Master’s Thesis

Molecular dynamics simulation of ion and cluster bombardment of metal surfaces—craters and sputtered clusters

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Chapter 1  

Introduction

Sputtering is the ejection of particles from a solid due to irradiation. The incident particle may be a photon, an electron, or an ion. One could include meteorites into this list, since sputtering by ion irradiation and the ejection of matter by meteorite impacts have some common features [1]. The surface under irradiation may be any solid, perhaps even the moon in the case of the meteorite (although meteorite impacts are not conventionally called sputtering).

Although sputtering by ion irradiation is an old concept, some basic issues are still poorly understood. These include surface changes and cluster sputtering during heavy ion or projectile irradiation of dense metals. In this work molecular dynamics simulations are used to investigate these topics. The emphasis will be on metals, so semiconductors will not be discussed at all.

The earliest historical evidence for sputtering can be dated back to 1852, to an article by W. R. Grove [2]. The author describes several experiments involving electric discharges between a metal plate (e.g. platinum and copper) and a needle in a low pressure atmosphere consisting of mixes of oxygen, nitrogen and hydrogen. Cathode material was observed to be deposited on the glass walls containing the electrodes and the gas, with various efficiencies depending on the metals and gaseous mix used. Although the concept of sputtering was not invented at this time, some of the results described by Grove can in retrospect be understood as caused by sputtering. The physics underlying sputtering became clear some 50 years after Grove’s article, but a quantitative description was not developed until the 1950s [3].

One of the largest applications of sputtering is the deposition of thin films on various substrates. These may have areas ranging from several square meters to those used in microelectronics [3]. These films can be used in areas such as microelectronics (e.g. single-electron transistors based on Al, Ta and Cr [4]), optical coatings (e.g. mirrors and large architectural windows [5, 6]), magnetic recording layers and hard wear resistant coatings [7]. Superconducting thin films [8] as well as conventional low-temperature and ceramic high-temperature superconductors [9] may also be manufactured using sputtering.

Irradiation in combination with simultaneous evaporation may be used to manufacture multispecies films. For example, a chromium nitride layer may be produced by evaporation of chromium combined with simultaneous nitrogen irradiation [10].

Heavy ion irradiation may be used to prepare superinsulating surfaces, for example 7.5 MeV/u Xe ions on a mica sample [11]. Mica is an insulator with high mechanical strength and heat resistance. The intrinsic tensile stress in refractory metal films increases as the deposition temperature is lowered. This is a problem for adhesion of the film to the substrate. When the film is thick enough the stress may become so high it produces loss of adhesion. The strain may be reduced by use of ion irradiation. For example, a 1 μm Cr film can be irradiated with 75 MeV Ni ions, with reduction in strain as a consequence [12].
Ion irradiation is a tool to investigate the erosion of fission and fusion reactors. When pellets of solid hydrogen are injected into the plasma in a fusion reactor electrons may be sputtered from the pellets. These electrons in turn may induce sputtering in the surrounding reactor material, primarily the first wall [13]. Even tungsten may be eroded when suffering impacts by high energy neutrals. The accumulation of defects caused by keV He ions produces significant hardening and embrittlement, even at high temperatures. This is due to the fact that helium interacts strongly with lattice defects. Hydrogen is also capable of inducing unrecoverable damage in the first wall [14].

Atoms removed from a solid via sputtering can be analyzed in a mass spectrometer and hence give information about the surface concentration of different atomic species. If the sputtered material is analyzed continuously, the depth profile (concentration as a function of the depth under the surface) of the solid may be obtained. Sputtering is also used to produce changes in surface structure and topography, especially for the purpose of etching, polishing and cleaning [3].

Analytical methods that use sputtering are 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. how different elements or substances are depth-distributed inside a sample.
Chapter 2

Physical background and simulation tools

2.1 Introduction

This chapter provides a broad and somewhat extensive overview of the physics underlying the phenomenon of energetic ions moving through a solid and the interactions therein this produces. The foremost theoretical tool of investigation in this area of physics is the computer simulation method known as molecular dynamics, in which the interaction between point-like entities is studied. The principles of this method will also be briefly reviewed.

2.2 Crystal structure and defects

Crystalline solids have a strict ordering of their constituents. At its most fundamental level, the crystal order reduces to the lattice, which is a regular pattern of atoms, ions or molecules. A crystal can be regarded as produced by repeated translations of the unit cell of the lattice [15]. Examples of latter include the simple cubic (sc), body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal closed packed (hcp) lattices ([16], ch. 1). These issues will be further discussed in connection with the presentation of the method of molecular dynamics in Sec. 2.10.

However, real crystals in comparison to ideal ones, suffer from residual defects. These may exist in the solid even after a relatively long period of annealing. Annealing is a treatment which induces recovery of the solid and hence destroys defects therein. Often an annealing treatment takes the form of long term heating at elevated temperatures.

The defects can be classified according to their dimensionality. Point defects are point-like and can be isolated or clustered. The most common types are vacancies and interstitial atoms. A vacancy is an empty lattice site, whereas an interstitial atom is an atom located outside the perfect crystal ordering, e.g. between some lattice sites. If the solid consists of ions of different kind, there is the additional possibility of substitutional impurities. Such a defect is made up of an atom located at a site that belongs to an atom of the other species. When there is an equal number of vacancies and interstitial atoms, one of each kind is taken together and called a Frenkel pair [17]. If the interstitial atom that is associated with a vacancy has migrated to the surface and therefore has left the bulk, the vacancy is often called a Schottky defect. Vacancies and interstitial atoms may also form clusters, thereby producing three-dimensional defects in the solid.
Two examples of one-dimensional defects are the so called edge and screw dislocations [17]. These appear during slip of atom planes, occurring when the shear stress exceeds some critical value, illustrated in Fig. 2.1. The presence of dislocations weakens the shear strength of a crystal.

These damage types listed above occur in bulk. At surfaces there are additional ones, like adatoms and craters. An adatom is simply an atom that has taken residence on top of the surface, whereas a crater is a void that intersects the surface. The conceptual difference between a large multiple vacancy (i.e. a vacancy cluster) and a small crater is somewhat vague, both terms may be used. Usually, the atoms that have been excavated from the solid have been deposited onto the surface or sputtered, i.e. ejected out from the surface and no longer attached to the other atoms in the solid.

During annealing treatments the defects become mobile. As a consequence, Frenkel pairs are annihilated, local stresses releaved, etc. However, some spontaneous annealing may occur even at a quite low temperature. For example, the members of a Frenkel pair may combine spontaneously, if the interstitial is inside a critical region concentrated on the corresponding vacancy. This region is usually called the spontaneous recombination volume (SRV).

Many major experimental techniques exist to investigate damage, namely Transmission Electron Microscopy (TEM) to study defect clusters [18] and Scanning Probe Methods (SPM) to investigate surfaces. Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) are the most common examples of scanning probe methods and are the most important techniques in connection with this work.

In STM a sharp metal needle (often made of tungsten) sweeps over the surface under investigation without touching it and the current of electrons tunneling between the needle and the surface is measured [19]. The tunneling current depends exponentially on the needle-surface distance, allowing high sensitivity in the measurements. To achieve a resolution of the order of 1 Å piezoelectric crystals are utilized to move the needle horizontally and vertically over the surface.

There are mainly two ways of investigating the surface. First, keeping the current and voltage at constant values and measuring the vertical movement of the needle as its horizontal position is varied, an image of the surface structure can be obtained. Second, holding the needle fixed and observing the current dependency on the voltage between the needle and the surface, the electron density at the surface can be measured. Varying the horizontal position of the needle the local electron density, the position of the surface atoms, and even the chemical bonds between them can be investigated.

The most important application of STM is the imaging of metal and semiconductor surfaces; surface structure and spontaneous rearrangement of atoms and foreign species may be investigated. Since the electron density depends on the species, chemical analysis can in principle be conducted in order to map the species distribution or to investigate chemical reactions.

STM can be used in usual air atmospheres, vacuum is not required for most substances. The method has been used to map DNA and certain viruses. STM is however limited to conducting surfaces. In order to investigate insulators (and other materials), atomic force microscopy may be used. In AFM the force between the needle and the surface is measured instead of the tunneling current. A resolution of 30 Å was obtained in the first studies using this method.
However, caution is necessary when analyzing the images obtained in STM and AFM, which is illustrated in the following. Surface damage on a graphite surface due to incident Ar$^+$ ions at 40-80 eV has been studied with STM and AFM by Hahn et al. [20]. The authors found that a surface vacancy visible in the STM image is missing in the AFM image. The explanation for this is that STM measures the *partial* electron density near the Fermi level while AFM sees the *total* electron density. This latter one is not changed much by the presence of the vacancy, which explains why AFM sees nothing where STM does the opposite. The authors note that the interpretation of images obtained through the method of scanning probe microscopy is enhanced by supporting information, like defect production obtained by other techniques. The motivation for this is the above mentioned difference in which electron density that is measured, but also the low sensitivity of the force microscopies for imaging atom-size defects.

Electron diffraction techniques are used in order to identify the internal structure of solids [21]. In electron transmission microscopy a beam of electrons (typically 50-200 keV) pass through the sample and form a diffraction pattern, from which information of the sample structure can be obtained. TEM differs from other electron microscopy techniques in that sample preparation is often destructive, since the sample needs to be thinned to a thickness of several 1000 Å for the electron diffraction through the sample to be successful. The sample may be polycrystalline (e.g. consisting of single-crystal grains) or monocrystalline. As an example, the crystal structure of Ni$_2$Al$_3$ and NiAl, which are connected via a phase transition, may be probed with the use of TEM.

### 2.3 Cascades

#### 2.3.1 Definition

Consider a projectile impinging on a target of solid material. The projectile may be a single atom, a molecule or a cluster, and it may be electrically charged or neutral. The projectile, or the target atoms that it strikes, may travel far into the material, initiating recoils along its path. All the atoms set in motion by the projectile constitute the *cascade*. Often one requires that this volume of temporarily moving particles is confined to a specific region to constitute *one* cascade, since energetic recoils may in turn generate relatively isolated *subcascades*.

#### 2.3.2 Linear cascades

The most simple kind of cascade is called *linear* or *ballistic*, where the particle collisions are governed by a linear Boltzmann transport equation [22]. A common feature for this kind of cascades is the relatively low density of collisions and deposited energy. In fact, the collisions are most often treated as binary, that is, involving only two participants.

A schematic linear cascade is illustrated in Fig. 2.2. An ion penetrates the surface and suffers mostly binary collisions along its path, finally coming to rest inside the solid. The primary recoils initiated along the path of the ion, which in this case acts as a primary knock-on atom (PKA), in their turn generate secondary recoils, and so on. The PKA is the particle that initiates the cascade, and it may be a target atom or the incident ion. The resulting defects will mostly consist of isolated vacancies and interstitial atoms, and some atoms will be ejected from the solid.

At the heart of linear cascade theory lies the linear Boltzmann transport equation

\[
-\frac{1}{v} \frac{\partial}{\partial t} G(x, v_0, v, t) - \frac{\partial}{\partial x} G(x, v_0, v, t) = n \int d\sigma \left[ G(x, v_0, v, t) - G(x, v_0, v', t) - G(x, v_0, v'', t) \right],
\]

(2.1)
where \( \mathbf{v} \) is the velocity of the impinging primary particle, \( \mathbf{v}' \) the velocity of the scattered primary particle, \( \mathbf{v}'' \) the velocity of the recoiling target atom (secondary particle), and \( n \) the density of target atoms. Also,

\[
d\sigma = d\sigma(v, v', v'') \equiv K(v, v', v'')d^3v'd^3v''
\]

(2.2)

is the differential scattering cross section.

In deriving the Boltzmann transport equation one has assumed that an atom starts its motion at a time \( t = 0 \) in a plane \( x = 0 \), with an arbitrary velocity vector \( \mathbf{v} \). The basic quantity that is of interest is

\[
G(x, v_0, v, t)d^3v_0dx,
\]

(2.3)

which is the average number of atoms moving at a time \( t \) in the interval \((t, t + dt)\), at a position \( x \) in the interval \((x, x + dx)\) and with a velocity \( v_0 \) inside a velocity element of size \( d^3v_0 \). The number of atoms with velocity \( v_0 \) that penetrate the plane \( x \) in a time interval \( dt \) is

\[
G(x, v_0, v, t)d^3v_0\left|v_{0x}\right|dt,
\]

(2.4)

where \( v_{0x} \) is the \( x \) component of \( v_0 \). The backscattering yield of a target with a plane surface at \( x = 0 \) is then

\[
S_b = \int d^3v_0\left|v_{0x}\right|\int_0^\infty dtG(0, v_0, v, t),
\]

(2.5)

where the \( v_0 \) integration includes all \( v_0 \) with negative \( v_{0x} \) large enough to overcome the surface binding. In the same manner of reasoning, the transmission sputtering yield through a planar surface at \( x = d \) is
where \( \nu_{0x} \) must be positive.

The transport equation above does not rule out many-body interactions. According to Sigmund these may be included by using the appropriate scattering cross section \( \sigma \). The expressions for \( \sigma \) presented here apply only to binary collisions.

For linear cascades, the most used scattering cross section is that of Thomas-Fermi, and especially the so called power approximation

\[
\frac{d\sigma}{dE} = \frac{C_d T}{E^{m} T^{1+m}}. \tag{2.7}
\]

where \( 0 \leq m \leq 1 \), \( E \) is the primary particle energy and \( T \) the recoil energy of the secondary particle. The multiplicative constant \( C \) contains information of the primary and secondary, e.g. their species. Note that this expression assumes an interatomic potential of the form \( V \propto 1/r^m \). A value \( m = 1/2 \) is suitable in the keV-region and \( m = 1/3 \) in the lower-keV and upper-eV region. In the eV-region \( m \) may be taken to be close to zero.

In this context the (stationary) secondary is the atom that the moving primary strikes. Note that the primary may be the projectile ion or a displaced target atom, and that the secondary may be a target atom or the slowed down projectile ion.

According to Sigmund [23] the number of displaced atoms created in a linear cascade can be calculated from the so called Kinchin-Pease formula

\[
N_{\text{def}} = \frac{E}{2E_d} \propto E, \text{ for } E \gg 2E_d, \tag{2.8}
\]

where \( E \) is the energy of the primary knock-on atom and \( E_d \) an effective threshold displacement energy. The effective displacement threshold energy \( E_d \) is the energy required for a target atom to be permanently removed from its original location.

According to Sigmund, there are some basic assumptions underlying the Kinchin-Pease formula, Eq. (2.8). These are also the basic rules which constitute the binary collision approximation (BCA), to be discussed later. The first of the assumptions is that the particles do not move in any preferred directions, which exist in e.g. a crystalline target. Second, the projectile and the target atoms experience only elastic collisions. Third, the scattering is thought to be made up of hard-sphere collisions, that is, the particles are viewed as classical "billiard balls" in the collisions. In order for the Kinchin-Pease formula to be valid, all these assumptions must be satisfied.

