Electron promotion and electronic friction in atomic collision cascades

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Abstract. We present a computer simulation model for the space- and time-resolved calculation of electronic excitation energy densities in atomic collision cascades. The model treats electronic friction as well as electron promotion as a source term of electronic energy that is carried away from the original point of excitation according to a nonlinear diffusion equation. While the frictional source is treated within the Lindhard model of electronic stopping, electron promotion is described using diabatic correlation curves derived from ab initio molecular orbital energy level calculations in combination with the Landau–Zener curve crossing model. Results calculated for two selected collision cascades show that the electron promotion mechanism may contribute significantly to the excitation energy density in the cascade volume, giving rise to distinct peaks of the local electron temperature at the surface. This contribution is essentially restricted to the first 100 fs after the projectile impact and may therefore be of significance for either external or internal kinetic electron emission. At later times, where the bombardment-induced particle kinetics lead to the sputter ejection of material from the surface, the excitation is shown to be primarily governed by electronic friction. This finding is important in light of excitation and ionization probabilities of sputtered particles.

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1. Introduction

The bombardment of a metal surface with keV ions initiates a complex series of atomic collisions in a near-surface region. It is well known that the temporal and spatial evolution of atomic collision cascades does not only lead to the emission of particles from the surface (‘sputtering’), but also induces electronic excitations in the substrate, which manifest, for instance, in the excitation or ionization of sputtered species [1], in ion induced kinetic electron emission (KEE) [2]–[4] or, very recently, in the experimental detection [5] of hot electrons with excitation energies below the vacuum level.

In particular, the accurate account of the ionization probability of sputtered atoms, which is directly related to the generation and transport of kinetically induced excitation energy in the collision cascade, constitutes a vivid field of research and may be considered as ‘the most urgent unsolved problem in atomic collisions in solids’ [6] due to its central role in the quantitative analysis of secondary ion mass spectra (SIMS).

From a theoretical point of view, the two excitation mechanisms usually taken into account during keV-bombardment of metals are (i) direct collisions of the projectile with conduction electrons close to the Fermi-level and (ii) electron promotion in close atomic collisions. The collective electron excitation induced by process (i), i.e. the direct collisional transfer of kinetic energy from both the projectile and low-energy recoils to electrons can to first order be described in terms of the Lindhard–Scharff–Schiott (LSS)-model [7] giving rise to a velocity-dependent electronic stopping power, whereas electron promotion is mostly treated within the Fano–Lichten model [8] of quasi-molecular orbital (MO) crossing.

However, despite the existence of well-established physical models for both excitation mechanisms, theoretical studies on the relative significance of both processes for the kinetic electronic excitation and, consequently, the ionization probabilities of sputtered particles as well as either external or internal KEE seem to be completely lacking.

Due to the fact that an ab initio calculation of large-scale particle dynamics, which would directly include electronic excitations, is still too complex and therefore not feasible for a sputtering scenario, several attempts [9]–[13] have been made to incorporate electronic excitation processes into standard molecular dynamics computer simulations. In all of these approaches electrons only play a passive role either as a static medium acting as a friction force, which is calculated within the framework of the LSS-model or similar approaches employing local electron densities [14], leading to a slowing down of moving atomic particles, or as a non-relevant...
by-product accompanying the deep level core hole generation in a hard binary collision event. In addition, we emphasize that published models neither feature a simultaneous quantitative treatment of both excitation sources nor do they take into account any excitation energy transport.

In order to close this gap, we have developed an alternative computer simulation concept [15]–[17] which treats the electronic energy loss of all moving atoms as an excitation source feeding energy into the electronic sub-system of the solid. This is combined with a diffusive description of the excitation energy transport in order to calculate a four dimensional excitation energy density profile \( E(\vec{r}, t) \) across the volume affected by a collision cascade. In a third step, this profile is parametrized in terms of a time- and space-dependent electron temperature distribution \( T_e(\vec{r}, t) \) as discussed in detail in [18]. In the framework of our model, the particle kinetics determining the excitation source are delivered by classical molecular dynamics. The diffusivity \( D \) describing the spread of electronic excitation energy constitutes the essential physical input parameter of the transport model. Starting from the assumption of a constant diffusivity [15], we have recently extended this model [17] to include a space- and time-dependent diffusivity \( D(\vec{r}, t) \) which is self consistently determined from the local lattice order parameter \( \Lambda(\vec{r}, t) \), the momentary lattice temperature \( T_l(\vec{r}, t) \) and electron temperature \( T_e(\vec{r}, t) \) itself.

First results obtained for one selected ion impact event (5 keV Ag → Ag(111)) have revealed interesting temporal dynamics of the substrate excitation at the surface: immediately following the projectile impact excitation energy densities are reached that correspond to electron temperatures of several thousand Kelvin. This initial excitation rapidly dissipates due to the onset of fast diffusion in the ideal metal lattice. After approximately 300 fs the electron temperature rises again due to the trapping of excitation energy caused by impact-generated lattice disorder, which reduces the diffusivity \( D \) via a reduction of the electron free mean path. It was shown that this leads to a second maximum of the surface electron temperature with values of about 1000 K depending on the radial distance from the impact point. This finding is of utmost significance, since (i) the timescale at which these temperatures are reached almost exactly coincides with that of maximum particle emission [17] and (ii) those temperatures are sufficient to have an effect on the electronic state of sputtered particles.

