [83].

In the present simulations clusters containing 13 atoms were used as projectiles. Each cluster had icosahedral symmetry, having one center atom and 12 nearest neighbors, due to the face centered cubic (FCC) lattice structure. The cluster was rotated with a random polar and azimuthal angle, and translated a random distance \( a_x \in [0, a] \) and \( a_y \in [0, a] \), \( a \) being the lattice parameter, in the \( x \) and \( y \) directions, respectively. The species’ of the cluster atoms and the substrate atoms were the same, either Pt or Pd.

Each simulation lasted 50 ps. This time was enough to cool down the system and achieve a stable crater, as determined by visual inspection. For each irradiated sample the crater size \( N_{cr} \) was calculated as the sum of the number of sputtered atoms and adatoms (atoms situated on top of the original
surface): \( N_{cr} = N_{\text{sput}} + N_{\text{ad}} \). This practically equaled the number of excavated atoms, since there were almost no vacancies outside the crater itself.

The crater size is illustrated in Fig. 5(a). In Fig. 5(b) the same data are plotted, but now scaled with the ratio \( T_{\text{melt,B}} / T_{\text{melt,A}} \). Now the crater sizes agree within the uncertainties.

The results can be interpreted as follows. For the potentials Pt-A and Pt-B with same cohesive energy \( E_{\text{coh}} \) but different melting temperatures \( T_{\text{melt}} \) Fig. 5(a) indicates that

\[
\frac{N_{\text{cr,A}}}{E_{\text{cl}}} = a, \quad \frac{N_{\text{cr,B}}}{E_{\text{cl}}} = b. \tag{13}
\]

Here \( a \) and \( b \) are material-dependent constants, and \( E_{\text{cl}} \) is the energy of the incident cluster ion. From Fig. 5(b):

\[
\frac{N_{\text{cr,A}}}{E_{\text{cl}}} = \frac{N_{\text{cr,B}}}{E_{\text{cl}}} \times \frac{T_{\text{melt,B}}}{T_{\text{melt,A}}}. \tag{14}
\]

Therefore,

\[
\frac{N_{\text{cr}} T_{\text{melt}}}{E_{\text{cl}}} = \text{const} \quad \Rightarrow \quad N_{\text{cr}} \propto \frac{E_{\text{cl}}}{T_{\text{melt}}}. \tag{15}
\]

Including the cohesive energy dependence known from before, see Eq. (11), with \( n = 1 \), the results show that

\[
N_{\text{cr}} \propto \frac{1}{E_{\text{coh}} T_{\text{melt}}}. \tag{16}
\]

This scaling behavior can be understood by recalling that one factor of \( 1/E_{\text{coh}} \) is observed for macroscopic cratering, where melting usually plays no role. The present observation of another factor \( T_{\text{melt}} \) in the denominator is a direct verification of the assumption that the difference between the two regimes is due to liquid flow.
Figure 5: (a) Crater size $N_{cr}$ as a function of the kinetic energy $E_{cl}$ of the bombarding cluster. Pt-A and Pd-A are the original Foiles interatomic potentials [75], Pt-B and Pd-B the models where the melting point has been modified to be close to the experimental value [83]. (b) is as (a), but here the results for potentials Pt-B and Pd-B are multiplied by the ratio $T_{melt,B}/T_{melt,A}$ where $T_{melt,x}$ is the melting point for model $x$, with $x$ equal to A or B. From publication I.
5.2 Sputtering of clusters

Turning to single-atom ions incident on equally dense metals, but focusing on the excavated material rather than the surface topology, Fig. 6 shows the total sputtering yield $Y$ and the fraction $f$ of atoms in large clusters as a function of time, resulting from 20 keV Xe impacts on Au. The data demonstrate that several tenths of all sputtered atoms are bound in clusters, and are not isolated.

Figure 6: Total yield (a), as well as the fraction of atoms in large clusters ($n \geq 4$) (b), as a function of time, for 20 keV Xe on Au. From publication III.