The Kinchin-Pease formula (2.8) can be modified to give an upper limit

\[
N_{\text{def}} = \frac{6E}{\pi^2 U} \ln(1 + \frac{U}{E_d}) \propto E, \tag{2.9}
\]

where \( U \) is a binding energy lost by the atom when it leaves a lattice site [23]. This formula neglects replacement collisions. An estimate by Sigmund yields about 150 % the number of defects in Au calculated with use of the formula

\[
N_{\text{def}} = \chi \frac{E_\nu(E)}{E_d}, \tag{2.10}
\]

called the modified Kinchin-Pease formula. This expression includes electronic stopping, but disregards hard-sphere scattering. Here \( E_\nu(E) \) is the amount of incident energy deposited into elastic
collisions. If \( \eta(E) \) is the fraction of energy \( E \) that results in electronic excitation and atomic ionization, it holds that \( \nu(E) + \eta(E) = 1 \). The factor \( \chi \) depends on the atomic interaction. \( \chi = 0.84 \) is a possible approximation, when \( m \) in Eq. (2.7) is close to zero [24].

According to Thompson [18] in his review of linear and non-linear cascades and their experimental evidence, it is possible to determine the distribution of deposited energy from the so called statistical cascade dimensions. Furthermore, a model by Sigmund et al. (see ref. in [18]) correlates the statistical cascade dimensions to those of an individual one.

The spatial distribution of deposited (elastic-collision) energy [25, 18]

\[
F_D(x, y, z, E) = \frac{E \nu(E)}{\sqrt{(2\pi \alpha \beta)^3}} \exp \left( -\frac{1}{2} \left[ \frac{(x-a)^2}{\alpha^2} + \frac{y^2 + z^2}{\beta^2} \right] \right),
\]

(2.11)

where \( a = \langle X \rangle_D \) (mean deposited energy range), \( \alpha^2 = \sigma_x \langle \Delta X^2 \rangle_D \), and \( \beta^2 = \sigma_y \langle Y^2 \rangle_D \). The quantities \( \sqrt{\langle \Delta X^2 \rangle_D} \) and \( \sqrt{\langle Y^2 \rangle_D} \) are the longitudinal and transverse stragglings, respectively. \( \sigma_x \) and \( \sigma_y \) are the correlation factors, relating the individual cascade to a statistical one.

One also defines the quantity

\[
\theta_D = \frac{F_D}{n},
\]

(2.12)

which is the (elastic-collision) energy density.

From the number of displaced atoms and the spatial distribution of the deposited energy, the average (elastic-collision) energy density \( \langle \theta_D \rangle \) and the average fractional damage \( \langle f_D \rangle \) over the cascade volume can be calculated. The density [26] is by definition

\[
\langle \theta_D \rangle = 0.2 \frac{E \nu(E)}{N_v R_v},
\]

(2.13)

where \( N_v \) is the number of atoms in the cascade core, i.e. within a spheroid with the axes defined by the longitudinal and transversal stragglings. \( R_v \) is the ratio between the statistical and the individual cascade volumes.

The fractional damage [26] is

\[
\langle f_D \rangle = 0.2 \frac{N_D^*}{N_v R_v} = \frac{N_D^*}{E \nu(E)} \langle \theta_D \rangle,
\]

(2.14)

where \( N_D^* \) is the number of displaced atoms per ion. For metals, the use of Eq. (2.10) may overestimate the number of defects [18].

The experimental determination of \( N_D^* \) is difficult due to mainly two reasons [18]. First, significant annihilation of close Frenkel-pairs occur below 40 K. Second, in regions of high defect density, vacancy rich cascade centers form. These may collapse into vacancy dislocation loops. Some analytical techniques rely on channeling and backscattering to measure the defect concentration, and since vacancy dislocation loops do not act as backscatterers, these techniques will report a too low value for the number of defects.

The kind of cascades described here are called ballistic or simply linear. The reason for this is apparent in the linear energy dependence of \( \langle \theta_D \rangle \), the number of defects and spatial distribution of energy. The same dependence is found in sputtering from linear cascades [22]. Sputtering and other surface effects will be discussed later.
2.3.3 Overview of non-linear cascades

In the above discussion, the expressions for the number of point defects, Eq. (2.8), (2.9) and (2.10), the spatial distribution of energy Eq. (2.11) and the deposited energy density Eq. (2.12), are all linear in the PKA energy $E$. However, when the mass of the impinging particle and the mass of the target atoms are large, the density of recoil atoms and deposited energy grow rapidly. At sufficiently high values the assumptions of the BCA (see Subsec. 2.3.2) no longer apply, and the above quantities become non-linear in the PKA energy. Such cascades are generally referred to as high density cascades, where one may emphasize the density of either moving atoms (i.e. deposited energy) or displacements.

A high density cascade may be an elastic collision spike or an ionization spike, of which the latter is more appropriate for insulators and therefore will not be discussed here. The elastic collision spike in turn can be divided into three somewhat distinct types. These are the displacement spike, thermal spike and the plasticity spike [18].

Displacement spikes. When the energy of a moving particle is below some critical value $E^*$, the average distance between displacement collisions approaches the interatomic separation. A net outward motion of atoms will occur along the path of the moving particle, creating a vacancy rich core and an outer shell rich in interstitial atoms [27, 28]. This region constitutes a displacement spike, also called a depleted zone, since many particles present before the cascade have been displaced from their lattice sites and moved away. This cascade type is also called a displacement spike [18]. Heavy ions ($m > 100$ u) with energies between 10 and 60 keV would typically result in a displacement spike extending over almost the entire cascade volume.

Thermal spikes. When an atom has slowed down so that it no longer can create displacements, it will share its energy with neighboring atoms, dissipating energy as lattice vibrations (“heat”). This region where this takes place is called a thermal spike [18]. If the recoil density is high enough and excited regions of the cascade overlap before significant energy dissipation can occur, then almost the entire cascade becomes a thermal spike. For a high enough energy density, the whole cascade will become liquid-like, i.e. the local lattice melts.

Without a displacement spike there can be no thermal spike, since the latter requires a high density of displaced or energetic atoms. If this density is low, there will probably be no region of high density of atoms dissipating their energy as lattice vibrations at the final stages of their displacement motion.

It is meaningful to talk about a thermal spike only if its lifetime $\tau_s$ is long compared to the period of lattice vibration. Assuming a spherical cascade with an initial radius $r_0$, a (lattice) thermal diffusivity $D$, atomic density of initial target material $n$, total damage energy contained in the cascade $E_D$, and a characteristic temperature $T_x$,

\begin{align}
\tau_s &= \frac{r^2 - r_0^2}{4D}, \quad (2.15) \\
 r_s^2 &= \left( \frac{E_D}{4\pi k_BT_x n} \right)^{2/3}. \quad (2.16)
\end{align}

Here the lifetime of the cascade $\tau_s$ is defined as the time required for the temperature of a cascade containing the damage energy $E_D$ to fall below the characteristic temperature $T_x$. For example, the lifetime of a 5 keV cascade in Cu, with $T_x = T_m$, the melting temperature, and assuming $D = 10^{12}$ nm$^2$/s, is 2.5 ps. This is significantly longer than the period of lattice vibrations. Using this formulation of $\tau_s$, it is clear that a cascade ends in a thermal spike provided the characteristic temperature $T_x$ (or a corresponding characteristic energy $E_x \sim k_BT_x$) is sufficiently low [29].

Plasticity spikes. The third type of an elastic collision spike is the plasticity spike, also called a shock wave. In this case the high density cascade is assumed to create a local transient in temperature and pressure. If the average velocity of the atoms exceeds the velocity of sound $c_L$ in the solid ($\sim 2 - 5$ km/s), the outward directed pressure may compress the surrounding medium, creating a shock wave.
If the induced stress is larger than the elastic limit, a permanent, plastic deformation will take place. For example, if the energy density in the cascade is 1 eV/atom, the associated pressure will be $\sim 1$ GPa, much larger than the elastic limit in metals. Under certain conditions a shock wave could lead to surface spalling (i.e. fracture and emission of some of the surface parts) as the wave is reflected from it. This would create a high sputtering yield.

In general, this division of a elastic collision spike into the three classes described above is often not done in the literature. Usually an elastic collision spike is simply called a displacement spike or a thermal spike. In this work this tendency will be followed. Hence the term ”thermal spike” will be used in all three cases presented above, since they concentrate on three different aspects of what basically is part of the same process.

### 2.3.4 Thermal spikes

In this paragraph the basic physics underlying the thermal spike as presented by Brinkman [27, 28] will be reviewed. If a target atom in a collision with an energetic projectile receives a high enough recoil energy, it may be unable to return to its original position. It then becomes a displaced atom. Atoms of this kind are often energetic enough to displace additional atoms before coming to rest. If the material is crystalline, i.e. all atoms in the material are ordered in a lattice, then the displaced atom becomes an interstitial atom, leaving behind a vacant lattice site. In short, a Frenkel pair is created. The energy needed to displace an atom, $E_d$, depends on the position of the atom in the lattice, or more exactly, in the unit cell. In this discussion this threshold displacement energy may be taken to be constant for a given metal.

As mentioned earlier, an atom that is displaced due to interaction with an energetic projectile or displaced target atom, is called a primary knock-on atom (PKA). Atoms that are displaced due to collisions with the PKA are called secondary PKA’s, etc. According to the Kinchin-Pease-formula above, Eq. (2.8), the number of displacements is proportional to $E/(2E_d)$. Because of this, a PKA with energy $4E_d$ will create a second Frenkel pair, after it has traveled a distance approximately equal to the mean free path from the site of the creation of the first Frenkel pair. These two Frenkel pairs will form a double vacancy together with two interstitial atoms. In general, a vacancy will multiplicity $m$ and a number of $m$ interstitial atoms will be created when the projectile energy is $2mE_d$.

As a result, a region with a depleted central core, essentially consisting of one large vacancy, and an outer shell rich in interstitial atoms will be produced in the target, see Fig. 2.3.

In most metals the concentration of interstitial atoms give rise to a pressure wave, with values up to 10 GPa. According to Brinkman, the region enclosing the interstitial atoms will be heated well above the melting point, producing a thermal spike. Without a constraining solid lattice, the atoms are free to flow back into the depleted zone, annihilating a large fraction of the initial Frenkel pairs. As a result, most of the crystal structure will be regenerated.

The displacement spike may be modeled according to Fig. 2.4. Since the material loses its strength upon melting, the high-pressure interstitial atom shell will travel inwards as a pressure wave, with a speed close to that of sound, i.e. $\sim 10^3$ m/s. Putting the radius of the outer shell to 20 Å, Brinkman estimates the time required for the wave to reach the center of the spike region as 2 ps.

In order to arrive at a critical projectile energy, below which no displacement spike will be produced, the following reasoning may be carried out. Assuming a point-like source of thermal energy $Q$ is inserted into the solid, at time $t$ after insertion the temperature at a distance $r$ from the point will be given by the expression

$$T = \frac{Q\sqrt{\pi}}{8\sqrt{(\pi\kappa t)^3}} \exp \left[-C r^2/(4\kappa t) \right],$$

(2.17)
Figure 2.3: A schematic view of a displacement spike, as described in ref. [28].

![Schematic view of a displacement spike](image)

Figure 2.4: A model for the displacement spike.

![Model for the displacement spike](image)

where $C$ is the specific heat of the material and $\kappa$ is the thermal conductivity. For $C$ one may use the lattice heat capacity, since the electronic heat capacity is generally small and the time short enough (about 100 ps, according to Brinkman) that the lattice and electronic systems have not had time to reach a common equilibrium. Brinkman presents the estimate...
for the center of the thermal spike to cool to the melting point $T_m$ of the material. Putting 2 ps (obtained above) equal to the time in Eq. (2.18), one obtains the critical energy $Q_{\text{crit}} = 350$ eV. This represents the part of the incident PKA energy that is dissipated to the target atoms. The second part consists of electronic heating, and the third and last part is stored as formation energy in the created interstitial atoms and vacancies. According to Brinkman, the second part is negligible if the PKA energy is less than 1 keV. The third can be estimated to be $N_{\text{def}} \cdot 5$ eV $= E_{\text{spike}}/(2E_d)5$ eV. Here $E_{\text{spike}}$ is the minimum energy which may be given to a PKA, which can result in the production of a displacement spike. 5 eV is an estimate for the energy needed to create a displacement. Putting

$$E_{\text{spike}} = Q_{\text{crit}} + \frac{E_{\text{spike}}}{2E_d} 5\text{eV},$$

(2.19)

and using $E_d = 25$ eV, one obtains $E_{\text{spike}} \approx 400$ eV. A PKA with an energy less than this value will not produce a displacement spike.

It may be noted that there are additional critical energies besides the threshold displacement energy $E_d$ and the threshold displacement spike energy $E_{\text{spike}}$. The maximum displacement spike energy, $E_{\text{spike, max}}$, is the largest energy a PKA can possess when it initiates a displacement spike. A particle with $E > E_{\text{spike, max}}$ must therefore experience several collisions at relatively large distances from each other, before its energy has dropped to $E = E_{\text{spike, max}}$ and it may initiate a spike. All these three energies $E_d, E_{\text{spike}}, E_{\text{spike, max}}$ are independent of the nature of the PKA (e.g. its species and mass). A fourth critical energy determines the maximum energy that can be given to a PKA (or any other particle) in a collision, and is given by

$$E_{\text{PKA, max}} = \frac{4mM}{(m + M)^2} E,$$

(2.20)

where $m$ is the mass of the primary particle, $M$ the mass of the secondary particle, and $E$ the energy of the primary particle.

As a comparison to Brinkman’s estimate of thermal spike lifetime, Thompson and Nelson [30] approximate the time required to distribute the PKA energy over a region 50 Å in diameter in heavy elements ($M_2 \sim 100$ u) as $\sim 0.1$ ps. Furthermore, ten atomic oscillations are approximated to occur before the Maxwell-Boltzmann law can be applied to the spike, making the relaxation time of the order of 1 ps. The authors furthermore estimate the spike lifetime to be $\sim 10$ ps. By considering the times between ion-ion and electron-electron collisions Thompson and Nelson estimate that the electron system comes into equilibrium much sooner than the ion system. Together with the observation that the time required for ‘cool’ electrons to quench the ‘hot’ ion system is relatively long (10$^5$ atomic oscillations, or $\sim 100$ ps or more for $M_2 = 200$ u), the conclusion is reached that the electron system and electron-ion coupling need not be considered in thermal spikes.

Analytical thermal spike models of e.g. sputtering usually start out with a spatial distribution of deposited energy, Eq. (2.11) above, and assume that classical theory of heat flow can be applied to describe the dissipation of heat and the evolution of the thermal spike [18]. In one dimension the heat equation is

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2},$$

(2.21)

where $D$ is the coefficient of thermal diffusion. The value depends on which thermal region is investigated. There are mainly two thermal regions used, the prompt and the slow. The prompt thermal region, spanning $\sim 1$ ps, is the time required for the vibrational temperature to be established, i.e.
for the ion system to relax and reach thermal equilibrium, providing the conditions for Maxwell-Boltzmann thermodynamics to apply. During the slow thermal region, spanning \( \sim 100 \) ps or more, the ion and electron systems reach a common equilibrium, \( i.e. \) the vibrational and electronic temperature attains the same value, which equals the macroscopic target temperature.

Attempts to actually measure the lifetime of the thermal spike have been made. In an experiment carried out by Stuchbery and Bezakova [31] Ir and Pt ions were implanted into a target whose surface consisted of sequential layers of Ir and Pt. These layers were sputtered onto a Fe foil, which in turn was backed by a layer of Cu. The in-bound ions had an average energy of 7.5 MeV, and stopped in the Fe layer after about 0.75 ps. Measurements of the hyperfine magnetic fields that the implanted nuclei experience combined with a simple model of how the fields depend on time, yields a thermal spike lifetime \( t_s = (7.3 \pm 0.8) \) ps in Fe. A more sophisticated model gives basically the same result, however it is pointed out by Stuchbery and Bezakova that the above value for \( t_s \) may be a slight overestimate. The authors find a value \( t_s \approx 6 \) ps more comfortable.