A shortcoming of the published model is that collisional excitations have not yet been taken into account. In this paper, we present another extension, which allows the incorporation of those processes in a straightforward manner. The extended model is applied to calculate the temporal and spatial excitation energy density for one selected trajectory, which is identical to that already investigated in [17]. This particular trajectory was selected since it was shown to produce a very dense cascade with many atoms being simultaneously in motion, thus leading to a relatively high sputter yield. It was deliberately selected here in order to discuss the relative role as well as the characteristics of different excitation mechanisms by comparison with corresponding calculations switching either electronic friction or electron promotion on and off. In order to get a feeling for the significance of that particular selection, the calculations were repeated for a second ‘reference’ trajectory, which was previously shown to generate a less dense cascade being much closer to the typical event produced under the prevailing bombarding conditions. Once the model is completed, the calculations will of course be expanded to a set of many different impact points in order to assess the statistics of the excitation processes.

The ultimate goal of this study is to provide an accurate description of \( T_e(\vec{r}, t) \), which can be employed in order to predict electron emission and secondary ion formation using published theory. These results can then be compared to a wealth of experimental data.
2. Description of the calculation

2.1. Particle kinetics

The atomic collision cascade described here is initiated by normal incidence of a 5 keV silver atom on to a monocrystalline (111)-oriented silver model crystallite consisting of 4500 atoms. This self-sputtering system is chemically inert and simplifies the calculations since only one parametrized potential is needed to describe the interaction among all particles of the system. In analogy to a variety of previous studies [17, 19] we use a standard molecular dynamics code [20] in connection with the molecular dynamics/Monte Carlo-corrected effective medium (MD/MC-CEM) many-body-potential [21] which has been fitted to the properties of solid silver. In view of the fact that hard binary collisions have to be detected during the time integration of the trajectory we use a dynamical timestep adjustment that limits the maximum allowed position change during one single integrator step to 0.01 Å.

2.2. Electronic excitation mechanisms and transport

The atomic collision cascade is assumed to be embedded in a quasi-free electron gas with Fermi energy $E_F$ and an electron mean free path $\lambda$. The amount of excitation energy is quantified by a local excitation energy density $E(\vec{r}, t)$ which may be parametrized in terms of a space- and time-dependent electron temperature $T_e(\vec{r}, t)$ via the definition of electronic heat capacity.

2.2.1. Electronic friction. As a first physical mechanism constituting a source of excitation energy, we regard electronic friction experienced by all moving particles traversing the Fermi gas. Within the Lindhard model of electronic stopping [7] the energy which is fed into the electronic system at location $\vec{r}$ within the time interval $[t, t + dt]$ due to the motion of $N$ silver particles moving at location $\vec{r}_i(t)$ with kinetic energy $E_{i,k}(\vec{r}_i, t)$ is given by [15]

$$dS_1(\vec{r}, t) = A \sum_{i=1}^{N} E_{i,k}(\vec{r}_i, t) \cdot \delta(\vec{r}_i - \vec{r}) \, dt.$$  

(1)

The constant $A$ depends on the projectile as well as the density of the (homogeneous) electron gas and is evaluated as $2.9 \times 10^{12} \text{s}^{-1}$ (see [15]) for an Ag atom moving in silver. In equation (1) the essential inputs $\vec{r}_i(t)$ and $E_{i,k}(\vec{r}_i, t)$ are delivered by the corresponding molecular dynamics trajectory calculation.

2.2.2. Collisional excitation. The second source of excitation energy to be considered is the promotion of d-electrons to energies above $E_F$ in violent binary collisions. In a simple physical model these excitations can be described on the basis of the curve-crossing theory of Fano and Lichten [8, 22, 23] originally developed for inelastic collisions in gases. In this picture, quasi-MOs are transiently formed by two hard colliding atoms. As the distance of the two nuclei decreases, some orbitals may be promoted to higher energies due to the competing effect of the increased nuclear charge in the quasi-molecule with decreasing internuclear distance and the increase in kinetic electron energy caused by increased localization [24]. When two levels of the same symmetry cross in a non-adiabatic picture, exchanges between them are possible, and higher levels, unoccupied before the collision, can be partially filled.
Ab initio calculation of MO energies versus interatomic distance corresponding to a quasi-molecule consisting of two silver atoms. RHF single-point energy calculations were performed using GAUSSIAN03 [25] in 1 Angstrom steps. In the region of strong interaction (between 2 and 0.4 Å) the step size was refined to 0.1 Å. In order to include all electrons in the mathematical description of the Ag–Ag wavefunction we have used the 3-21G standard basis rather than pseudopotentials. We note that preliminary calculations for the binary Ga–Ga System were found to be in agreement with earlier calculations carried out by Lorincik [26]. The dotted lines constitute the diabatic MO-level constructed from the adiabatic ones by connecting the gap between the energy curves at avoided crossings with an inverse hyperbolic cosine function. The density of states (DOS) data have been taken from [27].