In addition to 20 keV Xe ions incident on Au, the bombardment of Ag by 15 keV Xe ions has been studied for the ejection of clusters and their subsequent fragmentation. An illustration of a cluster sputtering event is given in Fig. 7, showing the dispersing cloud of clusters and the hot crater rim.
resulting from an event of 20 keV Xe ion impinging on Au. The images in this figure show that ejected clusters also originate from the crater rim, and not only the hot liquid-like region created by the ion.

Figure 7: Snapshots from a simulation of 20 keV Xe incident on Au. Displayed is a part of the sputtered material at times between 16 and 19 ps. The large continuous group in the lower part of the figures represents the crater rim that has been formed on the surface by the impinging ion. The labels 'A' and 'B' show clusters that are fragmenting, and 'C' illustrates late sputtering: a cluster separates from the surface after the displacement cascade has ended. From publication III.
The evolution of the sputtered, hot clusters was followed for long times after ejection, up to one microsecond for the case of 15 keV Xe on Ag, in order to clarify the extent of fragmentation. An appropriate measure of this is the size distributions of nascent and fragmented clusters. Another measure is the fraction of atoms in different-sized clusters, shown in Table 1. These numbers tell that fractions taken for the final distributions are without exception smaller than those taken for the nascent distributions. This consistency is a strong indication for extensive breakup of large clusters.

Table 1: Fraction of atoms in clusters with sizes larger than $N$. From publication III.

<table>
<thead>
<tr>
<th>$N$</th>
<th>15 keV Xe on Ag</th>
<th>20 keV Xe on Au</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nascent (%)</td>
<td>final (%)</td>
</tr>
<tr>
<td>4</td>
<td>53 ± 5</td>
<td>5.0 ± 0.8</td>
</tr>
<tr>
<td>10</td>
<td>37 ± 5</td>
<td>2.5 ± 0.8</td>
</tr>
<tr>
<td>20</td>
<td>30 ± 5</td>
<td>1.5 ± 0.7</td>
</tr>
<tr>
<td>30</td>
<td>25 ± 4</td>
<td>0.5 ± 0.5</td>
</tr>
<tr>
<td>40</td>
<td>22 ± 4</td>
<td>0.5 ± 0.5</td>
</tr>
<tr>
<td>50</td>
<td>19 ± 4</td>
<td>0.5 ± 0.5</td>
</tr>
<tr>
<td>60</td>
<td>16 ± 4</td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>12 ± 4</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>10 ± 3</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>10 ± 3</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>8 ± 3</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>3 ± 2</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>2 ± 2</td>
<td>0</td>
</tr>
<tr>
<td>250</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The (monomer-normalized) size distributions $(n,Y(n))$ for nascent and final clusters, as well as the results of fitting the inverse power law $Y(n) = Y_1 n^{-\delta}$ to the data, are shown in Figs. 8 and 9. Here $n$ is the number of atoms in the cluster, and $Y(n)$ is the number of clusters containing $n$ atoms, divided by the total number of ions incident on the target during the experiment or simulation. Using this definition, $Y(n)$ is also called the partial yield. For the sake of clarity in plotting, the data for intermediate and large clusters are summed up, in order to get rid of points with $Y(n) = 0$. For the fitting of the data to the inverse power law the original data were used, without any summing up.

During the fitting procedure it became obvious that the fitted exponent $\delta$ depends strongly on the lower limit of the data set. This can be seen in the figures: exponents $\delta$ obtained for the data sets $n \geq n_1$ (including data points with $Y(n) = 0$) with $n_1 = 1, 2, \ldots, 6$, are listed. The various curves are plotted for $n \geq 1$ although they are fitted to subsets of this interval.

