Modelling electron beam induced dynamics in metallic nanoclusters

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Abstract

We present a computational scheme to simulate beam induced dynamics of atoms in surface dominated, metallic systems. Our approach is based on molecular dynamics and Monte Carlo techniques. The model is tested with clusters comprised of either Ni, Ag or Au. We vary their sizes and apply different electron energies and cluster temperatures to elucidate fundamental relations between these experimental parameters and beam induced displacement probabilities. Furthermore, we demonstrate the capability of our code to simulate beam driven dynamics by using Ag and Au clusters as demonstration systems. Simulations of beam induced displacement and sputtering effects are compared with experimental results obtained via scanning transmission electron microscopy. The clusters in question are synthesised with exceptional purity inside inert superfluid He droplets and deposited on amorphous carbon supports. The presented results may help to understand electron beam driven processes in metallic systems.

Keywords

clusters; time-resolved STEM; knock-on damage; beam damage; electron beam induced atom dynamics

Introduction

With the advent of aberration corrected electron optics, scanning transmission electron microscopy (STEM) has proven its excellent capability of characterising nanomaterials. However, due to the high current densities occurring in such a highly focused electron beam, STEM has to be classified as a destructive method in many cases. Beam induced sample changes in metallic nanomaterials have commonly been reported in literature. Already in the early beginnings of high-resolution STEM, Isaacson et al. reported beam induced motion of single metallic atoms and clusters on a carbon support.¹ Similar observations were also presented in a more recent work by Batson.² Beam driven dynamics was also reported for metallic nanoparticles, for instance by Smith et al. who observed structural rearrangements of gold particles,³ by Han et al., who described the elongation of Au clusters parallel to the electron beam⁴ and Jones et al. who observed atom dynamics and surface sputtering while studying Pt clusters.⁵ Therefore, changes of cluster morphology and composition must be considered during the design of cluster experiments, as demonstrated in previous related work.⁶⁻¹⁰ All these reports indicate that beam induced sample changes pose a main limitation to material characterisation with electron probes.

However, it was shown that a finely focused electron beam could also be used as a tool to modify the composition and structure of certain materials in a highly localised manner, which may be used for possible applications in nanotechnology. For instance the electron beam induced fabrication of self-organised metallic nanostructures,¹¹ the formation of crystalline Si nanodots in a SiO₂ film¹² and the creation of hollow and toroidal NiO clusters¹³ were reported. Furthermore, STEM has also been used as an *in situ* tool to observe defect

generation and impurity diffusion in 2D materials¹⁴⁻¹⁸ as well as to study cluster sintering.¹⁹ The underlying physics of such beam driven dynamics has been studied thoroughly in literature. Notable attempts were done by Egerton,^{20,21} Reimer and Kohl,²² Lai et al.²³ and Jiang.²⁴ It was shown that the degree of sample modification does not only depend on electron energy and dose, but also is often characterised by a complex interplay of different damage mechanisms, which depend on the material, its conductivity of heat and charge, sample geometry and orientation with regard to incident electrons, atomic bond energies and local chemical environment. Beam driven dynamics is significant especially for samples with a high percentage of low-coordinated, and thus weakly bound atoms at surfaces, grain boundaries and interfaces.

For the simulation of beam induced effects molecular dynamics (MD) is an appropriate choice since it provides solutions of the equations of motion for each single atom in the system and, therefore, intrinsically accounts for the ballistic motion of atoms and the subsequent thermalisation of the system after scattering. Although, MD is widely used to obtain valuable information about the mechanisms of sputtering effects with ion radiation,^{25–27} there are only few attempts in literature harnessing such simulations to study electron beam induced effects in solids.^{14,28–31} The focus of all these studies laid in the simulation of beam damage in 2D materials, based on the McKinley and Feshbach approximation of the scattering cross section, which is valid only for elements with an atomic number Z < 21.^{32–35} In the following we provide a more generalised scheme to simulate such electron beam induced effects without prior knowledge of the local atomic configuration and displacement threshold energies, also for heavier elements.

Methodology

In the common picture electrons interact with matter via elastic and inelastic interactions. Elastic forward scattering of energetic incident electrons from the Coulomb field of atomic nuclei is the most important type of interaction of electrons with matter in electron microscopy.