Figure 1 shows ab initio calculated adiabatic \( \sigma_u \) MO energies for a binary Ag–Ag collision as a function of internuclear distance. It is quite obvious that the 9\( \sigma_u \) MO, which in the separated atom limit corresponds to the 4d–4d orbital, is quickly promoted with decreasing internuclear separation thereby exhibiting avoided crossings with the energetically higher 10\( \sigma_u \), 11\( \sigma_u \) and 15\( \sigma_u \) MOs. From the adiabatic MOs we derive the diabatic MOs by connecting the gap between the energy curves at avoided crossings with smooth, continuous curves which are then taken to substitute the former ones in the crossing region. Thus, this geometrical construction, which is in analogy to the one proposed in [26], leads to a ‘diabatic’ 9\( \sigma_u \) energy curve \( E_{9\sigma_u}(r) \) which for the ease of computations is approximated by an inverse cosine hyperbolicus dependence \( E_{9\sigma_u}(r) = a + b/\cosh (\gamma r) \) (dashed line, \( a = -7.1, b = 1657, \gamma = 4.75 \)) as already used by Sroubek [24].
Now, considering a violent collision within a solid metal, we are confronted with the problem, how to match the binary collision description of a promoted localized energy level with the band structure of the solid. For that scenario, we correlate the 4d–4d energy level, to which the $9\sigma_u$ MO converges in the limit of large interatomic distance to the energy corresponding to the centre of gravity of the density of states in the d-band of silver. Under the assumption that the MO energy levels originating from the localized d states for a Ag–Ag collision in the gas phase do not significantly differ from those evolving in a solid silver environment, the $9\sigma_u$ level energetically crosses the Fermi energy level at an interatomic distance $r_c$ of 1.5 Å (see figure 1). Thus, whenever the internuclear separation in a binary collision falls below this critical value, promoted electrons may undergo a transition from the promoted state to unoccupied levels in the continuum leaving either a localized 4d hole on one of the colliding atoms (binary picture) or a hole in the d band after the collision is completed. So far, the description is identical to that employed by others in order to explain the generation of inner shell vacancies. Here, we are interested in the fate of the liberated electron which may in principle end up in all possible excitation states between the Fermi level and the maximum energy corresponding to the distance of closest approach. Assuming a resonant transition at an internuclear distance $r^* = r(t^*)$ we arrive at an additional source term

$$ (E_{b\sigma_{\text{u}}}(r^*) - E_F)\delta(\vec{r}^* - \vec{r}) =: S_2(\vec{r}), $$

(2)

to incorporate into the nonlinear diffusion model.

At this point, it is obvious, that for each hard collision occurring within the cascade, the total amount of excitation energy $S_2$ fed into the electronic sub-system strongly depends on the...
interatomic distance \( r^* < r_c \) at which the transition occurs. In order to calculate the transition probability as a function of interatomic distance we employ the Landau–Zener curve crossing formula to describe the transition from a diabatic potential energy curve to the (horizontal) free electron states in the conduction band. Let us consider two diabatic potential energy curves crossing at \( r \). According to the classical Landau–Zener approximation the transition probability is given by

\[
p(r) = \left[ 1 - \exp \left( \frac{-2\pi H^2}{\hbar v(r)a(r)} \right) \right],
\]

where \( a \) denotes the modulus of the difference in the derivatives of the curves, \( v \) constitutes the relative velocity of the two nuclei and the parameter \( H \) represents the transition matrix element. All quantities are evaluated at the crossing distance.

Now, let us consider the case that during a violent binary collision within a solid, one energy curve \( E(r) \)—which has to be identified with the diabatic MO energy curve—overlaps with the conduction band (see figure 2). For the purpose of the present study, we assume the conduction band states to be a continuum of unoccupied free electron states with the Fermi energy \( E_F \) intersected by \( E(r) \) at an interatomic distance \( r_c \).

The detailed binary collision dynamics, i.e. the trajectory path \( r(t) \) and the corresponding relative velocity \( v(r(t)) \) between \( r_c \) and the distance of closest approach \( r_{\text{min}} \) are provided by the molecular dynamics simulation at discrete times \( t_i \). Note that the time intervals \( \Delta t_i = |t_{i+1} - t_i| \) and, thus, the intervals \( \Delta r_i = |r(t_{i+1}) - r(t_i)| = |r_{i+1} - r_i| \), are not necessarily of equal length due to a dynamical time-step adjustment.