From the curves in Fig. 8 it is clear that the inverse power law is a good fit only for $n \geq 4$. The fits to the Ag data behave in a similar manner. The behavior is not as dramatic as for the Au case, but
Figure 8: Monomer-normalized size distributions of (a) nascent and (b) final clusters for 20 keV Xe on Au fitted to the power law $Y(n) = Y_1 n^{-\delta}$, using the data sets $n \geq n_1, n_1 = 1, \ldots, 6$. The largest cluster detected contained $N$ atoms. For the nascent clusters $N = 256$, and for the final clusters $N = 154$. From publication III.

can nonetheless be observed in part (b) of the figure, where the dimer point clearly deviates from the other points.

In Table 2 the values of the exponent $\delta$ obtained from the best fits of cluster data (usually for $n \geq 4$) to the inverse power law are presented. In order to make the results comparable to studies where all cluster data have been used for the fitting, also exponents fitted to all cluster sizes (including monomers) are shown. These values are labeled ' $n \geq 1$'.

The lower limit of cluster sizes has a strong impact on the inverse power law exponent. This sensitivity
may be due to the fact that the dimer yield tends to be "too large" as compared to the monomer and trimer yields, as observed in our simulations and in experiments [17] carried out for 15 keV Xe impacts on Ag. These observations raise the question if it is correct to consider the cluster size distribution being well approximated by a power law. After all, if the data for small clusters (those containing less than four atoms) are consistently in conflict with the power law model based on data for large clusters, then the true model expression cannot be a power law.

The application of an inverse power law despite it being warranted by the complete data set can be understood from the following discussion. In several studies [14; 18; 84] the shock-wave model for cluster sputtering developed by Bitensky and Parilis [19] is preferred over the thermodynamical model
of Urbassek [20] when it comes to explaining the observed dependence of the partial yield \( Y(n) \) on the cluster size \( n \). The former model predicts an asymptotical power law dependence \( Y(n) = Y_1 n^{-\delta} \) with \( \delta = 5/3 \approx 1.7 \) or \( \delta = 7/3 \approx 2.3 \), i.e. \( \delta \sim 2 \). A similar asymptotical behavior is observed in our results. Therefore, instead of inventing a new model we consider our results being well modeled by an inverse power law, that holds in an asymptotical sense.

From Table 2 it seems that the representative values of the exponents \( \delta_1 \) and \( \delta_2 \) for the size distribution of nascent and final clusters, respectively, are relatively close to each other. A calculation shows that the ratio \( r = \delta_2/\delta_1 \), which may be considered a measure of the amount of fragmentation of hot, newborn clusters, is \( 1.2 \pm 0.2 \) for 15 keV Xe on Ag, and \( 1.3 \pm 0.4 \) for 20 keV Xe on Au. To summarize, despite the massive breakup of hot, newborn clusters, the exponent in the inverse power law fit to the size distribution does not change radically.

It was mentioned in section 4.2 that sputtering and cluster yields predicted by the EAM potential are in general higher than those obtained in experiments, or using the MD/MC-CEM potential, which is similar to the EAM. It is not obvious that this would affect the fragmentation behavior of the clusters. One might test this by using the ratio \( r = \delta_2/\delta_1 \). From the literature, one has for 0.5, 1.0, and 5.0 keV Ar impacts on (111) Ag surfaces that \( r = 1.3 \) (for all cases) when using the EAM potential [84], and \( r = 1.2 \) when using the MD/MC-CEM potential [76]. Although the MD/MC-CEM potential in general gives a better description of sputtering yields, these results indicate that the EAM potential need not be far off when it comes to describing the fragmentation of hot clusters.

6 SURFACE MODIFICATION BY LIGHT IONS

In the preceding sections some of the effects of heavy, energetic ion irradiation of dense metals were presented. Next, effects caused by ions with directly opposite mass and energy properties are dis-
The surface modification capability of the light ions H and He are investigated. The focus is on the formation of clusters in the surface-near layers of the target. A comparison of the cluster nucleation ability at low energy of H and He is given first, then the formation and growth of He bubbles in W is described.

6.1 Hydrogen vs helium

In the following the basic mechanism why H and He clusters form at vastly different depths under similar irradiation conditions is investigated.