2.4 Surface effects

2.4.1 Overview

When a cascade intersects a solid surface, mainly two kinds of phenomena may occur. These consist of \textit{sputtering}, \( i.e. \) ejection of particles, and \textit{cratering}, \( i.e. \) the production of holes in the surface. These are the end-results of several processes, like liquid flow, pressure wave induced surface rupture and evaporation from hot regions close to the surfaces.

2.4.2 Surface damage mechanisms

In their MD simulations of Au on Au at 10 and 20 keV Ghaly \textit{et al.} [32] note that their cascades evolve much in the way described by Brinkman — many atoms are ejected from the cascade core and a depleted region develops. The authors observe traces of replacement collision sequences (repeated collisions where the primary comes to a halt after knocking the secondary from its lattice site), a shock wave traveling at a speed close to that of sound, melting of the lattice surrounding the cascade, and high pressure due to temperatures exceeding 6000 K for up to 3 ps. This leads to the formation of a cavity, which later contracts. In this case the cavity does not intersect the surface, but otherwise it may have a greater importance in influencing the damage structure. This explosive flow of atoms from the melt to the surface, coined \textit{viscous flow}, ceases at about 12 ps, when the local melt starts to resolidify. Upon completion at 25 ps, many atoms are left on the surface, and hence few of them are available to fill the vacant lattice sites below the surface. In a related study adatom islands are observed on the surface [33]. The outgoing flow and adatom island formation take place if the liquid has a larger specific volume than the solid. If not, the formation of the melt introduces local, tensile stresses in the bulk, a phenomenon that may be termed a ”sucking” effect.

Complex dislocation structures are formed when the solid-liquid interface moves towards the center of the cascade during the resolidification process. No isolated vacancies and a very small number of interstitial atoms remain at the end of the simulations, at about 30 ps, due to the local annealing caused by the melting of the lattice. A corresponding local annealing has been experimentally observed by Averback and Merkle [34].

In their MD simulations of 10 keV Pt incident on Pt Ghaly \textit{et al.} [35] observe a phenomenon they call \textit{microexplosions}. A microexplosion is caused by high pressure and temperature, inducing surface rupture, flow of atoms to the surface, and ejection of many atoms. This occurs when the center of energy is close enough to the surface. Craters of sizes 450 times the atomic volume are observed as a consequence of the microexplosions. Most of the missing atoms are found on the surface as adatoms. Also, an increase in sputtering yield is noted during these events. The authors find that
microexplosion events are quite common in metals like Pt and Au, for which the energy density near the surface can be very large.

In some MD simulations of cascades in Cu and Ni at 50-200 keV ion energies a phenomenon which is coined coherent displacement has been observed [36]. This damage was present in one of seven Cu events, and in two of seven Ni events. In one 50 keV event a highly regular adatom island consisting of at least 117 atoms was observed. Among these were 60 randomly displaced atoms. The presence of this island was due to a liquid-like region forming inside the bulk. The large compressive stress created an interstitial dislocation loop. Driven by the high pressure this dislocation loop made planes of atoms slide coherently along one of the slip directions of fcc metals, towards the surface. The reason why all events did not show this kind of damage is due to the fact that the shearing stress required to initiate the slip often was very near the theoretical threshold value [37].

2.4.3 Sputtering

There are three kinds of sputtering. First, surface atoms with sufficient kinetic energy may overcome the surface binding energy and be ejected, producing sputtered particles that may be single atoms or clusters. Measurement of the sputtering yield, i.e. number of ejected particles divided by the number of incident particles, as well as the energy and angular distributions of sputtered atoms, give information on the recoil energy distribution in the surface region [18]. The sputtered material may consist of single, neutral or ionized atoms, and neutral or ionized clusters. Second, photons are emitted as the result of de-excitation of ejected particles. Third, electrons can be emitted. Here only the first phenomenon will be further discussed.

Sigmund presents a model of sputtering based on linear cascade theory, which yields a linear dependence on the projectile energy [22]. The theoretical results were initially verified, but some results indicated non-linear dependency of damage as function of projectile energy [18].

Some experimental studies by Andersen and Bay may also be mentioned. In 1972, these authors noted a non-linear sputter yield in cases of 45 keV ions incident on Cu targets [38]. They attributed this effect to be due to neglect of electronic energy losses in the theoretical considerations of Sigmund [22]. Later, in 1973, the same authors studied 45 keV ions incident on Si and Ag [39], and found similar non-linear effects. This time the effects were attributed to thermal spikes occurring in the solid targets. This lends direct support to Sigmund’s proposal [25] that thermal spike effects are due to the breakdown of the linear transport theory at low recoil velocities.

Still later, conclusive evidence for non-linear effects were obtained [18].

Merkle and Jäger [40] present a model intended to explain the surface craters and the sputtering-yield enhancements in heavy metals under high-energy heavy-ion bombardment. This model is based on experiments with Bi⁺ and Bi₂⁺ irradiation of Au at energies between 10 and 500 keV. It is the opinion of the authors, that the models by Sigmund [25] and Kelly (ref. in [18]) cannot account for the magnitude and energy dependence of the observed enhancements in the sputtering yield in Au and other heavy metals. Building on the thermal spike theory of Kelly, Merkle and Jäger propose that the enhancements in sputtering yield is due to high-energy-density cascades or sub-cascades occurring close to the surface. These cascades are coined surface spikes. These surface spikes are produced with low but finite probability, which explains why they are not present in every cascade.

Thermal spike theory is used to explain sputtering in terms of evaporation from a hot surface region. Taking the prompt and slow thermal regions as mentioned above into consideration, and considering the thermal spike to essentially be a liquid-like region — in comparison to Brinkman’s ”depleted zone”-concept — the following picture of a thermal spike emerges. First, energy is deposited and produces an initial (vibrational) temperature, after the ion system has reached equilibrium. Second, the hot zone is quenched (cooled down) through heat transport processes, and thermal evaporation takes place on the hot surface region of the spike. Several initial temperature distributions have been proposed. These include an initial point source (ref. in [18]), a spherical [30], a cylindrical [41], and a spheroidal distribution (refs. in [18]).
According to a brief review on analytical models for sputtering carried out by Bringa et al. [42], the sputter yield $Y$ may be defined as an integral of the surface temperature $T_{surf}$

$$Y = \int_0^\infty dt \int_S dS \Phi(T_{surf}, U_s), \quad (2.22)$$

where $\Phi$ is the particle flux, $U_s$ the surface binding energy, and the integration is performed over the surface of the solid target. Five analytical models for calculating $Y$ in the case of sputtering by evaporation may be mentioned: Johnson-Evatt, Sigmund-Claussen (e.g. [43]), Urbassek-Sigmund [44], Urbassek-Michl [45], and Bitensky-Parilis [46]. Some of these (e.g. [43, 45]) give relatively good agreement (at least qualitatively) when compared to experimental data. There is however no general consensus which of these or other models is the most generally suitable one.

As a concrete example, one may take the Sigmund-Claussen model, without corrections for temperature effects due to evaporation [43]. In this model the energy transport is determined by a temperature dependent thermal diffusivity obtained from kinetic gas theory,

$$K = \frac{25}{48} \frac{1}{N \lambda_0 a^2} \sqrt{\frac{k_B T}{\pi M}}, \quad (2.23)$$

where $\lambda_0 \approx 24$ and $a \approx 0.0219$ nm when a Born-Mayer interatomic potential is used. With the additional assumption of a cylindrical spike region the heat equation (2.21) can be solved. The resulting sputtering yield is

$$Y = 0.036 \frac{\lambda_0 a^2}{U_0^2} \left( \frac{F_D'(0, E, \eta)}{3} \right)^2 f \left( \frac{3 U_0}{3 (\theta_v)} \right), \quad (2.24)$$

where $F_D'(0, E, \eta)$ is the energy deposited per unit path length, and

$$f(u) = (1 + u - u^2) \exp(-u) + u^3 \int_u^\infty dt \frac{e^{-t}}{t}. \quad (2.25)$$

According to the authors (Sigmund and Claussen) this model is in good qualitative agreement with data, at least in the case of Sb$_n$ ($n = 1, 2, 3$) ions incident on Ag.

### 2.5 Primary stopping

A particle (e.g. an electron) traveling in any medium but vacuum will lose energy due to interactions with particles and quanta. Interactions with quanta will not be considered here. There are in general two possible types of interaction, elastic and inelastic. During elastic interactions the total momentum and kinetic energy of the system of interacting particles is conserved. This is the case when e.g. charged particles are deflected in an electric field, or during the collision of rigid bodies. Inelastic interactions, on the other hand, conserve the total momentum but not the kinetic energy. Examples include collisions of particles resulting in emission of quanta, for example the excitation and de-excitation of an atom by an impinging ion.

The slowing down of an ion traveling through solid matter is due to interaction with electrons and nuclei. The two most important mechanisms are elastic and inelastic collisions with the electrons and elastic collisions with the nuclei. These mechanisms are called electronic and nuclear stopping, respectively. However, some authors prefer to include only inelastic collisions in the electronic stopping. In this work this latter definition of electronic stopping will not be used. For the sake of consistency, electronic stopping mentioned in referenced articles will be assumed to agree with the definition used in this work. Any resultant error will be conceptual, since no numerical calculations will be carried out based on the referenced models of electronic stopping.
The remaining possibility of interaction is inelastic collisions with nuclei. This type of interaction is significant only when the energy of the ion is so large that nuclear reactions may occur. This will not be relevant in this work, and hence is not considered.

Let

\[ dP = n\delta_x d\sigma \]  \hspace{1cm} (2.26)

denote the probability that a primary with initial energy \( E \) undergoes a collision when traveling a short distance \( \delta_x \) through a material with particle density \( n \) [47, 29]. The collision is specified by the scattering cross-section \( \sigma \), which satisfies \( d\sigma = \sigma_d d\Omega = N_s / \Phi \), where \( \sigma_d \) is the differential scattering cross-section, \( N_s \) the number of particles scattered into the solid angle \( d\Omega \) per unit time, and \( \Phi \) is the incident flux density. The cross-section depends on the interatomic potential.

If \( E \) is the energy of the primary particle and \( T \) the recoil energy of the secondary particle, then the average energy loss during a collision is

\[ \delta E = \int T dP = -n\delta_x \int_{T=0}^{T=T_m} T d\sigma, \]  \hspace{1cm} (2.27)

where \( T_m \) is the maximum transferable energy. Hence knowledge of the cross-section allows evaluation of the stopping. The stopping power is by definition

\[ \frac{dE}{dx} = -n \int_{T=0}^{T=T_m} T d\sigma = -nS(E), \]  \hspace{1cm} (2.28)

where \( S(E) \) is the stopping cross-section. The total stopping power is

\[ \frac{dE}{dx} = \left( \frac{dE}{dx} \right)_n + \left( \frac{dE}{dx} \right)_e + \left( \frac{dE}{dx} \right)_Q, \]  \hspace{1cm} (2.29)

where the subscripts \( n \) and \( e \) denote nuclear and electronic, respectively. \( Q \) symbolizes the stopping not already accounted for. If one can assume the nuclear and electronic stopping powers to be independent of each other, and neglect the residual stopping symbolized by \( Q \), then the total stopping power is

\[ \frac{dE}{dx} = -n [S_n(E) + S_e(E)]. \]  \hspace{1cm} (2.30)

Inverting this, the path length traveled by the primary is obtained from the expression

\[ R(E) = - \int_C \frac{dE}{nS(E)}, \]  \hspace{1cm} (2.31)

where \( C \) denotes the path taken by the primary.

In Figs. 2.5, 2.6, and 2.7 is illustrated the nuclear and electronic stopping power for three different ion-target combinations, namely He on Pt, Xe on Pt, and Pt on Pt [48].
Figure 2.5: Nuclear and electronic stopping for He incident on Pt.

Figure 2.6: Nuclear and electronic stopping for Xe incident on Pt.

2.6 Ion-electron interaction

The interaction between ions is determined by the interatomic potential, which will be discussed in a later section. Here the interaction between the primary ion and electrons in the target will be considered.

Electronic stopping is the dominant mode of energy loss at energies $\sim 10^6$ eV, but decreases to
Figure 2.7: Nuclear and electronic stopping for Pt incident on Pt.

20 – 30% at \( \sim 10^4 \text{ eV} \) and to about 8% at about 25 eV [49]. For ions having kinetic energies between about 25 eV and \( \sim 10^{-2} \text{ eV} \), the electron-phonon interaction may become the dominant mode of energy loss. These numbers apply to Cu.

Figure 2.8: Electronic stopping in the case of He on C. \( v_B \) is the Bohr velocity.
2.6.1 Electronic stopping at different energies

The energy loss due to electronic stopping, \( S_e(E) = -1/n dE/dx \), can be divided into three approximate regions, as outlined in Fig. 2.8. The first and third region are most easily treated in an approximative manner, the second region will not be discussed here.

**Low-energy ions.** For slow ions satisfying \( v < v_B Z_1^{2/3} \) (region 1 in Fig. 2.8) Firsov (ref. in [50]) derives the expression

\[
S_e(E) = 0.325(Z_1 + Z_2) \left( \frac{E[\text{eV}]}{M[\text{amu}]} \right)^{1/2} \text{eV } \text{Å}^2.
\]  

(2.32)

Here \( Z_1 \) and \( Z_2 \) denote the nuclear charge of the primary particle and the secondary particle, respectively. \( v_B \) is the Bohr velocity, \( v_B = e^2/\hbar = 2.1877 \times 10^{16} \text{ Å/s} \). \( M \) represent the mass of the secondary and \( m \) the mass of the primary. The expression above is partly based on the Thomas-Fermi model of the atom (see [47], ch. 3 and 4).

Loss of kinetic energy of the primary is due to passage of electrons from the primary to the secondary. When the primary moves away from the secondary, the electrons return. The process can be described roughly as a collision between two isolated atoms, leaving their electronic shells undistorted.

Lindhard and Scharff [51] use a model of a slow heavy primary moving in a uniform electron gas. Electrons impinging on the primary transfer net energy proportional to their drift velocity relative to the primary. The electronic energy loss in this model can be written

\[
S_e(E) \approx 8\pi e^2 \frac{\hbar^2}{m_e e^2} \frac{Z_1^{7/6} Z_2}{(Z_1^{2/3} + Z_2^{2/3})^{3/2}} \cdot 6.343 \times 10^{-3} \sqrt{\frac{E[\text{eV}]}{m[\text{amu}]}} \text{eV } \text{Å}^2/\text{atom}.
\]  

(2.33)

Using the local density approximation, Kitagawa and Ohtsuki [52] derive two approximate expressions for the electronic stopping. The local density approximation means treating the solid target as a plasma of electrons, having density \( n(r) \). In the case of a high density electron gas,

\[
- \frac{dE}{dx} \sim Z_1^2 e^4 m_e^2 \frac{\hbar}{24\pi^3 e_0^4} \nu \ln \left( \frac{4\pi e_0 \hbar v_F}{e^2} \right),
\]  

(2.34)

which agrees with an earlier result of Fermi and Teller [53]. Here \( \nu \) is the velocity of the incident ion (the primary) and \( v_F \) the Fermi velocity. For a low density electron gas,

\[
- \frac{dE}{dx} \sim 0.32 \pi^{7/3} Z_1^2 \hbar v n^{2/3}.
\]  

(2.35)

Here \( n \) is the electron density. However, most metals exhibit a dependence somewhere between these two extremes. Still, the models presented here have one common property, namely the dependence

\[
S_e(E) \propto v,
\]  

(2.36)

which can be written

\[
S_e(E) = \lambda E^{1/2},
\]  

(2.37)

where \( \lambda \) is a model-dependent constant ([47], ch. 4).