Then, we assume—provided that the transition has not taken place in any of the previous intervals \( \Delta r_j \) with \( 1 \leq j < i \)—the probability \( \tilde{p}_i \) for a transition within the \( i \)th interval to linearly scale with the Landau–Zener term (3) as well as with the number of states \( N_i = [\Delta r_i \cdot \frac{\partial E}{\partial r}|_{r_i}] \) crossed within \( \Delta r_i \). Thus, we have

\[
\tilde{p}_i = \frac{1}{\xi} \cdot \left[ 1 - \exp \left( \frac{-2\pi H^2}{\hbar v(r_i)a(r_i)} \right) \right] \cdot \Delta r_i \frac{\partial E}{\partial r}|_{r_i}
\]

with

\[
\xi = \max \left\{ \Delta r_i \frac{\partial E}{\partial r}|_{r_i} \right\} .
\]

In equation (4) the normalization factor \( \xi \) has to be introduced in order to be able to define the counter probability \( q_i \) as \( q_i = 1 - p_i \). In order to account for the prerequisite that the transition must not have taken place in any of the preceding intervals \( \Delta r_{j<i} \), the probability \( \tilde{p}_i \) has to be multiplied with a factor \( \prod_{j=1}^{i-1} (1 - p_j) \), thus, leading to the recursion

\[
p_i = \frac{1}{N} \cdot \frac{1}{\xi} \cdot \left[ 1 - \exp \left( \frac{-2\pi H^2}{\hbar v(r_i)a(r_i)} \right) \right] \times \Delta r_i \frac{\partial E}{\partial r}|_{r_i} \times \prod_{j=1}^{i-1} (1 - p_j),
\]

with \( p_1 := \tilde{p}_1 \). The normalization constant \( N \) can be determined in a straightforward way, since at \( r_{\text{min}} \) the radial velocity vanishes leading to a singularity in the denominator of the argument of the exponential function which is equivalent to a transition probability equal to one. Thus, it is
clear that the transition must take place somewhere on the trajectory path from $r_c$ to $r_{\text{min}}$, which is equivalent to

$$N = \sum_{i=1}^{n} p_i = \sum_{i=1}^{n} \left\{ \frac{1}{\xi} \cdot \left[ 1 - \exp \left( \frac{-2\pi H^2}{\hbar v(r_i) a(r_i)} \right) \right] \times \Delta r_i \frac{\partial E}{\partial r} \bigg|_{r=r_i} \times \prod_{j=1}^{i-1} (1 - p_j) \right\}. \quad (7)$$

Figure 3 displays the calculated transition probability density $p_{\text{dens}}(r)$, i.e. $p_i/\Delta r_i$, as a function of radial interatomic distance for different coupling parameters $J := H^2/\hbar a(r)v(r)$. In the case of strong coupling of the quasi-MO with the continuum states (i.e. $J = 10^2 \gg 1$) the resulting probability density distribution is a delta-function centred at the critical distance $r_c$, i.e. the electron will be fed into the conduction band directly at the Fermi edge provided that there are unoccupied states, of course. Thus in this case the electron promotion process does not lead to the formation of hot electrons in the conduction band.

With decreasing coupling strength ($J \approx 0.5$) the delta peak loses approximately one half of its height in favour of the evolution of a small peak at the turning point $r_{\text{min}}$ as well as in favour of a nonzero probability density in the intermediate region between $r_c$ and $r_{\text{min}}$. Comparing $p_{\text{dens}}(r_c)$ with $p_{\text{dens}}(r_{\text{min}})$ one observes that a transition at the Fermi edge is by one order of magnitude more probable than a transition at the turning point.

Considering the case of weak coupling (i.e. $J = 10^{-2} \ll 1$), we still observe a rather high probability density of approximately 20 Å$^{-1}$ at $r_c$ which is followed by a steep exponential-like decay up to an interatomic distance of approximately 0.9 Å. Directly at the turning point the transition probability density again exhibits a second very sharp maximum, which, now, exceeds the one localized at $r_c$ by a factor of two. Thus, for that particular choice of $J$, a transition at
the turning point—which ‘generates’ a hot electron in the conduction band—appears to be more probable than a transition directly at the Fermi edge. Finally, figure 3 displays the resulting distribution for very low coupling constant $J \approx 10^{-4}$. It is clearly visible that for this particular choice of $J$ the probability for a transition to occur at the turning point is by two orders of magnitude larger than to occur at $r_c$. In the limiting case $J \to 0$ the corresponding distribution will converge to a delta function localized at the turning point.

Thus, the above analysis demonstrates the strong dependence of $p(r)$ on the coupling matrix element $H$, which in the present study constitutes a parameter that is associated with a high level of uncertainty. As a crude approximation, one could use published values of d-level broadening due to resonances with an sp-band, which typically are of the order of 0.5 eV [28]. Substituting this value for $H$ into equation (3), this translates to an average coupling parameter $J \approx 5 \times 10^{-4}$, thus indicating the weak coupling limit to be a reasonable approximation. Therefore, in order to estimate the excitation energy produced by electron promotion, we assume for each hard collision the transition to take place at the distance of closest approach $r_{\text{min}}$ with unit probability, provided that $r_{\text{min}} < r_c$, of course. It should be emphasized that this procedure results in a superior estimate of the maximum possible total excitation energy generated by electron promotion processes. For the sake of consistency with energy conservation, the generated excitation energy is subtracted from the total energy within the molecular dynamics calculation. In analogy to [29], this is done for each violent collision by symmetrically shifting the interatomic distance of the colliding atoms by an amount that lowers the potential energy between them by a value corresponding to the generated excitation energy above the Fermi level. This correction is performed one molecular dynamics time step after the distance of closest approach has been reached.