Before the actual calculations, an evaluation of the force models of the density-functional and molecular dynamics calculations was performed. Single H and He atoms were placed at the tetra- and octahedral interstitial lattice sites in W, and the formation energies were calculated. For H in W, the density-functional theory calculations (DFTC) and molecular dynamics simulations (MDS) predicted that the tetrahedral site is the ground state, in accordance with experiments [85; 86; 87; 88]. The DFT results for He in W were not conclusive, the energies for the octahedral and tetrahedral sites were within 0.3 eV of one another, with the tetrahedral one lower in energy. However, it should be noted that the DFT calculations had not reached convergence to this level of accuracy. The MDS predicted the same energy difference between the interstitial sites, with the octahedral position deeper in energy. There are no experimental data verifying which one is the correct ground state. Nevertheless, this does not affect the main results on the differences in cluster formation mechanisms, as explained below.

The basic difference in cluster depths should be related to the energetics of the clusters. It suffices to investigate the energy landscape of H and He pairs, as will be shown. Inserting H or He pairs into interstitial locations in perfect W, H at tetrahedral and He at octahedral sites, and relaxing to zero Kelvin using MDS, the results in Fig. 10 were obtained.

The results show that H atoms placed initially at separations of 1-2 Å are found far from each other after relaxation, indicating the initial configuration is very unstable. It is possible keep two H atoms at about the same distance they have in the gas phase, 0.7 Å, but this state is very high in energy. It is practically impossible for two migrating H atoms to come this close to one another, due to the formidable barrier of at least 3 eV. Both the MDS and DFTC predicted a weakly bound state for two H atoms at a separation of about 2.2 Å, but the binding energy was so low (DFTC gave less than 0.1 eV, MDS gave 0.3 eV) that it can not bind the H atoms for significant times even at room temperature.
Figure 10: Initial and final distances between atoms for (a) H-H and (b) He-He in W, as well as potential energy of the (c) H-H and (d) He-He pair in W, as a function of the relaxed distance between the impurity atoms, as predicted by the MDS. From publication IV.

Previous studies on H-H interactions in BCC metals have not been conclusive on the nature of the interaction. Analysis of solubility measurements and jellium calculations have indicated that the interaction can be either repulsive or attractive [89; 90]. In a review of defect trapping of gas atoms in metals, Picraux [91] discussed self-trapping of H as a possible trapping mechanism without reaching any definite conclusions. The present results clarify the situation for W, showing that H self-trapping in W is not possible at room and higher temperatures.

The results also show that two closeby He atoms form a stable pair, having a bond length of about 1.6 Å and a binding energy of about 1 eV both in DFTC and MDS. This distance is about half the W lattice parameter, which is 3.16 Å. In the calculations the octahedral site was taken to be the ground state for He in W. Above it was mentioned that there is no direct experimental proof for this. To see why this is not crucial for the outcome of the present results, the following arguments can be made. Two tetrahedral He atoms in W are at a separation of 1.6 Å, corresponding to the bound octahedral configuration, when they are next-nearest neighbors. The difference between this configuration and
the corresponding octahedral one is then only in the locations of the He atoms relative to the W lattice. Above it was mentioned that the tetrahedral and octahedral sites differ in energy by no more than 0.3 eV, the tetrahedral site possibly being the true ground state. Therefore the $\sim 1$ eV binding energy of the octahedral configuration is a lower estimate of the true binding energy, which should not exceed $\sim 1 + 2 \times 0.3 \text{ eV} \sim 1.6 \text{ eV}$. This does not alter the present result that two closeby He atoms are strongly bound.

At larger distances both H and He have some fluctuations because different crystal directions give slightly unequal results. MDS indicate these peaks in potential energy do not constitute a barrier for atomic motion, since the atoms can find migration paths around the maxima.

These results explain why He atoms in W form clusters close to the surface while H atoms do not. For He, the strongly bound pairs will act as seeds for further growth. For H, on the other hand, no stable pairs can be formed, and thus no nucleation centers for H bubbles can be generated. These results hold for H and He atoms in perfect W, and are therefore relevant to spontaneous cluster formation — also known as self-trapping — under non-damaging irradiation conditions.