**High-energy ions.** Energetic (region 3 in Fig. 2.8) primary particles interact mainly with the bound electrons of the secondary particle. If the electron that interacts with the primary is considered to be initially at rest, the kinetic energy loss of the primary is simply determined by the momentum of the electron after the interaction.
Calculations of electronic stopping in this region have been carried out by Bethe and Bloch (refs. in [47]). According to Bethe,

\[ S_e(E) = 4\pi \frac{Z_1^2 e^4}{(4\pi \epsilon_0)^2 m_e v^2} Z_2 \ln\left(\frac{2m_e v^2}{I}\right), \]  

(2.38)

where \( I \) is the mean excitation energy for the atom in its ground state, a quantity which is difficult to estimate exactly, and \( m_e \) is the electron mass.

Also, a result due to Bohr (refs. in [28]) can be mentioned:

\[ S_e(E) = 4\pi \frac{Z_1^2 e^4}{m_e v^2} Z_2 \ln\left(\frac{4.123\pi \epsilon_0 m_e v^3}{Z_1 e^2 \omega}\right), \]  

(2.39)

where \( \omega \) is some average oscillation frequency of the electron in the atom. This formula gives a reasonable description of the electronic energy loss of slow alpha particles and heavier nuclei.

Also note that \( S_e(E) \sim 1/v^2 \) in this high-energy ion region ([47], ch. 4).

### 2.6.2 Application to target ions

All of the above models for electronic stopping predict

\[ S_e(E) = \lambda E^{1/2} \]  

(2.40)

at low energies for the primary. Since

\[ \frac{dE}{dx} = -n S_e(E) = -\lambda n E^{1/2}, \]  

(2.41)

one obtains

\[ \frac{dE}{dt} = v \frac{dE}{dx} = -\lambda n v E^{1/2} = -\lambda n \left(\frac{2}{m}\right)^{1/2} E \equiv -\frac{1}{\tau_v} E. \]  

(2.42)

Here \( m \) is the mass of the primary. The quantity

\[ \tau_v = \frac{1}{\lambda n} \left(\frac{m}{2}\right)^{1/2} \]  

(2.43)

can be considered the lifetime of the kinetic energy \( E \).

The energy and momentum transfers when the primary interacts with an electron are small compared to the energy and momentum of the particle. The transfers give in practice a straight trajectory of the primary. Hence, the electronic energy loss can be incorporated into the classical equations of motion as a continuous loss mechanism:

\[ m \frac{d^2 \mathbf{R}}{dt^2} = \mathbf{F} - \beta \frac{d\mathbf{R}}{dt}, \]  

(2.44)

where \( \mathbf{F} \) is the interatomic force and \( \beta \) is given by

\[ \beta = \frac{m}{\tau_v} = m \lambda n \sqrt{2/m}, \]  

(2.45)

representing the electronic energy loss. For example, for Cu \( 0.3 < \lambda < 2.5 \text{ eV}^{1/2} \text{ Å}^{2} \), which yields \( 2.3 \times 10^{-14} \text{ eV} < \lambda < 19.5 \times 10^{-14} \text{ eV} \), and a relaxation time \( \tau_v \) satisfying \( 0.27 \times 10^{-12} \text{ s} < \tau_v < 2.3 \times 10^{-12} \text{ s} \), i.e. \( \tau_v \sim 1 \text{ ps} \) [49].
2.6.3 Electron-phonon interaction

According to Caro and Victoria [49], most of the heat is transported by electrons for metals at equilibrium. The quenching in the lattice (cooling down by the surrounding undamaged lattice) of a cascade will depend on the thermal conductivity of the solid and the coupling between the primary particles (atomic parts of the projectile and the target atoms, collectively referred to as "ions") and the electrons. Electrons and ions are two different systems, each with their temperature-dependent heat capacities and thermal conductivities. The two systems are coupled together via the so called electron-phonon interaction. Observe that both of the two systems are out of global equilibrium in the thermal spike, because this develops on a time scale of 0.1 ps, which is of the same order as the period of lattice vibrations.

Note that a weak electron-phonon coupling means that the mean free path of the electrons in the corresponding liquid is some hundred Ångströms. That is, the electron mean free path is larger than the linear dimension of the cascade. Hence, the energy of the electrons far from the energetic ions will decay at the early stage of the cascade. Since the thermal conductivity of the electronic system is two orders of magnitude larger than the phonon one, the electronic thermal spike moves faster and produces a sphere of hot electrons about ten times larger than the cascade radius. The decaying electron energy feeds energy back into the ions, especially those that are outside the cascade.

To consider the electron-phonon coupling, one may use the classical stochastic Langevin equations. These describe the interactions of an ensemble of classical particles (e.g. ions and electrons) with an irreversible heat bath (e.g. the undamaged lattice surrounding the cascade). It is generally thought that the Langevin equations generate the canonical ensemble, i.e. the NPT ensemble, having fixed values for particle number, pressure and temperature.

The Langevin equations of motion are

\[
\frac{d^2 \mathbf{R}}{dt^2} = \mathbf{F} + \eta(t) - \beta \frac{d\mathbf{R}}{dt}, \tag{2.46}
\]

where \( m \) is the mass of the ion in question. Here the positive multiplicative constant \( \beta \) measures the strength of the coupling to the heat bath, always yielding a retarding force term, and \( \eta(t) \) is a random (stochastic) force, which obeys

\[
\langle \eta(t) \rangle = 0,
\]

\[
\langle \eta(t_1) \cdot \eta(t_2) \rangle = 2\beta k_B T \delta(t_1 - t_2), \tag{2.47}
\]

\[
P(\eta(t)) = \frac{1}{\sqrt{2\pi \langle \eta^2(t) \rangle}} \exp\left(-\frac{\eta^2(t)}{2\langle \eta^2(t) \rangle}\right), \tag{2.48}
\]

where \( T \) is the temperature of the heat bath. Since this term is missing from equation (2.44), \( \eta(t) \) may be interpreted as representing the electron-phonon coupling.

When comparing (2.44) and (2.46), the question arises if \( \beta \) could be having one and the same value in both regimes. In fact, these two values for \( \beta \) may differ by up to two orders of magnitude.

If equation (2.46) is taken to apply for all particle energies, one needs to know how \( \beta \) varies from one regime to the other. Caro and Victoria propose an empirical fit to different models,

\[
\beta = A \log_{10}(\alpha \rho^{1/3} + b), \tag{2.49}
\]

where \( \alpha = 4(3\pi^5)^{1/3} \epsilon_0 \hbar^2/(e^2 m) \), the fitting parameter \( A \sim Z^2 e^4 m^2/(24\pi^3 \hbar^3 \epsilon_0) \), and \( b \) is an adjustable parameter depending on the energy regime. The above expression can be used most efficiently in cases where the interatomic potential is a function of the electron density \( \rho \).
The random force may be neglected if the electron-phonon interaction is estimated to have a small influence of the development of the cascade. Then the atoms in the target obey the equation of motion

$$ \frac{d^2 \mathbf{R}}{dt^2} = \mathbf{F} - \beta \frac{d \mathbf{R}}{dt}, $$

(2.50)

with $\beta$ given by equation (2.49).

According to Flynn and Averback [54] a strong coupling between the electrons and the ions means that the electrons absorb a relatively large power from the lattice, i.e. the electronic heat capacity is large. In these materials the mean free path of the electrons is usually less than the linear dimension of the cascade. And since the electrons usually have a large thermal conductivity, much heat will be carried away from the cascade core very fast, reducing the maximum spike temperature. Hence, a strong coupling may totally suppress a heat spike.

Finnis et al. [55] derive two coupled differential equations describing the local electronic and ion temperatures and their gradients. Simplified forms of these are included into MD simulations of cascades in Cu and Ni via application of a damping force acting on the ions and proportional to the velocity. The authors find that their model gives satisfactory agreement with the results of Caro and Victoria [49]. The simulations of 2 keV cascades in Cu and Ni yield a reduction in the number of defects when the electron-phonon coupling is included, in larger extent in Ni than Cu, as well as faster cooling of the cascade.

Koponen [56] discusses the electron-phonon coupling in an article presenting a theory of the energy transfer between valence electrons and ions in dense displacement cascades in metals. According to the author, electronic stopping is less important than electron-phonon coupling in a cascade where the ions have energies below a few eV. In this case only energy transfer via electron-phonon coupling can significantly change the cooling rate of the thermal spike. Some experimental findings give support to the hypothesis that electron-phonon coupling is operating in thermal spikes, through agreement with calculations of so called ion-beam mixing (a measure of the relocation of the target atoms during irradiation). This support is however indirect and inconclusive, according to Koponen.

In an MD study Nordlund et al. [57] compare experimental values of ion-beam mixing with those obtained from MD simulations. The authors find that the effect of electron-phonon coupling on the dynamics is much less significant than believed for Ni, Pd and Pt bulk affected by up to 200 keV cascades. However, the authors cannot exclude the possibility that the coupling may influence the mixing by a factor up to $\sim 1.3$. Still, this largely differs from the theoretically calculated values of $3 - 10$. The difference between the MD results and those derived from theoretical models the authors attribute to the fact that the models are based on equilibrium concepts whose validity is questionable in the highly disordered state that is typical for the cascade. The conclusion is that the electron-coupling plays only a minor part in cascade dynamics for Ni, Pd and Pt.

### 2.7 The interatomic potential

#### 2.7.1 Classical potentials

The classical interatomic potential $V = V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ for a $N$-body system is generally of the form [58]

$$
V = \sum_i V_1(\mathbf{r}_i) + \sum_i \sum_j V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \sum_j \sum_k V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \ldots
\equiv \sum_i V_1(\mathbf{r}_i) + \sum_i \sum_j V_2(\mathbf{r}_i, \mathbf{r}_j) + V_{\text{many-body}}.
$$

(2.51)
Here $V_1$ is a potential due to an external field, $V_2$ is a pair-potential, $V_3$ is a three-body potential, etc. This potential form is labeled 'classical' since it does not include quantum mechanical considerations in any direct ways. The potential energy of atom $i$ is

$$V_i = V_1(r_i) + \sum_{j, j \neq i} V_2(r_i, r_j) + \sum_{j, j \neq i} \sum_{k, k \neq i, j} V_3(r_i, r_j, r_k) + \ldots$$

(2.52)

The pair-potential states that atom $i$ obtains a contribution to its potential energy due to each and every one of the other atoms, where these are considered separately. On the other hand, the three-body term contributes for each combination of two neighbors $k_1$ and $k_2$, the potential term depending on the spatial configuration $(i, k_1, k_2)$.

Examples of pair potentials are the $(A, B)$-Lennard-Jones, Morse, Born-Mayer, and Buckingham potentials (refs. in [47]):

$$V_{L-J}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^A - \left( \frac{\sigma}{r} \right)^B \right],$$

(2.53)

$$V_{\text{Morse}}(r) = D \left[ e^{-2\alpha(r-r_m)} - 2e^{-\alpha(r-r_m)} \right],$$

(2.54)

$$V_{\text{B-M}}(r) = Ee^{-F(r-r_m)} - \frac{G}{r^6} - \frac{H}{r^8},$$

(2.55)

$$V_{\text{B}}(r) = Ie^{-r/\rho} - \frac{J}{r^6},$$

(2.56)

where various constants are fitted to experimental data. However, from the functional dependences one can for example deduce that $\epsilon$ determines the cohesive energy. The last two potentials are often used at short-range separations in the case of ionic compounds. In these cases a screened Coulomb potential is often used at greater separations. The screened Coulomb potential can be of the form

$$V(r) = \frac{Z_1(r)Z_2(r)e^2}{4\pi\epsilon_0 r},$$

(2.57)

where $Z_1$ and $Z_2$ are so called screened charges. These could be of the form

$$Z_i(r) = Z_{0,i}(1 + \beta r^\nu) e^{-\alpha r},$$

(2.58)

where $\alpha$, $\beta$ and $\nu$ are adjustable parameters and $Z_{0,i}$ the number of valence electrons of atom $i$ [47]. Alternatively, one may use a screening function, in which case the potential becomes

$$V(r) = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r} \chi\left( \frac{r}{a_0} \right),$$

(2.59)

where $\chi$ is the screening function and $a_0$ the screening distance, such that the screening becomes insignificant at interatomic separations less than $a_0$.

However, the pair potentials may not always be sufficient. They are often used for noble gases and ionic compounds (e.g. Xe and NaCl), but not for materials having closed-packed crystal structure (fcc and hcp) (e.g. Pt and Au), or materials that are covalently bonded (e.g. Si and C). In these latter materials many-body potential terms are needed to provide a more accurate description. Pair potentials are unable to describe complicated situations like surfaces and fracture of a metal in the presence of hydrogen, a phenomenon called hydrogen embrittlement [59, 60].
2.7.2 Quantum mechanical models

One way to treat many-body effects is *density functional theory* (DFT). According to Hohenberg and Kohn [61], essentially all system properties may be derived from the electron density \( n(\mathbf{r}) \) of the corresponding system, hence the name DFT. Kohn and Sham [62] present a way to solve for the electron density from a given interatomic potential \( V(\mathbf{r}) \). Consider the energy of an *interacting* inhomogenous electron gas,

\[
E = \int d^3r V(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + G[n],
\]

where \( G \) is a universal functional of the density. Write \( G[n] = T_e[n] + E_{xc}[n] \), where \( T_e \) is the kinetic energy of a system of *non-interacting* electrons with density \( n(\mathbf{r}) \) and

\[
E_{xc}[n] = E_x[n] + \int d^3r n(\mathbf{r}) \varepsilon_c(n(\mathbf{r})),
\]

where \( E_x \) is the exchange energy of a system of electron density \( n(\mathbf{r}) \) and \( \varepsilon_c \) the correlation energy per particle of a homogeneous electron gas. A variational condition leads to the system of equations

\[
\left[ -\frac{1}{2} \nabla^2 + V(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{d(n(\mathbf{r})\varepsilon_c)}{dn(\mathbf{r})} \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}),
\]

\[
n_1(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \psi_i(\mathbf{r})\psi^*_i(\mathbf{r}'),
\]

from which the \( N \) single electron wave functions \( \psi_i \) can be iterated. The total energy is

\[
E = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3r d^3r' \frac{n_1(\mathbf{r}, \mathbf{r}') n_1(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + \int d^3r n(\mathbf{r}) \left[ \varepsilon_c(n(\mathbf{r})) - \frac{d(n(\mathbf{r})\varepsilon_c)}{dn(\mathbf{r})} \right].
\]

This formalism is used as a starting point for *e.g.* the Embedded Atom Method, which is discussed next.