We note that the electron transition from the promoted level to an unoccupied state in the conduction band is naturally accompanied by the simultaneous creation of a d-hole in the valence band. Due to the relatively narrow width of the silver 4d band, along with the fact that the crystallographic order is heavily disturbed during most of the collision cascade, these d-shell excitations will remain localized on the specific atom where they have been created on a timescale of at least femtoseconds. At larger times, the d-hole will be shared among neighboured atoms and delocalize. However, the decay of d holes represents another source of excitation energy which is outside the scope of the present study.

2.2.3. Excitation energy transport. The transport of excitation energy as well as numerical implementation details have already been discussed in [17]. Therefore in the following we will only give a brief outline of the basics of the transport model. The spread of electronic excitation energy around the original point of generation is modelled by the full three-dimensional, nonlinear diffusion equation

$$\frac{\partial E(\vec{r}, t)}{\partial t} - \vec{\nabla} \cdot \left( D(T_l(\vec{r}, t), T_e(\vec{r}, t), \Lambda(\vec{r}, t)) \vec{\nabla} E(\vec{r}, t) \right) = A \sum_{i=1}^{N} E_i^{k}(\vec{r}_i(t)) \cdot \delta(\vec{r}_i(t) - \vec{r}(t))$$

$$+ \sum_{\kappa} \frac{E_{\text{exc}} \left(t^{(\kappa)}_{\text{dca}}(t) - E_F\right)}{\Delta t} \cdot \delta \left( t - t^{(\kappa)}_{\text{dca}} \right) \cdot \delta \left( \vec{r} - \vec{r}^{(\kappa)}_{\text{dca}} \right)$$

with an excitation energy diffusivity $D$, which is for each time self-consistently determined from the lattice temperature $T_l$, the electron temperature $T_e$ itself and an additional lattice order parameter $\Lambda$. Note that the last sum in equation (8) with index $\kappa$ loops over all hard binary
collisions. For the exact evaluation formulae and further discussion on the parameters entering $D$, the reader is referred to [17]. Equation (8) is numerically solved within the complete half-space below the surface using a finite differences approach [17]. At the surface plane itself a Neumann boundary condition is enforced in order to inhibit outward diffusion of excitation energy into the vacuum. It should be noted that this boundary condition neglects the energy loss induced by electron emission from the surface. Under the bombarding conditions employed here, however, typical electron emission yields are of the order of unity with typical emission energies being of the order of eV. This means that on the average only one electron is emitted during the entire simulation, rendering this energy loss negligible.

3. Results

The above combination of molecular dynamics and nonlinear diffusive transport of excitation energy has been applied to calculate the time- and space-resolved excitation energy density within the atomic collision cascade initiated by a 5 keV silver atom impinging on to an Ag(111) surface under normal incidence.

In order to study the relative role of the two excitation mechanisms (electronic friction + electron promotion) the calculations are carried out (i) with as well as (ii) without the collisional source term $S$. The temporal and spatial evolution of the electronic excitation energy density will be discussed in respect to the ionization probability of sputtered particles and KEE.

In order to get a first impression of how the atomic collision cascade studied here develops in time and space, figure 4 shows perspective snapshots of the simulation volume at different stages after the projectile impact for the calculation including electron promotion. Simultaneously to the atomic particles, which are diagrammed as small coloured balls, the electronic subsystem is represented by a gas cloud whose colourization reflects the momentary local excitation energy density as calculated by equation (8).

The first snapshot is taken shortly after the primary particle (red colour) penetrated the uppermost crystal layer (green colour) under normal incidence. At that time, the highly energetic projectile is the only atom which is not at rest and, thus, the only particle transferring part of its kinetic energy into the electronic subsystem via electronic friction. Due to the still undisturbed lattice the transport of excitation energy takes place very rapidly ($D \approx 180 \text{ cm}^2 \text{ s}^{-1}$) without any preferences in lateral direction. In direction perpendicular to the surface plane, however, any flux of excitation energy in outward direction is inhibited by Neumann boundary conditions, whereas diffusion in bulk direction is not restricted at all. These symmetries directly transfer to the resulting distribution $E(\vec{r}, t)$ which clearly exhibits radial symmetry around the impact point and peaks at an excitation energy density of approx. $5 \times 10^{-3} \text{ eV } \text{ Å}^{-3}$ in its centre of symmetry. Note that all excitation energy generated so far solely originates from electronic friction, since the primal electron promotion event occurs 2 fs after this snapshot was taken.