Kinetic Monte Carlo simulations (KMCS) were used to verify the validity of the MDS and DFTC results. For He, the DFTC and MDS results warrant the assumption that two He atoms are able to form a bound state when their separation is 3.16 Å or less. Using experimental He fluxes and temperatures [45; 92], average depths of clustered He atoms of $\approx 50$ Å (trapped by irradiation defects) and $\approx 2300$ Å (self-trapped), respectively, were obtained. These values are in good agreement with the experimental results.

In KMCS of H cluster formation in W the H atoms were first intentionally allowed to bind with other H atoms, contrary to what the DFTC and MDS indicate. Using experimental fluxes and temperatures [46; 47; 48] average depths of $\sim 100$ Å for clustered H atoms were obtained. This is orders of magnitude lower than what has been found in the experiments, where the depths are $0.5 – 10$ μm. Obviously, an assumption of self-trapping of H atoms leads to bubble depths inconsistent with experiments, and therefore supports the conclusion that H self-trapping does not take place.

H atoms must trap with something in W, since clusters are formed also for non-damaging irradiation. Not all native defects can act as seeds for bubble growth. For instance, MDS indicated that a single vacancy may bind one or two H atoms but not more. Defects which can bind several H atoms and thereby act as bubble nucleation centers may be called ”multitraps” to distinguish them from traps which can bind only single H atoms.

The possibility of building H clusters from defect traps was investigated using KMCS. From various studies a range of natural trap concentrations [93; 94] have been obtained. These traps are typically
such that they can bind single H atoms, and have quite a high concentration, $\gtrsim 10^{24}$ traps m$^{-3}$ (to be compared with the atom density of $6.3 \times 10^{28}$ W m$^{-3}$). There are no indications these traps can act as seeds for bubble growth. In fact, KMCS with such high multitrap concentrations give bubbles right at the surface. Since a reasonably well-defined natural multitrap concentration $c_T$ for H in W is unknown, in the KMCS a homogeneous $c_T$ was assumed as a free parameter. Subsequent MDS showed that a multitrap concentration of $\sim 10^{21}$ traps m$^{-3}$ leads to an average bubble depth of $\sim 1 \mu$m, comparable to the experimental depth values.

### 6.2 Formation and rupture of helium bubbles

The results in the preceding section predict that He ions implanted into W are able to self-trap close to the surface, whereas H ions migrate to vastly larger depths before becoming trapped, most likely by defects. This makes it possible to study the growth mechanisms of He clusters in W, as well as their effects on the target, using molecular dynamics simulations.

Investigations of He cluster formation in W were carried out using 50 eV, 100 eV, and 200 eV He ion irradiation of an initially perfect lattice. The time between the impacts was 5 ps, making the flux of the order of $10^{27} - 10^{28}$ He m$^{-2}$ s$^{-1}$, depending on the size of the simulation box. The samples were irradiated up to fluences of $10^{19} - 10^{20}$ He m$^{-2}$. The longest implantation series consisted of 15000 irradiation events. Three series of 50 eV, four series of 100 eV, and one series of 200 eV He implantations were carried out.

#### 6.2.1 Cluster formation and growth

The three 50 eV implantation series using targets with the temperature scaled towards 0 K (two series) and 300 K (one series), and the first 100 eV series, were analyzed for cluster nucleation and growth mechanisms. The analysis was carried out up to the first significant cluster rupture event. In these events the number of He atoms emitted from the cluster was on average about 30 or larger.

From visual and numerical inspection of the simulations it became clear that single He atoms become trapped in the surface-near layer of W, also when the target temperature is 300 K. Pairs of He atoms are formed when additional He ions are trapped by the resident He atoms. The small clusters formed in this way continue to grow by further trapping of incident ions.