2.8 Embedded atom method

A quantum-mechanical, many-body potential especially well suited for metals is the so called *embedded atom method* (EAM), derived by Daw, Baskes, Finnis and Foiles [59, 60, 63, 64]. However, in the case of hexagonally close-packed (hcp) lattice structure it turns out that some bulk properties cannot be fitted to the potential. This is the case for the elastic constants, which determine the behavior of the bulk when it is subjected to elastic stress and strain, for Cd, Zn, Be, Y and Zr [65]. Still, the agreement in several cases between predictions by simulations using EAM-potentials and experiments makes the EAM a practical method for study of defects, surfaces and impurities in metals, according to Daw and Baskes [60].
Hohenberg and Kohn [61] have shown that the electron density determines the total energy in a solid, 
Eq. (2.63), to within an additive constant. Stott and Zaremba [66], on the other hand, have shown that 
the energy of a host containing an impurity is a function of the electron density of the unperturbed 
host, i.e. the host with the impurity absent. Thus,

\[ E_{\text{tot}} = \mathcal{F}(Z, R, \rho_h (r)), \]  

(2.64)

where \( Z \) and \( R \) are the type and position of the impurity, and \( \rho_h (r) \) the electron density of the 
unperturbed host. The functional \( \mathcal{F} \) is universal and independent of host type [59].

One may view each atom in a solid as an impurity in the host of all the other atoms, and make the 
Ansatz

\[ E_{\text{tot}} = \sum_i F_i(\rho_h (r_i)), \]  

(2.65)

where \( F_i \) is the so called embedding energy and \( \rho_h (r_i) \) the electron density of the host at position \( r_i \),
but without atom \( i \) present [60]. The embedding energy is the difference between the energy of the 
atom inside the electron gas relative to the energy of the atom when it is separated from the electron 
gas. There is no simple connection between the functional \( \mathcal{F} \) and the function \( F \).

However, the above equation (2.65) leads to unrealistic properties of the solid. Partly because it 
assumes complete uniformity, and it neglects the repulsion between the ion cores. To account for 
this, one may write the total energy as

\[ E_{\text{tot}} = \sum_i F_i(\rho_h (r_i)) + \frac{1}{2} \sum_{i,j: j \neq i} \phi_{ij} (R_{ij}), \]  

(2.66)

where \( R_{ij} \equiv |r_i - r_j| \) is the distance between atoms \( i \) and \( j \), and \( \phi_{ij} \) is a short-range, repulsive pair 
potential. This equation can be simplified by writing the unperturbed host electron density as

\[ \rho_h (r_i) = \sum_{j: j \neq i} \rho_j^A (R_{ij}), \]  

(2.67)

i.e. by approximating the host density at position \( r_i \) by a sum of the atomic electron densities \( \rho_j^A \).

Note, that \( \rho_j^A \) is the contribution to the total electron density due to atom \( j \), but \( \rho_h (r_i) \) is the electron density at the position of atom \( i \), created by all the atoms in the solid but with the “impurity atom” \( i \) absent. Now

\[ E_{\text{tot}} = \sum_i F_i \left( \sum_{j: j \neq i} \rho_j^A (R_{ij}) \right) + \frac{1}{2} \sum_{i,j: j \neq i} \phi_{ij} (R_{ij}) \]

= \sum_i \left[ F_i \left( \sum_{j: j \neq i} \rho_j^A (R_{ij}) \right) + \frac{1}{2} \sum_{j: j \neq i} \phi_{ij} (R_{ij}) \right]. \]  

(2.68)

One EAM-like potential is the Finnis-Sinclair potential [63]. Here \( F(\rho_i) \) is simply \( -C \sqrt{\rho_i} \), where \( C \) 
is a multiplicative constant. There are explicit EAM-potentials for Ni, Pd, Pt, Cu, Ag, Au and alloys 
of these [67].

When forming alloys or adding real impurities (e.g. Cu in a solid consisting of pure Au) it is necessary 
to know the embedding function \( F \) for each element (e.g. \( F_{\text{Cu}} \) and \( F_{\text{Au}} \)), and the potential \( \phi_{ij} \) for 
each kind of pair (e.g. \( \phi_{\text{Cu}-\text{Cu}}, \phi_{\text{Cu}-\text{Au}} \) and \( \phi_{\text{Au}-\text{Au}} \)). All these functions must often be found 
empirically.
The repulsive pair potential may be written as a screened Coulomb potential with modified nuclear charges, Eq. (2.57). Alternatively, one may use the Coulomb potential with unmodified nuclear charges but multiply by a screening function. This could be the Moliere (M) or the screening function for the so called ZBL universal potential [68], both having the form

\[ \chi(x) = \sum_{i=1}^{4} a_i e^{-b_i x}, \]  

(2.69)

where \( a_i, b_i \) are empirically fitted parameters and \( x = r/a_0 \), where \( a_0 \) is the screening length [47].

### 2.9 Binary collision approximation

#### 2.9.1 BC simulations

One way to learn about the damage caused by a penetrating ion or a recoil inside a target is by computer simulation. The binary collision (BC) simulation method accomplishes this, using the binary collision approximation (BCA) to calculate the paths of the particles in the cascade. The conditions under which the BCA is valid has been presented earlier, in Subsec. 2.3.2.

The simulation starts with a primary recoil of specified velocity and position. This is followed through a series of inelastic binary collisions, i.e collisions including only two particles. Between the collisions the particles travel in straight line segments, which are the asymptotes of the paths of the particles in the laboratory system. If the energy a particle receives in a collision is larger than some threshold value, it is included in the cascade. To simulate the development of the cascade in time, the simulation follows the current fastest particle. When the energy of a particle falls below some threshold value, or e.g. when it escapes from the target, the particle is excluded from the cascade.

The collisions are considered to be composed of a quasielastic part and a separate electron excitation (inelastic) part. The quasielastic part is governed by a repulsive pair potential. The inelastic energy loss may be continuous and dependent on the traveled path length, or discontinuous and occurring only at the moment of collision between primary and secondary.

![Figure 2.9: The center of mass view of a binary collision.](image)
The BC code MARLOWE adapted for crystalline targets [50] uses a screened Coulomb potential with the screening function

\[
\phi(x) = 0.35y + 0.55y^4 + 0.10y^{20},
\]
\[
y = e^{-0.3x},
\]
\[
x = r/a_0,
\]

which is Moliere’s approximation to the Thomas-Fermi screening function. Here the screening length of Firsov has been used,

\[
a_0 = \left( \frac{9\pi^2}{128} \right)^{1/3} \frac{a_B}{(\sqrt{Z_1^0 + Z_2^0})^{2/3}}.
\]

Inelastic (electronic) energy losses are included by using a model of Firsov, in such a way that a specific amount of energy is subtracted from the energy of the impinging particle in each elastic, nuclear collision. \( Q \) depends on the incident energy of the primary.

The energy transfer to the secondary in a nuclear collision is

\[
T = \frac{4mME_0}{(m + M)^2} \left( \sqrt{1 - \frac{Q}{E_0} \frac{m + M}{M} \sin^2 \frac{\theta}{2}} + \frac{1}{2} \left[ \frac{5}{2} - 2 \frac{Q}{E_0} \frac{m + M}{M} - \sqrt{1 - \frac{Q}{E_0} \frac{m + M}{M}} \right] \right),
\]

where \( Q \) is the energy lost by electronic excitation, \( E_0 \) is the energy of the impinging particle, \( \theta \) is the scattering angle in the center of mass (CM) system, \( m \) is the mass of the primary, \( M \) is the mass of the secondary, and \( A = M/m \). The energy of the primary after scattering is

\[
E_1 = E_0 - T - Q.
\]

Another BC code named TRIM (TRansport of Ions in Matter) can be used for amorphous targets [69]. Here particles lose energy in discrete amounts in nuclear collisions and lose energy continuously due to electronic stopping. For the nuclear interaction a screened Coulomb potential of Moliere type is used at high energies, and an unscreened Coulomb potential at low energies. The potential used in [69] is the same as used in the MARLOWE calculations mentioned above, but here the screening function is

\[
\chi_M(x) = 0.35e^{-0.3x} + 0.55e^{-1.2x} + 0.1e^{-6x}.
\]

Later versions of TRIM (e.g. [70]) use a ZBL universal potential (see Sec. 2.8).

The energy transfer to the secondary is given by Eq. (2.72) for \( Q = 0 \):

\[
T = \frac{4mM}{(m + M)^2} \frac{E_0}{\sin^2 \frac{\theta}{2}}.
\]

The scattering angle in the laboratory system is related to the one in the CM system by the expression

\[
\tan \psi = \frac{\sin \theta}{\cos \theta + m/M}.
\]

The electronic energy loss is related to the path \( L \) traveled,
\[ \Delta E_e = \ln S_e(E). \]  
(2.77)

The Bethe-Bloch formulation is used for the electronic stopping at high energies, and Lindhard-Scharff theory at low energies. At low energies, \( S_e(E) \equiv S_e^L(E) = kE^p \), the Lindhard-Scharff formula \([51]\) predicts

\[
k = 8\pi e^2 \frac{h^2}{m e^2} \frac{Z_1^{7/6} Z_2}{(Z_1^{2/3} + Z_2^{2/3})^{3/2}} 6.343 \cdot 10^{-3} \sqrt{\frac{1}{m[\text{amu}]}} \text{ eV } \AA^2 \text{ atom}^{-1}, \tag{2.78}
\]

with the energy given in units of eV, and \( p = 1/2 \). Compare with Eq. (2.33).

At high energies, \( v > v_B Z_1^{2/3} \) and \( v > v_B \sqrt{Z_2} \), the Bethe-Bloch formalism becomes valid. The non-relativistic expression for the stopping is given by a particular form of Eq. (2.38):

\[
S_e^H(E) = \frac{8\pi Z_1^2 Z_2 e^4}{2m_e v^2} \ln \left( \frac{2m_e v^2}{Z_2 I_0} \right), \tag{2.79}
\]

where the Bloch constant \( I_0 \) can be given as \( I_0 = 12 + 7/Z_2 \) for \( Z_2 < 13 \) and \( I_0 = 9.76 + 58.5/Z_2 \).\(^{19}\) otherwise.

The expressions for the electronic stopping at low and high energies are fitted together at intermediate energies, \textit{i.e.} region 2 in Fig. (2.8) in Subsec. 2.6.1.

### 2.9.2 Simulation method

Some of the basic rules for treating the binary collisions are as follows. Consider a collision from which the primary particle emerges having energy \( E_1 \), after transferring energy \( T \) to the secondary particle. The secondary joins the cascade with an energy \( E_2 \), which need not equal \( T \). The secondary is displaced if \( T > E_d \), where \( E_d \) is the displacement energy (see Subsec. 2.3.2), and is then given an energy \( E_2 = T - E_b \), where the binding energy \( E_b \) satisfies \( E_b \leq E_d \). The primary replaces the secondary on its lattice site when \( T > E_d \) and \( E_1 \leq \min\{E_c, E_d\} \). Here \( E_c \) is a threshold energy for atoms belonging to the cascade; atoms with energy less than \( E_c \) are not included in the cascade. Usually \( E_c \) is not directly related to \( E_d \) \([50]\).

This recipe gives the number and location of the interstitial atoms, vacancies and replaced atoms. There are two important limitations of the BC simulation method. One is the inability to treat many-body collisions, which are likely to be important in dense thermal spikes. The simulation method also fails in a serious manner at low recoil energies.

### 2.10 Molecular dynamics

#### 2.10.1 The algorithm

Since this work relies heavily on molecular dynamics simulations, a brief but somewhat comprehensive introduction is in order.

Atomistic simulations form a part of physics that by definition concerns itself with the computer aided simulation of the motion and interactions of indivisible entities. Compare with the greek word for atom, \textit{atomos}, which means precisely ’undividable’. In the special case of atoms and molecules, this method is called \textit{molecular dynamics} (MD).
The parts carried out in a MD simulation are illustrated schematically in Fig. 2.10.

**Initialization.** The first part concerns the determination of the initial positions and velocities for all particles whose interactions with each other are going to be simulated. Often one begins with the selection of a simulation cell. This could be in the form of a parallelepiped (i.e. an elongated cube with all four corner angles preserved), having the side lengths $L_x$, $L_y$ and $L_z$. For convenience, the cell if often centered on the origin, leaving the surfaces at $x = \pm L_x/2$, $y = \pm L_y/2$ and $z = \pm L_z/2$. 
In cascade simulations the size of the simulation cell (the number of atoms) is by a rule of thumb set to larger than 16 to 20 times the energy of the primary ion in electron volts (eV).

One often wishes to simulate an infinite medium, not a region bounded by a surface. In this case so called *periodic boundary conditions* are applied. This is implemented in such a way, that if a coordinate (e.g. $x$) lies outside the simulation cell, then the corresponding side length (e.g. $L_x$) is repeatedly subtracted from the coordinate, until this lies inside the cell (e.g. $x \in [-L_x/2, L_x/2]$). It should be noted, that this actually yields a *finite* but unbounded simulation cell, in the same manner as the surface of the Earth is finite but unbounded (one can travel in a straight line and never come to any boundary).

Most often the simulated material is crystalline. Then the atoms and/or molecules order themselves in a *lattice*, whose smallest building block is the *unit cell*. The unit cell of a lattice may be constructed in different ways. The kind of unit cell that has three orthogonal axes is often simplest to handle, so this is called the *conventional unit cell* — in the case of cubic lattices this unit cell is simply a cube. Examples of cubic lattices and corresponding conventional unit cells are presented in Fig. 2.11. Unit cells for face-centered cubic (fcc), body-centered cubic (bcc) and simple cubic (sc) lattice are shown.

The simulation cell usually consists of multiples of the unit cell, *e.g.* there are $N_x$ unit cells in the $x$ direction, $N_y$ unit cells in the $y$ direction and $N_z$ unit cells in the $z$ direction. Here $N_x, N_y, N_z = 1, 2, 3, \ldots$.

The initial velocity of all secondary particles should be set according to the simulated temperature, $T$. One could *e.g.* use a Gaussian distribution for the velocity components. Then the probability density for the velocity component $v_{i,x}$ is given by
\[ \rho(v_{i,x}) = \sqrt{\frac{m_i}{2\pi k_B T}} \exp \left( -\frac{m_i v_{i,x}^2}{2k_B T} \right), \]  
(2.80)

where \( m_i \) is the mass of particle \( i \) and \( T \) the temperature of the simulated material \[71\].

Equilibration of the simulated material is often needed. In this way the initial guess for a material’s lattice parameter(s) may be adjusted, allowing the system to reach a state closer to what it would be in reality. The system has equilibrated when the relevant physical quantities have reached stable values, e.g. the instantaneous pressure and/or energy.

The event starting the simulation could be a primary impinging on the target surface, or alternatively some ion inside the target recoiling with a specified velocity (magnitude and direction).

**Boundary conditions, image cells and potential cutoff.** For each direction, it should be decided whether periodic boundary conditions should be used or not. If periodics are applied, the simulated material may be thought of consisting of the simulation cell surrounded by an infinite amount of *image cells* in all directions. These image cells are duplicates of the original simulation cell. If an atom e.g. exits the simulation cell in the positive \( x \) direction, it will reappear into the cell from the other side, still going in the positive \( x \) direction.

![Figure 2.12: Demonstration of the potential cutoff radius applied to atom \( i \) in a periodic, two-dimensional lattice. The original simulation cell is surrounded by image cells.](image)

The size of the side lengths of the simulation cell leads to physical implications, which depend on the investigated phenomenon and the *potential cutoff radius*. When using periodics and a potential cutoff
radius $R_c$, only the neighbors inside the sphere with radius $R_c$ concentrated on particle $i$ contribute to the total force acting on this particle. See Fig. 2.12.