The next picture taken at $t = 75$ fs shows a crystal which appears to be almost undisturbed apart from some defects in the uppermost surface layer. The excitation energy distribution strongly deviates from the one at $t = 5$ fs in mainly two points. Firstly, the lateral symmetry is broken and, secondly, the maximum of excitation energy density is no longer located in the uppermost surface layer at the impact point, but in approximately 12–15 Å depth near the front-right crystal edge. This finding already indicates that the collision cascade predominantly propagates in that particular direction beneath the surface, thereby continuously heating up the electron gas. Unfortunately, in this representation of calculation results it is not possible to...
Figure 4. Temporal snapshots of the exemplary collision cascade initiated by 5 keV Ag → Ag(111) bombardment. In addition to the illustration of atomic particles (blue: bulk atoms; green: surface atoms) the local excitation energy density (eV Å⁻³) is visualized using the indicated colourmap.

distinguish between excitation energy generated by electronic friction or electron promotion, respectively. This issue will be analysed and discussed in a separate figure in the course of the present paper.

The subsequent snapshot at \( t \approx 150 \) fs reveals the onset of sputtering with a total number of three particles already been emitted from the surface, which electronically has ‘cooled down’ to excitation energy densities of approximately \( 3 \times 10^{-5} \) eV Å⁻³ at the impact point due to (i) rapid transport of excitation energy in bulk direction and (ii) an additional lack of particles passing through the near sub-surface region. Moreover, the observation of plenty of particles knocked out from their original lattice sites at the right-front edge of the crystallite corroborates our aforementioned speculation about the direction of propagation of the cascade beneath the surface.

At \( t = 225 \) fs the excitation energy distribution \( E(\vec{r}, t) \) remains rather moderate with excitation energy densities of about \( 4 \times 10^{-5} \) eV Å⁻³ at the surface which correspond to electron
temperatures of about 500–600 K. Concerning particle dynamics eight atoms have already been sputtered from the very surface.

At a later time of about 300 fs, we interestingly observe a rise in excitation energy density particularly at the very surface, again. This effect must be ascribed to the augmented presence of secondary recoils in the proximity of the surface plane. In addition, the local atomic disorder induced by the projectile impact leads to a significant reduction of the excitation energy diffusivity by two orders of magnitude. Therefore, the electronic excitation generated by the persisting frictional source term becomes trapped within the crystal volume perturbed by the collision cascade. This leads to the occurrence of local ‘hot spots’ of electronic excitation, which may exhibit peak temperatures $T_e$ of about 1000 K and last some hundreds of fs during the late stage of the cascade (see last snapshot). We note that these ‘hot spots’ temporally overlap with the emission of particles from the surface. Particularly those atoms sputtered from these excited surface areas may constitute the fraction of secondary ions among the entire flux of sputtered particles.

A look at the last snapshot at the end of the total simulated time of $t = 750$ fs reveals that with increasing time the excitation energy density will naturally decrease due to the continuous decrease in the frictional source term, which is attended by additional kinetic energy losses in the form of sputtered particles and naturally superimposed by the dissipation of excitation energy in bulk direction, which can no longer be (over)compensated by an enhanced trapping of electronic excitation.

In summary, the qualitative analysis of the series of snapshots reveals the necessity to distinguish between two different stages of high density of excitation energy at the surface. First, directly after the projectile hit the surface an isotropic hot spot develops around the point of impact. This hot spot breaks down on a timescale of several ten fs due to the onset of fast diffusion and therefore will not have any direct effect on the electronic charge state of by far the majority of sputtered particles, which leave the surface at much later times. However, we consider this initial highly excited area to be responsible for KEE. The second kind of hot spot attributed to the increased confinement of electronic excitation in the later stage of the cascade strongly coincides with the sputtering of secondary recoils and, therefore its momentary electron temperature at the position a particle has been emitted from must be regarded as the crucial parameter for the determination of the individual ionization probability of that particular particle.

In view of the fact that the majority of particles are emitted from the uppermost surface layer [19], figure 5 focuses on the time evolution of the excitation energy densities at the surface for the calculations with and without collisional excitation. In order to allow a rather compact quantification of results, figure 5 shows the excitation energy density evaluated at two different radial distances from the impact point. Before analysing and comparing the calculation results in detail, we emphasize that the MD trajectories corresponding to both cases differ from each other as a matter of principle, since for every electron promotion process the collisional excitation energy is subtracted from the potential energy of the colliding atoms, thereby altering the subsequent cascade evolution. We note that these differences in particle dynamics influence the obtained sputtering yield, which is $Y = 21$ for the calculation with and $Y = 19$ for the calculation without electron promotion.