In order for the impurity clusters to grow, host lattice atoms need to be removed from the vicinity of the clusters. From the analysis of the simulations two clear mechanisms of cluster growth emerged: (1)
the formation of (111) crowdion interstitials, and (2) groups of these, essentially interstitial dislocation
loop punching. The mechanisms are illustrated in Figs. 11 and 12. A (111) crowdion interstitial is
formed when a (111) row of atoms displaces coherently in this crystal direction: atoms move from
one equilibrium site to the next. This occurs because the hot ion transfers some of its energy to the
clustered atoms, which start to move more violently, colliding with the surrounding He and W atoms.
Since the surface of the host is relatively closeby, violent enough collisions may displace entire rows
of W atoms. If the cluster is large enough, several adjacent rows of atoms can be displaced in the
(111) direction, or in a direction close to this one. This phenomenon can be called loop punching,
although one could perhaps also use the term "collective crowdion interstitials".
Figure 11: Sequence of snapshots from implantation run 378 in the first 100 eV He implantation series, displaying the formation of a (111) crowdion interstitial, involving 8 W atoms. The label 'A' shows the implanted He ion that has entered the W sample, whose surface is represented by the black horizontal line. The label 'B' indicates the W atom that is responsible for initiating the (111) crowdion interstitial, and the ellipses mark the regions where the crowdion interstitial is formed. In the last frame the (111) crowdion interstitial motion ends in the formation of a single adatom. From publication II.
Figure 12: Illustration of a loop punching event. **0.0 ps:** Initial configuration of atoms. Rows 1, 3 and 4 are clearly visible, row 2 is covered by row 1. Dark (blue) dots represent He atoms, light (yellow) dots represent W atoms. **0.2 ps:** Atoms in row 1 start to displace, especially atom A. **0.6 ps:** Atom A has relaxed backwards, atom B has moved slightly towards the surface. The surface atom in row 1 is close to making a displacement up onto the surface ... **0.8 ps:** ... but it is not able to go through with it. **1.7 ps:** The rows 1 and especially 2 are being compressed by the activity in the He cluster. Atoms in row 3 are about to start moving. Atoms in row 4 are off to a slow start. **2.0 ps:** Displacements in rows 1 and 2 are advancing. Atoms in row 3 are starting to move. **2.5 ps:** Atoms in rows 1 and 2 continue moving. The atoms in row 3 have been displaced by approximately one half the \( \langle 111 \rangle \) distance. Atoms in row 4 have moved forward somewhat. **3.4 ps:** The atoms in rows 1 and 2 have relaxed backwards and have nearly completed their displacements. Atoms in row 3 are more or less in their final states, after having relaxed somewhat in the backward direction. Atoms in row 4 are in 'mid-flight'. **3.7 ps:** Atoms in row 4 are more or less in their final positions, but some relaxation of the surface-near atoms is still going on. **5.0 ps:** Final configuration of atoms. A total of 19 W atoms were directly involved in this loop punching event. From publication V.
6.2.2 Rupture of clusters

The rupture of a surface-near He cluster is illustrated in Fig. 13. The bubble is able to form a temporary "channel" to the surface, enabling the He atoms to escape. The displaced W atoms do not travel far. Usually the bubbles have diameters on the order of Ångströms when they rupture.

Rupturing clusters are not associated with loss of host atoms (W), which occur independently, and should perhaps therefore more appropriately be referred to as sputtering. The erosion — or sputtering — yield can be found in Table 3. The values are in agreement with experimental ones [95].

Table 3: Yield of substrate erosion for the different implantation series. The yield is defined as $N_e/N_i$, where $N_e$ is the number of eroded W atoms, and $N_i$ is the number of implanted He ions. From publication V.