The cutoff radius must satisfy $R_c < L/2$, where $L$ is the smallest of $L_x$, $L_y$, and $L_z$. When deciding which particles that should be considered inside the cutoff region of particle $i$, one first has to make sure that every particle $i$ is located inside the simulation cell, i.e. $r_i = (x_1, x_2, x_3)$, with $x_1 \in [-L_x/2, L_x/2)$, $x_2 \in [-L_y/2, L_y/2)$, and $x_3 \in [-L_z/2, L_z/2)$. Next, the separation $R_{ij}$ between particle $i$ and every other particle $j$ in the simulation cell is calculated, according to

$$R_{ij} = \sqrt{R_{x_1,ij}^2 + R_{x_2,ij}^2 + R_{x_3,ij}^2},$$

$$R_{x_k,ij} = x_{k,i} - x_{k,j},$$

$$k = 1, 2, 3. \quad (2.81)$$

In Fig. 2.12 it seems that particle $A$ would be excluded from the calculation of the force on particle $i$, although it should be included, since its image in the cell left to the original simulation cell lies inside the cutoff radius. To correct for this, one defines the minimum image vector $R^*_{ij}$. Its magnitude is

$$R^*_{x_k,ij} = R_{x_k,ij} - L_k \cdot \text{INT}(\frac{R_{x_k,ij}}{L_k}),$$

$$k = 1, 2, 3, \quad (2.82)$$

where $\text{INT} : \mathbb{R} \rightarrow \mathbb{N}_0$ is a function returning the nearest integer of its argument [71]. For example, $\text{INT}(-1.6) = -2$, and $\text{INT}(1.2) = 1$. Now atom $j$ is included in the force calculation only if $R^*_{ij} < R_c$, and $R^*_{ij}$ is used as the separation distance, instead of $R_{ij}$.

![Diagram](image)

Figure 2.13: Neighbor list and potential cutoff radii.

The neighbor list. To speed up the force calculation, which often constitutes the most time consuming part of a MD simulation, a neighbor list is used. For each particle $i$, the neighbor list contains
all the particles that are at a distance of $R_{\text{nl}}$ or less from particle $i$. These particles may be called the neighbors of particle $i$. The neighbor list radius should be larger than the potential cutoff radius, $R_{\text{nl}} > R_c$. The neighbor list needs to be updated as soon as two particles have entered or left the cutoff region, which is the spherical shell with inner radius $R_c$ and outer radius $R_{\text{nl}}$, see Fig. (2.13).

**Time step selection and solution of equations of motion.** The motion of the particles in the simulation is determined by the ion-ion and ion-electron interactions. The former is governed by the interatomic potential, and the latter by the electronic stopping.

Before solving the equations of motion numerically, the time step size must be selected. The size of the time step is usually determined such that no atom travels farther than $a_0/20$, where $a_0$ is the lattice parameter, during a time step.

As mentioned earlier, the equations of motion of the ions in the solid may be written

$$m \frac{d^2 R}{dt^2} = F + \eta(t) - \beta \frac{dR}{dt}, \quad (2.83)$$

where $F$ represents the interatomic force, $\eta(t)$ a contribution due to electron-phonon interaction, and $\beta$ the electronic stopping. For EAM potentials one may use the expression

$$\beta = A \log_{10} (\alpha \rho^{1/3} + b). \quad (2.84)$$

The electron-phonon interaction may be neglected if e.g. the electron mean free path is less than the linear dimension of the cascade.

The numerical solution of the equations of motion is often done in such a manner, that the positions and velocities are first “predicted” using the interatomic force, then “corrected” by calculating the force at the predicted positions. A robust, 2-order algorithm that has long been used is the velocity Verlet algorithm, which is based on the original Verlet algorithm [72]. The predictor stage is

$$r(t + \Delta t) = r(t) + v(t) \Delta t + \frac{1}{2} a(t) (\Delta t)^2, \quad (2.85)$$

$$v^p(t + \frac{1}{2} \Delta t) = v(t) + \frac{1}{2} a(t) \Delta t. \quad (2.86)$$

Now the acceleration $a(t + \Delta t)$ is calculated using $r(t + \Delta t)$, i.e. $a(t + \Delta t) = F(r(t + \Delta t))/m$. The corrector is

$$v^c(t + \Delta t) = v^p(t + \frac{1}{2} \Delta t) + \frac{1}{2} a(t + \Delta t) \Delta t$$

$$= v(t) + \frac{1}{2} [a(t) + a(t + \Delta t)] \Delta t. \quad (2.87)$$

Hence the velocity Verlet algorithm is

$$r(t + \Delta t) = r(t) + v(t) \Delta t + \frac{1}{2} a(t) (\Delta t)^2, \quad (2.88)$$

$$v(t + \Delta t) = v(t) + \frac{1}{2} \left[ a(t) + \frac{1}{2} a(t) \Delta t \right] \Delta t. \quad (2.89)$$

Another popular method is the six-value (fifth order) Gear algorithm. Let

$$r_i(t) = \frac{(\Delta t)^i}{i!} \frac{d^i r(t)}{dt^i}. \quad (2.90)$$
A simple way to maintain constant temperature is to use Berendsen’s temperature scaling method [73]. If with the constant

temperature order to keep the pressure and temperature constant.

In the microcanonical, or constant-canonical or grand canonical ensemble, or variants of these.

Scaling of physical quantities

Simulation of the isothermal-isobaric, or constant-ensemble, has fixed values for the particle number, volume and temperature \( T \). When using Newton’s equations of motion measures must be taken to ensure constancy of temperature.

Simulation of the isothermal-isobaric, or constant-\( NVT \) ensemble, where the particle number, as well as the pressure \( P \) and the temperature have constant values, requires measures to be taken in order to keep the pressure and temperature constant.

When using the grand canonical, or constant-\( \mu VT \) ensemble, with fixed values for the chemical potential \( \mu \), volume and temperature, the particle number should vary in a reasonable manner.

A simple way to maintain constant temperature is to use Berendsen’s temperature scaling method [73]. If \( T_0 \) is the desired temperature, \( \Delta t \) the time step, \( \tau_T \) the time constant of the scaling (often \( \tau_T > 100\Delta t \)) and \( T \) the actual instantaneous temperature, then all velocities \( \mathbf{v} \) should be multiplied with the constant

\[
\lambda = \sqrt{1 + \frac{\Delta t T_0 - T}{\tau_T}}
\]  

(2.93)

after the solution of the equations of motion.

If on the other hand the pressure is to be constant, it can be achieved in a simple manner by Berendsen’s pressure scaling [73]. If \( P_0 \) is the desired pressure, \( \Delta t \) the time step, \( \tau_P \) the time constant of the scaling (often \( \tau_P > 100\Delta t \)), \( B \) the bulk modulus (1/\( B \) is the isothermal compressibility) and \( P \) the actual instantaneous pressure, then all positions \( \mathbf{r} \) and all three simulation cell side lengths (in \( x \), \( y \) and \( z \) directions) should be multiplied with the constant

\[
\mu = \left(1 - \frac{\Delta t P_0 - P}{\tau_P B} \right)^{1/3}.
\]  

(2.94)

Also, the volume should be multiplied by \( \mu^3 \).
**Calculation of physical quantities.** After scaling of physical quantities has been carried out, actual values for the most interesting quantities may be determined. A value for the quantity $A$ may be calculated from the instantaneous value $A$ according to

$$
A \equiv \langle A \rangle \equiv \langle A \rangle_{\text{ens}} = \frac{1}{\tau_{\text{obs}}} \sum_{\tau=1}^{\tau_{\text{obs}}} A(\Gamma(\tau)),
$$

(2.95)

Here $\tau_{\text{obs}}$ is a number of small time steps. $\Gamma(\tau)$ is the point in the $6N$-dimensional phase space that the system currently occupies.

Often the above time average is replaced by the spatial average

$$
A = \frac{1}{N} \sum_{i=1}^{N} A(i).
$$

(2.96)

The instantaneous temperature $\mathcal{T}$ of the system may be calculated from the expression

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

(2.97)

where $\mathcal{K}$ is the instantaneous kinetic energy of the system. When calculated in this way, $\mathcal{T}$ is called the *kinetic temperature* of the system. The instantaneous pressure, on the other hand, may be written as

$$
\mathcal{P} = \rho k_B \mathcal{T} + \mathcal{W}/V = \rho k_B \mathcal{T} + \frac{1}{3V} \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i,
$$

(2.98)

where $\rho$ is the density of the system, $\mathcal{W}$ the so called *internal virial*, $\mathbf{F}_i$ the force acting on particle $i$, and $N$ the number of particles in the system.

**Iteration or/and ending.** When the instantaneous physical quantities have been calculated the time is advanced with one step. If the last time point has been reached, final values for physical quantities are calculated and the simulation ended. Else control returns to the part of the MD algorithm that calculates the neighbor list. The list is updated if necessary. After this the equations of motions are solved for the next time step, and so on.
Chapter 3

Craters

3.1 Empirical observations

Craters have been observed in TEM studies, carried out by e.g. Merkle and Jäger [40]. These authors bombarded Au foils with thicknesses 60-80 nm with Bi and Bi\textsubscript{2} with energies between 10 and 500 keV. Craters were observed at energies larger than about 50 keV. Other TEM observations of defect structures produced by energetic cascades have shown the existence of small surface craters associated with individual displacement cascades in Au.

Merkle and Jäger found that craters are formed in individual displacement cascades. However, only about 1\% of the cascades showed visible craters. The size of the crater was considerably smaller than the cascade size. Assuming a hemispherical crater it was noted that about 2000 atoms must have been excavated from a crater 5 nm in diameter. This number is more than an order of magnitude greater than the average sputtering yield from a cascade. The authors also observed a linear dependence between the number of craters observed per incident atom and the energy per atom in the case of single atom bombardment. For Bi\textsubscript{2} bombardment this number showed a non-linear dependence on the energy per atom.

In a study of 200 keV Xe ions incident on thin Au foils Birtcher and Donnelly [74] observed holes in about 0.5\% of the bombardments. These holes had diameters between 5 and 10 nm. The authors note that no holes were created in regions where the thickness was about 50 nm and larger, a fact from which one may deduce that the average cascade had a vertical dimension of at most 50 nm. Craters were also observed, but they were more difficult to image than the holes. It was found that the excavated atoms had moved to the surface. Occasionally small particles appeared far from any hole or crater. Holes were annealed by the quench phase of their own cascade, but additional ion impacts were capable of producing further annealing by means of plastic flow. Changes in hole shape were generally due to cascade events that did not produce new holes but generated plastic flow near existing ones. In the opinion of Birtcher and Donnelly, Merkle and Jäger underestimated the number of crater creation events that occurred, while misidentifying the origin of the craters, since they assumed the craters to be the result of sputtering, not the flow of atoms.

In another work Donnelly and Birtcher [75], investigating Xe on Au at 50-400 keV, once again observed crater creation and annihilation. It was found that 2 \(-\) 5\% of the ions produced a crater. Occasionally a "lid" was associated with the production of a crater. These "lids" were attributed to the high localized pressure in the thermal spike, which generally may cause ejection of a fragment of solid material. In this study the ejection allowed molten gold to flow out onto the surface, from where it partially filled, and thereby annihilated, existing craters. The atoms were usually unable to overcome the surface binding and become sputtered.


3.2 MD simulations of craters

In MD simulations of 0.4 – 100 keV Xe impacts on Au Bringa et al. [76] followed the temporal and spatial development of craters. The authors observed craters and associated rims, isolated adatom islands, sputtered atoms and coherent displacements. The formation of the crater and its rim was due to liquid flow of atoms, which was created in the thermal spike and forced onto the surface due to the high pressure. The authors note that the lifetime of the spike was equally important as the energy density associated with crater production. Long-lived spikes will allow for ejection even at relatively low energy densities. The authors also found that the number of excavated atoms \( N_{cr} \) scaled with the cohesive energy as \( N_{cr} \propto 1/U_{co}^2 \).

MD simulations of Au clusters incident on Au at 16 keV have been carried out by Colla et al. [77]. The authors used clusters with 1, 2, 4, 8 and 12 atoms and noted that the larger the cluster, the lesser the fluctuations in the resulting damage. The damage is described in terms of e.g. microexplosions rather than surface evaporation. Craters with pronounced rims were formed, whose relaxation time were about 20 ps. Most of the sputtered chunks of matter emitted after 5 ps originated in the rims. The authors discern three separate stages in the development of the crater. Phase one lasted up to about 1 ps. During this time the energy in the core lead to a spherically symmetric outflow of atoms from the cascade center. This flow was bounded from outside by a shock front. During phase two, between 1 and 2 ps after impact, the spherical symmetry was broken by the surface. Particles and clusters were ejected, and a crater formed. During the last phase, flow processes took place on the thin melt that covered the crater and its rims. The flow direction was up and out, continuously extending the crater. The rims received molten matter, which contributed to the sputtering at later times.

3.3 Models

In MD simulations of Cu clusters containing 13 and 43 atoms incident on Cu at energies between 5 and 20 keV, Aderjan and Urbassek [78] found a qualitative analogy between microscopic ion and macroscopic projectile impacts. For macroscopic impacts like meteorites, one has that the number of excavated atoms, \( N_{cr} \), satisfies

\[
N_{cr} \propto \frac{E}{E_{coh}}, \quad (3.1)
\]

where \( E \) is the energy of the projectile and \( E_{coh} \) a corresponding cohesive energy of the target. On the other hand, experiments with micrometer-sized metal projectiles incident on metals (ref. in [78]) show that

\[
N_{cr} = 2300 \frac{E}{\text{keV}}, \quad (3.2)
\]

In their study, Aderjan and Urbassek obtained

\[
N_{cr} = 131 \frac{E}{\text{keV}} - 656 \quad (3.3)
\]

for impact energies larger than 5 keV.

Considerations based on dimensional analysis suggest that in the case of identical material in projectile and target, it holds that

\[
N_{cr} \propto f\left(\frac{E}{E_{coh}}, N\right), \quad (3.4)
\]
<table>
<thead>
<tr>
<th>Time (ps)</th>
<th>Reaction Image</th>
<th>Simulation Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image 1" /></td>
<td><img src="image2.png" alt="Image 2" /></td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Image 3" /></td>
<td><img src="image4.png" alt="Image 4" /></td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Image 5" /></td>
<td><img src="image6.png" alt="Image 6" /></td>
</tr>
<tr>
<td>10</td>
<td><img src="image7.png" alt="Image 7" /></td>
<td><img src="image8.png" alt="Image 8" /></td>
</tr>
<tr>
<td>20</td>
<td><img src="image9.png" alt="Image 9" /></td>
<td><img src="image10.png" alt="Image 10" /></td>
</tr>
</tbody>
</table>

Figure 3.1: The evolution of the crater between the times 1 and 20 ps since projectile impact. Data taken from a 20 keV Pt$_{13}$ projectile impact on Pt included in the present work (run 2.01).

where $N$ is the number of atoms in the projectile.
Aderjan and Urbassek observed that around small bombardment energies the craters had a tendency to be shallow, while at higher energies they became roughly hemispherical. Also, it was discovered that the crater walls were faceted. The observed craters were relatively small, a fact that was attributed to the mono-crystalline target, in which e.g. plastic flow is more difficult than in polycrystalline targets. Using modified interatomic potentials differing in cohesive energy, Aderjan and Urbassek found a dependence

\[ N_{cr} \propto \frac{E}{E_{coh}^2}, \quad (3.5) \]

which is in contradiction with Eq. (3.4), the established functional dependence for macroscopic craters. The authors have no explanation for this deviation.