Focusing on the trajectory simulated without electron promotion, we observe a steep initial rise of $E$ up to a maximum value of about $2 \times 10^{-2}$ eV Å$^{-3}$ at $t \approx 7$ fs. This initial maximum originates from the projectile penetrating the first layer of the model crystal and is followed

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Figure 5. Time evolution of the excitation energy density at the surface for two different radial distances from the impact point of the 5 keV silver projectile impinging on to Ag(111). The diffusivity $D$ varies in time and space according to a function of lattice temperature, atomic disorder and excitation energy density.

by a fast monotonic decay to values of about $2.6 \times 10^{-4} \text{ eV Å}^{-3}$ at $t = 12$ fs after the primary particle has completely passaged the uppermost layer. The extremely strong decay clearly mirrors the rapid transport of excitation energy at that early stage of the cascade. After the occurrence of a second maximum at $t \approx 15–20$ fs, which we ascribe to a fast recoil moving across the uppermost surface layer, the excitation energy density exponentially decreases—apart from some distinct fine structure from insular secondary recoils—up to a simulated time of approx. 150 fs. Shortly after, the excitation energy density at the surface increases again by almost one order of magnitude, a finding which is due to the enhanced confinement of electronic excitation within the cascade volume. At $t > 350$ fs, $E(t)$ exhibits a rather constant, plateau-like curve characteristics with values of about $1 \times 10^{-4} \text{ eV Å}^{-3}$, which translate to electron temperatures of about 800 K. For a larger radial distance from the impact point ($r = 15$ Å), figure 5 reveals similar curve characteristics with by far less pronounced maxima. The electron temperatures in the range from 250 to 750 fs are by one half of a magnitude lower than those calculated at $r = 0$ Å. However, one has to bear in mind that, dependent on the momentary lateral position at the surface, even temperatures above 1000 K are possible in local ‘hot spots’ as shown in figure 4.
Now, considering the calculation including electron promotion, the corresponding curves are within the first 150 fs rather similar to those of the case without collisional excitation, but additionally exhibit a set of sharp peaks. These structures originate either from electron promotion processes, which may occur either at that particular radial distance from the impact point, or, more likely, from contributions of collisional excitation generated somewhere else in the cascade. Within the first tens of fs after the impact the curves calculated without collisional excitation may be regarded as the inferior enveloping functions of the curves representing the calculation including electron promotion. At \( t = 7 \) fs and \( r = 0 \) Å, one observes a very steep peak evolving from the plateau of the initial maximum with an excitation energy density of 6 eV Å\(^{-3}\). This peak can be ascribed to the initial violent collision of the projectile with a target atom localized at the impact point in the uppermost surface layer. Moreover the detailed collision analysis of the MD-trajectory reveals that for this particular collision the distance of closest approach is 0.67 Å which is equivalent to an excitation energy of 127 eV. A close look at the fine-structures of the peaks reveals a characteristic fast exponential decay at the right slope, mirroring the fast transport of excitation energy, which can also be derived from the observation that there is hardly any temporal shift in the peaks from \( r = 0 \) Å to \( r = 15 \) Å. As a general tendency the peak heights as well as their occurrences decrease with increasing time as a consequence of successive partitioning of kinetic energy among the particles. The latest electron promotion process takes place 140 fs after the primary particle impact.

Taking into account the time interval from 100 to 750 fs, we again find an increase of excitation energy density in the time interval most particles are sputtered within. However, for both radial distances, the rises are retarded as well as less pronounced compared to those obtained without the collisional source term. This finding clearly reflects the fact that for each collision the excitation energy is subtracted from the potential energy of the colliding atoms, which, in turn, is converted into a—in comparison to an analogous elastic collision—diminished amount of kinetic energy. Integrated over all inelastic collisions, this leads to a significant reduction of the frictional source term. In order to determine the relative significance of both excitation mechanisms, the source terms \( dS_1/dt \) and \( S_2/\Delta t \) have been integrated over the complete model crystallite volume in timesteps of \( \Delta t = 1 \) fs. The resulting time evolution of the source terms is depicted in figure 6.

Directly after the impact, when the projectile penetrates the uppermost cell layer, the electronic friction source term raises to values of about 14.4 eV fs\(^{-1}\). This maximum corresponds to the situation where the bombarding energy has not yet been shared among the atoms and not been partially transformed into potential energy either. The initial rise is then followed by a rather slow exponential decrease of the frictional source term to values of about 2 eV fs\(^{-1}\) at \( t = 750 \) fs. The observed oscillatory structure in the time interval 0 to 50 fs reflects the conversion of kinetic into potential energy in close collisions, a finding which is corroborated by the fact that each minimum of kinetic energy is accompanied by a maximum of the electron promotion source term. With increasing time these oscillations disappear due to enhanced partitioning of energy among more and more particles, making violent collisions less and less probable.

Having a look at the source term \( S_2/\Delta t \) resulting from collisional excitations, we observe distinct peaks decreasing in height with increasing time. Each peak mirrors the promotion of a deep-level electron into an excited state above the Fermi level. This process becomes more and more improbable with enhanced kinetic energy dissipation and partitioning. The last electron promotion process occurs 127 fs after the impact of the primary particle and generates a hot
Figure 6. Volume-integrated source terms (solid line: electronic friction; dotted line: electron promotion) as a function of time after the projectile impact. The sub-window shows the total excitation energy generated within the first 750 fs after the initialization of the cascade.

electron at 0.4 eV above the Fermi level. Comparing the two datasets we observe the following interesting features.

1. Both excitation mechanisms exhibit completely different temporal dynamics. The occurrence of collisional excitation events is limited to short times (≈100 fs) after the projectile impact, whereas electronic friction constitutes a continuous source term lasting throughout the entire simulated time interval. Hence, the significance of the electron promotion mechanism for secondary ion formation in sputtering appears to be negligible, since by far the majority of particles are emitted at much later times.