The momentum transfer to the atom during an elastic scattering event can be neglected for the majority of electrons. Nevertheless, some of them are scattered to high angles and thus transfer energies up to several eV, which is in the energy range of atomic displacement and defect generation in many solid materials.^{21,36} The energy needed to displace an atom is also determined by its local bonding energy and by the availability of empty lattice sites in its neighbourhood. Consequently, beam induced atomic displacements lead to enhanced (surface) diffusion and even to mass loss due to sputtering of atoms from the surface.

While elastic scattering events are considered to be electron-nuclear interactions, inelastic scattering includes ionisation and excitation of sample electrons (electron-electron interactions). When atoms are ionised in a crystal, bond breaking can occur and if one atom gains enough momentum due to heat and/or Coulomb interactions with its neighbours, it leaves its lattice site. Such displacement events are referred to as radiolysis. In metals, however, vacancies in the electron shell, caused by inelastic scattering, are filled within very short time periods of below 1 fs due to the high electron density in their conduction band.³⁷ This time span is insufficient to accumulate enough energy for a displacement. Ionisation and excitation events are therefore reversible and do not lead to radiolytic damage in metals.

Furthermore, also heating and charging effects caused by electron irradiation can be neglected in our case. In a typical STEM experiment with beam sensitive specimens, beam currents of below 0.1 nA are used. This value equals an electron flux of 6.2×10^8 electrons/s, implying that on average every 1.6 ns an electron impinges the specimen and only a fraction of these electrons undergo scattering. Dissipation of kinetic energy brought in by a single scattering event usually occurs on a much shorter time scale in materials with a sufficiently high heat conductivity. The lifetime of phonon excitations in a nano scaled system is typically in the ps range.^{38,39} Accumulation of thermal energy, thus, can be neglected.^{40,41} The same holds true for the accumulation of charges, because in conductors electrons excited by the electron beam settle within a time span of less than 1 ps.²⁴

Accordingly, we rely on the assumption that any beam induced dynamics of supported clusters can be explained with elastic interactions of incident electrons with the clusters' atomic nuclei. We further assume that electron-atom interactions are temporally uncorrelated, which is reasonable due to the lack of charge or heat accumulation.

Based on these considerations we will introduce a computational framework for the simulation of beam induced changes in supported metallic clusters in the following. Our approach applies a combination of molecular dynamics calculations for the atomic movement and Monte Carlo based methods for the simulation of electron-atom interactions.⁴²

Description of knock-on displacements

Our simulation relies on tabulated differential elastic cross section values $\frac{\partial \sigma}{\partial \Omega}$ from the NIST database based on a model by Mott.^{43,44} These values are given as a function of scattering angle θ as exemplary shown in Fig. 1b at 100 and 300 keV electron energy for Au, Ag and Ni atoms. It is important to note that in general the total cross section for elastic scattering decreases with increasing electron energy and decreasing atomic number of the nucleus. The maximum energy transfer E_{max} from a relativistic particle with energy E and mass m_0 to a nucleus with mass m is given by following equation:

$$E_{\max} = \frac{2mE\left(E + 2m_0c^2\right)}{\left(m_0 + m\right)^2 c^2 + 2mE} \tag{1}$$

where c is the vacuum speed of light. For electron irradiation where $m_0 \ll m$ and $E \ll mc^2$ Eq. (1) can be simplified and the transferred energy E_t to an atom by an electron scattered to an angle θ can then be calculated via:

$$E_{t} = E_{\max} \cdot \sin^{2} \frac{\theta}{2}$$
with $E_{0} = m_{0}c^{2}$ & $E_{\max} = \frac{2E(E + 2E_{0})}{mc^{2}}$
(2)

In Eq. (2) the transferred energy is directly connected to the scattering angle. The elastic



Figure 1: (a) Elastic scattering event of an electron with momentum \vec{p} from an atomic nucleus. The nucleus gains the momentum $\vec{p'_n}$ after scattering. (b) Illustration of the NIST differential elastic scattering cross sections for 100 keV and 300 keV electrons, exemplary for Au, Ag and Ni as a function of the scattering angle θ ; The orange dashed lines corresponds to a typical maximum HAADF detection angle range of 60 - 200 mrad (3.4 - 11.5°); The green dotted line marks the scattering angle ($\approx 30^{\circ}$), at which a 300 keV electron transfers 0.3 eV to a Au atom (typical activation energy for surface diffusion in Au clusters).⁴⁵