### 3.4 Present work

#### 3.4.1 Overview

In the current work it is proposed that

\[ N_{cr} \propto \frac{E_1}{T_{mel} E_{coh}}, \quad (3.6) \]

where \( T_{mel} \) is the melting temperature, as an improvement of \( N_{cr} \propto E/E_{coh}^2 \), a dependence that has already been established, as mentioned above.

In order to investigate the current proposition, Eq. (3.6), one needs artificial potentials differing only in the melting temperature. It has been shown that it is possible to theoretically modify the melting point of a material without any effect on the cohesive energy or other equilibrium properties [79]. In that work, two different potential models, one for Pd and one for Pt, were constructed to test the effect of the melting point on ion beam mixing. The same potentials will be used here to compare cratering in the same material under identical conditions for each impact energy, so that the only difference is the melting point.

#### 3.4.2 Simulations

Two targets were used, Pd and Pt. Both targets contained 48 unit cells in all directions, two of them periodic, the \( z \) one being non-periodic. This yielded two free surfaces, one facing the positive \( z \) direction and the other the negative direction. The simulated bulk, created using the 0 K lattice parameter, was given an initial temperature of 0 K, which also was the value of the desired temperature. The temperature was scaled towards 0 K in three closest atom layers at all borders except the surface facing the positive \( z \) direction, using Berendsen’s method [73]. This scaling models the heat conduction into the rest of the solid, which takes place in every real solid.

The projectile was placed above the bulk in the positive \( z \) direction, outside the potential cutoff of about 5.5 Ångströms. A cluster of the same matter as the bulk, and containing 13 atoms, was selected as the projectile. A cluster was used instead of a single ion, since previous work has shown that the fluctuations in crater size are reduced with increasing cluster size [77]. Each cluster had icosahedral symmetry, having one center atom and 12 nearest neighbors. This type of cluster is easily created, since in the fcc lattice each atom has 12 nearest neighbors.

The cluster was rotated with a random polar angle, while the azimuthal angle was held at 25 degrees. The projectile was translated a random distance \( a_x \) and \( a_y \) in the \( x \) and \( y \) directions, respectively. Here \( a_x, a_y \in [-a_0/2, a_0/2] \), with \( a_0 \) being the lattice parameter. These rotation and translation operations
introduced an element of randomness into each simulation, as required to generate statistics. In order to start the cluster moving against the bulk surface, a kinetic energy of $E_0/13$ was given to each of the atoms in the cluster.

A potential based on the embedded atom method (EAM) by Foiles [80] was used to describe equilibrium properties. The modified potential version was designed to keep the equilibrium properties unchanged, but give a better description of the melting point than the original potential [79]. This was done by modifying the original potential with a function $f(r) = -a(r - r_i) + 1$ when $r < r_i$. When $r \geq r_i$, $f(r) = 1$. The value of $r_i$ was chosen to be less than the equilibrium nearest-neighbor distance to ensure that the equilibrium properties were unaffected. The parameters $r_i$ and $a$ were chosen to obtain a good reproduction of both the melting point and threshold displacement energy.

At close separations all the EAM potentials were smoothly joined to the universal ZBL interatomic repulsive potential [68] to realistically describe strong collisions. The original potentials, denoted by Pt-A and Pd-A, had melting temperatures of $1530 \pm 20$ K and $1415 \pm 5$ K, respectively. The modified potentials, denoted by Pt-B and Pd-B, had melting temperatures of $2130 \pm 10$ K and $1910 \pm 20$ K, respectively.

The electronic stopping was adapted from the ZBL model [68] and was applied to all atoms having a total energy exceeding 5 eV.

The temporal evolution, including the cluster hitting the bulk surface, the resulting cascade ending in a thermal spike, and finally the cooling down of the system, was followed for 50 ps, in all the cases of cluster energy, 2, 20 and 40 keV. This time was enough to cool down the system and obtain a stable crater, as verified by visual inspection.

As a rule, 14 simulations were carried out for each kind of cluster impinging on the surface of the bulk. Half of these used the modified potential. For example, in the case of 20 keV Pt$_{13}$ clusters impinging on Pt and using the potential denoted by Pt-A, 7 simulations were carried out. However, in the case of self-bombardment of Pt by 2 keV clusters, results were gathered from a total of $N_{\text{sim}} = 30 + 30$ simulations in order to obtain enough statistics.

### 3.4.3 Results

<table>
<thead>
<tr>
<th>Model</th>
<th>Energy (keV)</th>
<th>$N_{\text{cr}}$</th>
<th>$R_{\text{cr}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-A</td>
<td>2</td>
<td>111 ± 17</td>
<td>9.8 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1665 ± 61</td>
<td>24.9 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>3398 ± 265</td>
<td>32.9 ± 0.7</td>
</tr>
<tr>
<td>Pd-A</td>
<td>20</td>
<td>1971 ± 80</td>
<td>25.9 ± 0.5</td>
</tr>
<tr>
<td>Pt-B</td>
<td>2</td>
<td>67 ± 12</td>
<td>7.8 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1112 ± 68</td>
<td>21.3 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2372 ± 84</td>
<td>27.9 ± 0.7</td>
</tr>
<tr>
<td>Pd-B</td>
<td>20</td>
<td>1382 ± 89</td>
<td>23.4 ± 3.4</td>
</tr>
</tbody>
</table>

Crater sizes in the form of number of excavated atoms ($i.e.$ the size of the crater) and crater radii are presented in Tab. 3.1. $N_{\text{cr}}$ is simply the sum of the number of sputtered atoms and adatoms, $N_{\text{cr}} = N_{\text{sp}} + N_{\text{ad}}$. This number practically equals the number of excavated atoms, since there are almost no vacancies outside the crater itself, which may be viewed as a large multiple vacancy.

The crater radius $R_{\text{cr}}$ is derived from the expression $N_{\text{su}}/\sigma = A = \pi R_{\text{cr}}^2$, where $\sigma$ is the surface number density of atoms of the topmost bulk atom layer, and $N_{\text{su}}$ is the number of missing atoms.
in this layer, due to the presence of the crater. The expression is inspired by the roughly circular appearance of the crater wells in the cascade simulations initiated by 20 and 40 keV clusters.

Figure 3.2: A typical crater resulting from the impact of a 2 keV Pt cluster on Pt.

Figure 3.3: A slice through a typical crater resulting from 40 keV Pt cluster on Pt.

In Fig. 3.2 a crater resulting from bombardment with a 2 keV Pt\textsubscript{13} cluster on Pt is shown. The image is based on the final positions from a simulation having a crater size $N_{cr}$ and $R_{cr}$ very close to the average values. Fig. 3.3 illustrates a slice through a correspondingly average crater formed as the result of 40 keV Pt clusters on Pt. Note the faceting on the crater walls.

The crater size $N_{cr}$ for the simulated cases is illustrated in Fig. 3.4 (a). Since for each material the cohesive energy is exactly the same for the two models used, the crater size does not depend on the cohesive energy alone. In Fig. 3.4 (b) the same data is plotted, but now the data for models Pt-B and Pd-B is scaled with the ratio $T_{melt,B}/T_{melt,A}$. Now the crater sizes agree within the uncertainties. Bearing in mind that this result still has to be consistent with the previously observed dependence (Eq. 3.5) for the simpler modification of a potential (i.e. $T_{melt} \propto E_{coh}$), the result shows that the best way to describe the crater size dependence on material properties is

$$N_{cr} \propto \frac{1}{E_{coh}T_{melt}}. \quad (3.7)$$
Figure 3.4: (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, Pt-B and Pd-B the models where the melting point has been modified to be close to the experimental value. (b) is as (a), but here the results for potentials Pt-B and Pd-B are multiplied by the ratio $T_{m, B}/T_{m, A}$ where $T_{m, x}$ is the melting point for model $x$, with $x$ equal to A or B.

The scaling behavior observed here can be understood by recalling that one factor of $1/E_{coh}$ is observed for macroscopic cratering, where melting usually plays no role. The presence of another factor $T_{melt}$ (rather than $E_{coh}$) in the denominator for microscopic cratering indicates that the difference be-
tween the two regimes (macroscopic and microscopic) is due to liquid flow, i.e. the existence of the thermal spike.

In the modification of the potential all other quantities which could be expected to be relevant (e.g. elastic and heat conduction properties) are unchanged from the original EAM potential. Hence the crucial additional parameter is better described as the melting point rather than any of the other quantities.

It should be noted that at 2 keV the crater size still scales with the inverse of the melting point within the uncertainties, even though no long-lived thermal spike can form at this low energy.

In conclusion, the size of craters produced by energetic ion and cluster ion impact scales with the inverse of the product of the melting temperature and cohesive energy, when other material parameters are the same. This shows that the difference between the crater production mechanisms for macroscopic and microscopic crater impacts is due to liquid flow in the latter case.
Chapter 4

Cluster sputtering

4.1 Mechanisms and experiments

A brief review of the history of cluster sputtering shows that this phenomenon has been observed since the late 1960s [46]. As a matter of fact, the very first report on cluster emission during ion sputtering was made by Honig in 1958. Sputtering of charged clusters has been investigated by e.g. Staudenmaier, Wittmaack, and Hofer. On the other hand, studies of neutral clusters have been carried out by e.g. Gerhard and Oechsner.

According to Bitensky and Parilis [46] clusters are formed with the highest probability under bombardment by heavy ions. Under such conditions there is a sharp increase in the sputtering yield and a non-linear dependence on the deposited energy. The same effect results from bombardment with polyatomic projectiles. Some authors attribute the non-linearity to overlapping cascades, which may produce shock waves if there also is a region of high energy density deposition. The arrival of the shock wave at the surface causes tension. A tension that exceeds some critical value may produce cracking of the surface and separation of macroscopic pieces. The notion of a shock wave has been used to explain crater formation and sputtering.

Bitensky and Parilis use the following assumptions for the shock wave mechanism of cluster sputtering. First, energetic recoils near the surface create a dense cascade, which produces a high energy density elastic collision spike. Second, a shock wave forms, reaching up to the surface. At the front of the shock wave there is highly correlated motion. As a result, a group of atoms can gain large kinetic energy without breaking their bonds. Third, under molecular bombardment an elastic collision spike forms as the result of overlapping collision cascades initiated by the atoms in the molecule.

The calculation performed by Bitensky and Parilis are based on hydrodynamical considerations, since energy dissipation from a spike is more effective through hydrodynamical processes than thermodynamical ones. A cluster yield of the form \( Y(n) \propto n^{-2} \), where \( n \) is the cluster size, is obtained.

Urbassek has proposed a model for cluster sputtering near the critical point and on the coexistence curve [81]. A near-surface part of the elastic collision cascade is assumed to be in thermodynamical equilibrium, which means that clusters are continuously being created and destroyed. Upon expansion into the vacuum this region may undergo a liquid-gas transition. If this occurs near the critical point, the fluctuations are high enough to produce large clusters. According to Urbassek the critical point of a gas is described by a position in the temperature-pressure diagram where the interparticle binding is balanced by the kinetic energy.

Urbassek derives the formula

\[
Y(n) = Y_0 n^{-\tau} \exp \left[ \frac{G_2 - G_1}{k_B T} n - \frac{4\pi r^2 \sigma}{k_B T} n^{2/3} \right]
\]  

(4.1)
where $G_g$ is the Gibbs free energy of the gas, $G_1$ the free energy per particle in the liquid phase, $r$ the average atomic radius in a cluster, $\sigma$ the surface tension of a $n$-cluster, and $\tau \in (2, 2.5]$ is Fisher’s critical exponent (ref. in [81]). Two special cases are noted. First, at the critical point,

$$Y_{\text{crit}}(n) = Y_0 n^{-\tau}. \quad (4.2)$$

Second, on the coexistence curve,

$$Y_{\text{coex}}(n) = Y_0 n^{-\tau} \exp \left[ -\frac{4\pi r^2 \sigma}{k_B T} n^{2/3} \right] \approx Y_0' n^{-\tau'}, \quad \tau' > \tau. \quad (4.3)$$

The model is not sufficient to describe measured mass distributions since sputtered clusters are metastable and evaporate after formation, on their way to the detector. However, these and other anomalies are absent at times much less than 1 $\mu$s.

According to Wucher and Garrison [82], there are several models proposed to describe formation of sputtered clusters, either as ejection of clusters or agglomeration after ejection of individually sputtered atoms, i.e. along the lines of Urbassek’s model [81]. However, these mechanisms require the correlated ejection of atoms, which is difficult to describe by statistical means.

In an experimental study of 5 keV Ar$^+$ incident on Ag, Wucher et al. investigate sputtered clusters using laser photoionization [83]. In general, the clusters have to be ionized so that mass or energy analysis can be performed on them. The authors acknowledges the possibility of fragmentation due to multiphoton absorption processes and consequent corruption of the results.

Wucher [84] notes that the interpretation of experimental work performed on charged clusters is difficult due to the uncertainty of the ionization probability, which may depend strongly on cluster size. The ionization probability is defined as the number of clusters of a given size that leave the surface in a charged state, divided by the total number of clusters of the given size.

![Figure 4.1: Dependence of $\delta$ on total sputtering yield. The points labeled "n < 40" denote values obtained from experiments where the yield for clusters equal to or smaller than 40 atoms was measured. Correspondingly for "n > 500". The graph is obtained from [85].](image)

Figure 4.1: Dependence of $\delta$ on total sputtering yield. The points labeled "n < 40" denote values obtained from experiments where the yield for clusters equal to or smaller than 40 atoms was measured. Correspondingly for "n > 500". The graph is obtained from [85].
A review of several studies (refs. in [86]) show that the dependence \( Y(n) \propto n^{-\delta} \) is common. The compilation of empirical values for \( \delta \) as a function of the total yield is presented in Fig. 4.1.

In an experimental study conducted with 15 keV Xe ions incident on Ag, sputtered clusters with up to 60 atoms were detected by Staudt et al. [86]. Ionization of sputtered neutral clusters was achieved by means of single photon ionization, with a relatively low fragmentation rate. Staudt et al. found that a large total sputtering yield gives a low value of \( \delta \), i.e. a higher contribution of larger clusters. In the study a value of \( \delta = 3.7 \) was obtained. However, when post-acceleration was used in order to improve on the detection of large clusters, \( \delta \) was lowered to 3.3. It was not possible to achieve a saturation of \( \delta \) due to technical reasons, hence the authors do not rule out the possibility that \( \delta \) may still be lowered.

Clusters with 500 atoms and more has been detected in experiments with Ne, Ar, Kr and Au ions with energies between 400 and 500 keV incident on Au by Rehn et al. [85]. The yield dependence on cluster size was determined to be \( Y(n) \propto n^{-2} \), for \( n \geq 500 \). In this study the shock wave mechanism for sputtering as presented by Bitensky and Parilis [46] was adopted. The assumption that the heated volume pass through the liquid-gas coexistence region after reaching thermal equilibrium is not expected to remain valid over the wide range of ion masses used, hence the authors Rehn et al. did not consider the cluster sputtering model by Urbassek [81].

Rehn et al. found that sputtering of large clusters implies a large total yield. This in combination with the results in Fig. 4.1 is compelling evidence for the shock wave model. As the sputtering becomes more energetic, a fact indicated by the increased sputter yield, more of the subsurface displacement cascades generate shock waves strong enough to cause surface fracture. Hence the yield would approach the \( Y(n) \propto n^{-2} \) dependence, as proposed by Bitensky and Parilis [46].