2. Time integration of both source terms reveals that for times shorter than about 65 fs, electron promotion may constitute the dominating excitation process, at least within the upper estimate implied by our model assumptions. This finding is interesting in the context of KEE [3, 4] whose basic mechanisms and their relative significance are being actively discussed [26], [30]–[33]. Very recently, the relevance of electron promotion has not only been experimentally demonstrated for grazing incidence scattering of rare gases from a metal surface [31], but also observed for KEE from Al surfaces under bombardment with 1–8 keV Kr⁺ ions [30]. Therefore the calculation results presented in figure 6 may be treated as an additional indication for the prevailing role of electron promotion processes in ion-induced KEE.

3. The probably most relevant observation in figure 6 is the fact that—summed over electronic friction and electron promotion—about 3 keV of energy have been transferred into the electronic subsystem of the metal. Thus, over 60% of the kinetic energy originally imparted into the solid surface is dissipated into electronic degrees of freedom rather than by nuclear collision dynamics. It is important to note that essentially the same values are obtained for the ‘reference’ trajectory, thus indicating that this result is not restricted to superdense collision cascades (‘spikes’) but may be rather typical for the bombarding conditions.
employed here. We emphasize that the observed energy partitioning does not contradict the common notion that under these conditions nuclear stopping exceeds electronic stopping by approximately one order of magnitude. To illustrate this, let us look at the first stopping process, which is given by the impact of the projectile on to the central surface atom. A detailed analysis of the MD data [34] shows that in this collision the projectile loses about half of its kinetic energy (2500 eV), thereby generating a total of about 200 eV of excitation energy by electronic friction and electron promotion. Hence, the original electronic stopping power experienced by the projectile amounts to approximately 8% of the nuclear stopping power, which is in accordance with the results of Monte Carlo computer simulations using SRIM 2003 [35].

4. Conclusion

We present a computer simulation model for the calculation of electronic excitation energy densities \( E(\mathbf{r}, t) \) in atomic collision cascades in metals. This model treats electronic friction as well as electron promotion in close binary encounters as local and time-dependent sources of excitation energy, which is assumed to spread around the original point of generation according to a nonlinear three-dimensional transport equation. The latter is numerically integrated—in combination with molecular dynamics delivering the atomistic particle kinetics.

The resulting four-dimensional excitation energy density profile \( E(\mathbf{r}, t) \) reveals the temporal evolution of two different kinds of ‘hot spots’, i.e. highly electronically excited sub-areas of the model crystallite. The first ‘hot spot’ with excitation energies from \( 10^{-3} \) to \( 1 \) eV Å\(^{-3} \) arises directly at the particle impact, when the projectile penetrates the uppermost crystal layer. Our results indicate that electron promotion in close binary collisions may in principle be capable of playing a dominant role in the generation of excitation energy during this early stage. It should be emphasized again that the ‘weak coupling’ approximation employed here (cf section 2.2.2) leads to an upper estimate of this excitation mechanism, which may be ineffective in the opposite limit of ‘strong coupling’. Due to the rapid excitation energy transport at that initial stage of the atomic collision cascade, this primary ‘hot spot’ dissolves on the timescale of several ten fs and, therefore, will not significantly influence the formation of secondary ions, which are known to be sputtered mostly at a much later stage of the cascade. Nevertheless, this initial ‘hot spot’ may be of primary importance for ion-induced KEE.

The second kind of ‘hot spot’ emerges at times of approx. 300 fs after the projectile impact and is restricted to the very surface. This second maximum of excitation energy density results from an enhanced confinement of excitation in particularly those regions, which are affected most by the collision cascade. The calculations clearly show strong correlations between the presence of such a ‘hot spot’ and spatial and temporal emission characteristics of sputtered particles. Hence, we believe that it is exactly that coincidence which is of utmost relevance for the formation of secondary ions in sputtering.

Moreover, we find that about 60% of the kinetic energy imparted into the solid is at least temporarily dissipated into electronic degrees of freedom rather than directly into the collision dynamics. In the limit of long times, the system will of course be thermalized by electron–phonon coupling.
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Equation (8) contained an error. The correct version is given below:

$$\frac{\partial E(\vec{r}, t)}{\partial t} - \vec{\nabla} \cdot (D(T_l(\vec{r}, t), T_e(\vec{r}, t), \Lambda(\vec{r}, t)) \vec{\nabla} E(\vec{r}, t)) = A \sum_{i=1}^{N} E_k^i(\vec{r}_j, t) \cdot \delta(\vec{r}_j(t) - \vec{r}(t))$$

$$+ \sum_{\kappa} \frac{E_{\theta \kappa}(r_{dca}^{(\kappa)}(t)) - E_F}{\Delta t} \cdot \delta(t - t_{dca}^{(\kappa)}) \cdot \delta(\vec{r} - \vec{r}_{dca}^{(\kappa)})$$

(8)