<table>
<thead>
<tr>
<th>Series</th>
<th>$N_e$</th>
<th>Yield of substrate erosion ($N_e/N_i$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 eV, series 1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>50 eV, series 2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>50 eV, series 1, $T = 300$ K</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100 eV, series 1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100 eV, series 2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100 eV, series 3</td>
<td>2</td>
<td>$(3 \pm 2) \times 10^{-4}$</td>
</tr>
<tr>
<td>100 eV, series 4</td>
<td>1</td>
<td>$(1 \pm 1) \times 10^{-4}$</td>
</tr>
<tr>
<td>200 eV, series 1</td>
<td>4</td>
<td>$(8 \pm 4) \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Figure 13: Illustration of the cluster rupture in run number 2027 in the 50 eV He series 1. (a) The 50 eV He ion is incident on the target. (b) The ion has become trapped in a He cluster. (c)-(e) He atoms in the surface-near cluster are escaping from the target. (f)-(g) Some He atoms are still leaving the cluster. (h) Final relaxed state of the target. From publication V.
7 CONCLUSIONS

The surface modification effects of heavy and light ion irradiation of metallic surfaces have been investigated using classical molecular dynamics and kinetic Monte Carlo simulations.

It was shown that for heavy and energetic atomic clusters incident on the dense metals Pt and Pd, the size of ion-induced craters scales with the inverse of the product of the melting temperature and the cohesive energy. This proves that the difference between the crater production mechanisms for macroscopic and microscopic crater impacts is due to the presence of molten material in the latter case.

Moving on to the metals Ag and Au, it turned out that the size distribution of hot clusters sputtered by heavy, single-atom ions obey an inverse power law. The evolution of these newborn clusters were followed up to a time of one microsecond after ejection. The size distribution of the cooled-down clusters was observed to follow a similar inverse power law, but with a different exponent \( \delta \). The fragmentation of the hot clusters caused \( \delta \) to grow, but this change was not very dramatic. Including the uncertainties, the growth \( \delta_1 \Rightarrow \delta_2 \equiv r\delta_1 \) may be limited to a factor of \( 1.0 \leq r \leq 1.7 \).

The surface effects of heavy and energetic ions are more severe than those of light and low-energy ions, in terms of, for instance, the number of displaced atoms. Nevertheless, the study of the surface modification effects caused by light ions is not less important. For instance, light ions differing very little in mass can have vastly different effects on metals. This was shown for H and He atoms in W. The study of pairs of these elements, inserted into interstitial sites in perfect W, revealed that H atoms cannot bind with each other under non-damaging irradiation conditions, making them unable to spontaneously form clusters. He atoms, on the other hand, are able to form stable pairs, which act as seeds for further growth of bubbles.

Using the results that He clusters can form spontaneously in W, a study of 50-200 eV He implantation at high flux was performed. The findings show that He clusters are produced and grow mainly via the formation of (111) crowdion interstitials and interstitial dislocation loop punching. During the implantations W atoms are emitted, but not in association with rupturing of surface-near bubbles. The bubbles have diameters of the order of Ångströms when they rupture.

In summary, this thesis shows that atomistic calculations such as molecular dynamics and kinetic Monte Carlo simulations can be successfully applied to study a variety of erosion and surface modification phenomena that occur on spatial and temporal scales difficult to directly access in experiments.
ACKNOWLEDGMENTS

I wish to thank the current and former heads of the laboratory, Prof. Jyrki Räisänen and Doc. Eero Rauhala, for providing the facilities of the laboratory to my disposal.

I am also thankful to my supervisor Prof. Juhani Keinonen, the head of the Department of Physical Sciences, for the opportunity to conduct research at the department, and for kind advice and help during this work.

Special thanks are due to my principal supervisor Prof. Kai Nordlund, for introducing me to the world of computational physics, and for being a constant source of energetic inspiration, both in matters related and not so related to work.

Thanks are also due to co-workers and colleagues at the laboratory and the department.

Financial support from the Academy of Finland and Magnus Ehrnrooth’s Foundation is gratefully acknowledged.

Helsinki, July 22, 2005

Krister Henriksson
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59. PARCAS computer code, K. Nordlund, private communication. The main principles of the molecular dynamics algorithms are presented in [96; 97]. The adaptive time step and electronic stopping algorithms are the same as in [56].