### 4.2 Simulations of cluster sputtering

Wucher et al. [82] have performed MD simulations of Ar ions incident on Ag surfaces at energies between 250 eV and 5 keV. An EAM potential by Foiles [80] for the target atoms and a pair-potential of Moliere type for Ar-Ag interactions were used. The EAM potential was modified to include a repulsive potential at short separations. The authors emphasize that the EAM potential used is considered a model potential describing an arbitrary fcc metal rather than as an accurate description for Ag.

The yield of stable clusters with up to four atoms was determined. A cluster was considered stable if its total energy was less than the dissociation energy of the cluster. Candidates for the dissociation energy of an \( n \)-cluster were calculated as

\[
E'_d = E_a(n - m) + E_a(m) - E_a(n),
\]

where an \( n \)-cluster splits into an \( m \)- and an \( n - m \)-cluster. \( E_a \) is the atomization energy, i.e. the energy required to break up the cluster into atoms located infinitely separated from each other. The EAM potential was used to calculate the atomization energies using several possible stable configurations of the various clusters. The smallest of the \( E'_d \) values was chosen as the dissociation energy.

Wucher et al. found a cluster sputter yield of \( Y(1) = 6.085 \), \( Y(2) = 0.973 \), \( Y(3) = 0.028 \) and \( Y(4) = 0.002 \). A fit to the function \( Y(n) = Y_1 n^{-\delta} \) gives \( Y_1 = 6 \pm 2 \) and \( \delta = 3 \pm 2 \). The authors note that virtually all clusters with \( n \geq 5 \) were unstable. The average decomposition time was about 10 ps, practically independent of cluster size. During this time the particles traveled about 100 Å away from the surface, a distance too short for them to make it to the detector.

In a corresponding study Wucher et al. [84] observed Ar ions impinging on Ag surfaces at energies between 100 eV and 5 keV, using MD simulations and MC calculations. An EAM potential by Foiles et al. [80] and with modifications for use in sputtering calculations was used. It was found that the potential over-bound small gas phase Ag clusters by 60% (dimers and tetramers) to 90% (trimers).
The authors point out that the potential was considered a general one for metals, not an exact one for Ag (see corresponding note above).

The difference to the previous study [82] is the calculation of atomization energies for the various clusters. For clusters with 8 atoms and more, the approximation $E_a(n) = U_s(1 - cn^{-\kappa})$ was used, where $c$ and $\kappa$ were fitted to $E_a(n)$ values for $n < 8$. Here $U_s$ is the sublimation energy, directly obtainable from the EAM potential.

The cluster yield was found to be $Y(n) \propto n^{-\delta}, \delta = 3.9$. This value is smaller than the experimentally reported $\delta = 6.5$ [83]. This difference the authors contribute to the fact the EAM potential used over-bound the clusters.

### 4.3 Present work

#### 4.3.1 Overview

A total of 40 cases with a 20 keV Xe ion incident on a Au surface (100) in the $z$ direction were simulated. The simulations consisted of three types of targets, and two separate stages. The targets were a bulk specimen, a thick foil and a thin foil. Simulation of the cascade development was followed by a second stage where the motion of the ejected material was investigated.

#### 4.3.2 Simulation of the cascade

The very first atom configuration for each type of sample (bulk, thick and thin foil) was created using the 0 K lattice constant and assuming the crystal expands linearly in all dimensions when the temperature is raised to 300 K, the target temperature in the cascade simulations. This first configuration was simulated at this temperature in order to obtain the natural lattice parameter, which was indeed found to be close to the calculated one. The lattice parameter hereby obtained was used to create all needed atom configurations, i.e. the bulk, the thick and the thin foils. All these configurations were relaxed at 300 K before commencing the cascade, in order to establish a realistic atom configuration, where all particles are slightly displaced from their perfect equilibrium positions and have thermal velocities corresponding to the ambient temperature.

The bulk specimen contained 48 unit cells with side length $\approx 4.065$ Å in all directions, making a total of 442368 atoms due to the fcc crystal structure. All surfaces were non-periodic. All atoms within 5 Å of the free surfaces were fixed, i.e. their velocity held at 0 at all times. A surface is here defined as "free" if it is facing the impinging projectile or atoms are otherways allowed to enter and/or exit the specimen through it. The bulk had only one free surface.

The temperature of all atoms in three layers inside this region of fixed particles were scaled using Berendsen’s method [73], such that the temperature was maintained at roughly 300 K at the surface facing the inner parts of the bulk and 0 K at the surface facing the fixed atoms. No pressure scaling was carried out. Also, a maximum kinetic energy of 20 eV was allowed for atoms entering the region where the temperature was scaled.

For the thick foil the box length in the $z$ direction was changed to 28, all other parameters were set analogously to the case of the bulk. On the other hand, when simulating cascades in the thin foil the box length in the $x$ and $y$ directions was changed to 60 and to 16 in the $z$ direction. The latter setting gave rise to forward sputtering besides the back sputtering obtained for the bulk and thick foil specimens. Note that the foils had two free surfaces, the lower and upper one in $z$ direction, not just one as for the bulk.

An EAM potential by Foiles [80] was used at atomic separations corresponding to thermal equilibrium, and larger. The repulsive ZBL universal potential was applied to relatively close separations [68]. The potentials were fitted together at intermediate energies.
The electronic stopping was adapted from the ZBL model [68] and was applied to all atoms having a total energy exceeding 5 eV.

The Xe recoil was started from a vertical position about 5.55 Å outside the target. This distance equals roughly the potential cutoff of 5.5 Ångströms. The recoil was directed towards the surface at polar and azimuthal angles of 25 degrees, and with a speed corresponding to a kinetic energy of 20 keV. After 20 ps since impact the cascade was essentially over, but the material was still simulated to 50 ps in order to allow for any late sputtering.

### 4.3.3 Simulation of the sputtered material

When any simulation of the cascade was ended at 50 ps, the system consisted of a damaged specimen, with a crater facing the direction of the impinging ion in the bulk and thick foil cases, but facing the opposite surface in the thin foil case. Adatoms were scattered all over the cratered surface and a number of atoms were found outside the free surfaces. The transmission or forward sputtering simulations did not produce as much damage on the surface opposite the one facing the incoming projectile.

All atoms not connected to the appropriate free surface were extracted. In the case of the bulk and the thick foil, this only concerned atoms above the surface facing the incident particle — no forward sputtering was detected for the thick foil. Only ejected atoms facing the surface not hit by the impinging projectile were extracted for the thin foil.

After this, the sputtered material was simulated until the distribution of clusters no longer changed. The size distribution as a function of time has several plateaus where no change in the size of clusters occur, followed by short-lived intermediate states. Counting the number of time steps the size distribution remains unchanged one obtains a sequence of integers $n_1, n_2, \ldots$ denoting the number of subsequent identical cluster distributions. This sequence generally has small integers in the beginning and large ones towards the end, such that the last one is roughly 10 times the next to last one. Then the final cluster distribution may be labeled “stable”. This corresponds to the fact that the cluster distribution stabilizes as a function of time. Since the cloud of sputtered atoms grows outwards the probability for collisions where clusters could fuse or fragment each other diminishes, also any internal rearrangement within clusters leading to lower potential energy becomes less likely as the cluster atoms lose energy via stopping, as they interact within the clusters.

Since the damaged, post-cascade specimen (bulk, thick and thin foil) is missing from the simulation cell during the evolution of the sputtered matter, some of the stable clusters may travel into or beyond the (absent) post-cascade specimen. These clusters were excluded from the calculation of the final yield.

### 4.3.4 Results

**Backsputtering.** The data from the backsputter simulations is displayed in Tab. 4.1. $N_{\text{sprut}}$ is the number of sputtered atoms, $T_{\text{max}}$ is for how long time the sputtered clusters were simulated, and $T_{\text{last}}$ is the minimum lifetime of the stable clusters.

The total backspattering yield (from bulk and thick foil) is illustrated in Fig. 4.2. The yield for the 10 smallest clusters is shown in Fig. 4.3, whereas Fig. 4.4 display the distribution of clusters of
Table 4.1: Results from the backspattering of the bulk specimen (run number prefixed by 'b-') and the thick foil (run number prefixed by 'f-'). Runs excluded due to problems with the data are marked with an *.

<table>
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<th>Run</th>
<th>(N_{\text{spat}})</th>
<th>(T_{\text{max}}) (ps)</th>
<th>(T_{\text{last}}) (ps)</th>
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<td>b-1</td>
<td>47</td>
<td>500</td>
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</tr>
<tr>
<td>b-2</td>
<td>63</td>
<td>1000</td>
<td>714.5</td>
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<tr>
<td>b-3</td>
<td>121</td>
<td>1500</td>
<td>610</td>
</tr>
<tr>
<td>b-4</td>
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<td>500</td>
<td>500</td>
</tr>
<tr>
<td>b-5</td>
<td>260</td>
<td>1500</td>
<td>500</td>
</tr>
<tr>
<td>b-6*</td>
<td>401</td>
<td>5000</td>
<td>340</td>
</tr>
<tr>
<td>b-7</td>
<td>102</td>
<td>1000</td>
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<tr>
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</tr>
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<td>500</td>
<td>500</td>
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<td>3000</td>
<td>1150</td>
</tr>
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<td>500</td>
</tr>
<tr>
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<td>500</td>
</tr>
<tr>
<td>f-6</td>
<td>61</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
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<td>36</td>
<td>500</td>
<td>500</td>
</tr>
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</tr>
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<td>1000</td>
</tr>
<tr>
<td>f-10</td>
<td>224</td>
<td>2500</td>
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</table>

intermediate sizes. The large yield for monomers, dimers and trimers is largely due to sputtering from the linear (ballistic) cascade. It is reasonable that only very small clusters are produced at this early stage, when the displaced atoms are energetic and experience mostly binary collisions. Most of the larger clusters are then produced during the thermal spike. However, since the clusters in general may fuse and fragment, the thermal spike sputtering will also produce small clusters in the end, while it is unlikely that the small clusters created during the ballistic phase of the cascade come together
and form large clusters. Hence the tail of the cluster yield (roughly clusters with four atoms or more) will be dominated by thermal spike clusters.

**Forward sputtering** The forward sputtering data is shown in Tab. 4.2 and the yield of forward sputtered clusters is illustrated in Fig. 4.5. Some simulations have been excluded, namely those
that did not produce any forward sputtered atoms. No analysis will be carried out on these forward sputtered clusters, since there is not enough of them to provide good statistics.

### 4.3.5 Analysis of results

The cluster yield due to the thermal spike is the one that is of interest in this work. By the argument above, the head of the cluster yield distribution will be excluded when the data is fitted. In order to obtain a good fit the data has to be smoothed. For a brief discussion on smoothing, see [87]. In short, smoothing means that a given data interval $[x_1, x_M]$ is replaced by one data point $(x', y')$, such that the area under the curve is conserved and the overall behavior of the data not altered.

Assume the data is given as $M$ quartuples $(x_k, y_k, dx_k, dy_k, b_k)$, where $dx_k$ and $dy_k$ are the error in $x_k$ and $y_k$, respectively. The bin width of $x_k$ is given as $b_k$. The bin width is calculated as $b_k = (x_{k+1} - x_k)/2 + (x_k - x_{k-1})/2 = (x_{k+1} - x_{k-1})/2$ when $1 < k < M$. At the interval end points, the approximations $b_1 = x_2 - x_1$ and $b_M = x_M - x_{M-1}$ may be made. For the point $(x', y')$ substituting the interval $[x_1, x_M]$, the following properties hold:
Cluster size (number of atoms)

Figure 4.5: Forward sputtering yield.

\[
x' = x_1 - \frac{b_1}{2} + \frac{1}{2} \left[ x_M + \frac{b_M}{2} - \left( x_1 - \frac{b_1}{2} \right) \right],
\]

\[
= \frac{x_1 - b_1}{2} + \frac{x_M}{2} + \frac{b_M}{4}
\]

\[
dx' = \frac{1}{2} \sqrt{(dx_1)^2 + (dx_M)^2},
\]

\[
y' = \frac{[b_1 y_1 + \ldots + b_M y_M]}{b'},
\]

\[
gy' = \sqrt{(b_1 dy_1)^2 + \ldots + (b_M dy_M)^2} / b',
\]

\[
b' = b_1 + \ldots + b_M,
\]

where \(dx'\) and \(dy'\) are the errors associated with the new data \(x'\) and \(y'\), and \(b'\) is the bin width at \(x'\).

The data, with the head of the distribution excluded, is shown in Fig. 4.4, for \(n \geq 4\). Monomers, trimers and tetramers were not considered at all when the backspatter data was smoothed, the reasons are given above. Also, three cases of head exclusion were considered: one for which clusters having \(n \geq 4\), \(n \geq 5\), and \(n \geq 6\) are included in the smoothing.

Each smoothing operation (division into intervals and smoothing the points inside them) was performed as follows. All points between \(n_1\) and \(n_2\), where \(n_2\) is the size of the largest cluster observed, were always divided into smoothing intervals. \(n_1\) was initially set to the the value of \(n_1\) corresponding to the first point of zero yield, \(n_1^{\text{initial}} = n_0 = 17\). For each subsequent smoothing operation \(n_1\) was lowered by one unit, until \(n_1^{\text{final}} = 4, 5\) or \(6\) was reached, depending on the case. In this manner a total of \(n_1^{\text{initial}} - n_1^{\text{final}} = 13, 12\) or \(11\) smoothed data sets were obtained.

The length of the smoothing intervals followed the simple formula \(L_{i+1} = 2L_i, L_1 = 2\), that is, the size of the interval was doubled each time a new interval was selected. A linear folding is not suitable, since the data is degraded more than linearly for increasing \(n\).
Plots of smoothed data and their fits can be found in Figs. 4.6-4.8. In all three cases one obtains the power law exponent $1.8 \pm 0.2$. Observe, that the fit is based on all smoothed data sets for each of the cases $n_i^\text{final} = 4, 5$ or 6. The plots, on the other hand, are obtained from the last smoothed data set, the one having the smallest number of smoothed data points.

These results clearly show, that the power law exponent in the experimental formula for cluster sputtering is close to 2. This verifies the trend observed in experiments where the total cluster sputter
yield has been relatively large, as in [85], making the thermal spike important for the production of the not so small clusters. The present result also agrees with the model proposed by Bitensky and Parilis [46], where the thermal spike plays a crucial role in the emission of matter from the irradiated bulk. In combination with the fact that the cluster data investigated here is mainly due to thermal spike effects the obtained value for the exponent is highly realistic.
Chapter 5

Summary

In this work cratering and cluster sputtering for dense metals have been investigated through molecular dynamics simulations. It was found that the size of craters is better described by one factor of cohesive energy and melting temperature each, instead of the previously held notion of two cohesive energy factors. The presence of the melting temperature implies that liquid flow has to be considered for microscopic craters, even if the thermal spike that creates it may be short-lived. This again proves the importance of the thermal spike for effects in connection with ion irradiation of solids, as well as provides new information. These results have been accepted for publication in Applied Physics Letters.

Investigations of cluster emission and especially the yield showed that the number of large clusters is very close to inversely proportional to the square of the cluster size, when the effects of linear cascades are minimal. Comparison to recent experiments where the total yield was large and hence the presence of thermal spike effects relatively high, verifies this result. This once again indicates the significance of the thermal spike, for which molecular dynamics is the foremost tool of investigation.
Bibliography