scattering cross section integrated over an angular interval $[\theta_{\min}, \theta_{\max}]$ can be calculated via:^{46,47}

$$\sigma_{\left[\theta_{\min},\theta_{\max}\right]} = 2\pi \int_{\theta_{\min}}^{\theta_{\max}} \frac{\partial\sigma}{\partial\Omega} \cdot \sin\theta \cdot d\theta \tag{3}$$

where $\frac{\partial \sigma}{\partial \Omega}$ denotes the differential scattering cross section. With knowledge of $\frac{\partial \sigma}{\partial \Omega}$ the cross-section for a displacement σ_D event can be calculated using Eq. (4).^{24,48}

$$\sigma_D = 2\pi \int_{\theta_{\min}}^{\pi} P(\theta) \cdot \frac{\partial \sigma}{\partial \Omega} \cdot \sin \theta \cdot d\theta \tag{4}$$

where $P(\theta)$ denotes the probability that an atom is displaced after a certain energy transfer E_t .

The sputtering cross section σ_S can be defined in a similar way. Often $P(\theta)$ is assumed to be a step like function, being 0 below an energy threshold value E_d and 1 above. This approach follows from the naive model that damage will occur only if the incident electron has an energy greater than a threshold value, corresponding to a maximum energy transfer E_{max} in Eq. (1). Practically, for a metal this is a very rough approximation, because several different displacement mechanisms occur dependent on orientation and local configuration, each with a different E_d value. We will show that P < 1 for heavier elements, even for high scattering angles (Fig. 3). For high beam energies and/or light elements an electron may also displace more than one atom, resulting in a displacement cascade. All these influences render displacement and sputtering phenomena dependent on the local anisotropy and therefore on the geometry. For flat or tubular shaped nanostructures with a high geometric symmetry, like graphene or carbon nanotubes, an emission energy threshold E_d can be calculated as a function of the direction of the scattering vector $\vec{p_n}^2$.^{28,29} Due to the high amount of possible configurations this is not feasible for metallic clusters exhaustively. However, in the results section we estimate $P(\theta)$ for different cluster species, sizes, temperatures and electron energies to identify general trends. This knowledge could be valuable to design STEM experiments and give hints to minimise damage effects.

Molecular Dynamics

For the simulation of cluster dynamics the trajectory of each atom needs to be calculated under the influence of inter-atomic force fields. These trajectories are calculated by the numerical integration of Newton's equations of motion via the well established Velocity-Verlet algorithm.⁴⁹ A main advantage of this algorithm is the availability of both coordinates and velocity of each atom at every time step. We use this feature for the manipulation of the velocity vector of a certain atom at a given time-step to simulate scattering events.

In classical molecular dynamics, the force each atom exerts on its neighbours is modelled via empirical potentials. By choosing an appropriate model a trade-off between the computational effort and the proximity to reality has to be made. Details about the used potentials and parameters are found in the supplementary information.

Choice of Time Step

The choice of the time step is crucial since it determines the quality of the calculated trajectories. Metallic bonds and heavier atoms allow the choice of relatively large time steps.⁴⁹ Villarreal et al. suggested values of 20 fs, 16 fs or 14 fs for Au, Ag and Ni respectively, for temperatures below 1000 K.⁵⁰

For non-equilibrium systems, such as a cluster struck by a high energy electron, the time step needs to be adapted to the fastest atom in the system until the system reaches its equilibrium. To this end we chose an approach presented by Marks et al.⁵¹ They suggested to use the $|| F_{\text{max}} || \cdot \Delta t$ metric for the time-step adaptation. In every integration step Δt is chosen in a way to keep the factor $|| F_{\text{max}} || \cdot \Delta t$ constant. This approach guarantees that the time step is optimal for each step in the simulation while energy conservation is fulfilled. In order to control the temperature of the system we apply a modified Anderson thermo-

stat,⁵² by coupling the system to a heat bath of the desired temperature. In order to reduce perturbations of the system, only atoms in contact with the substrate are considered for the thermostat.⁵³ After each scattering event the thermostat is temporarily deactivated to preserve the dynamics of the system.

Modelling Beam Induced Displacements

Since the collision time of an electron with a nucleus is extremely short (in the order of 10^{-21} s) compared with the time step in the molecular dynamics run, atoms are considered to remain stationary during scattering (according to the Born-Oppenheimer principle).²⁶ For each scattering event a scattering angle θ is chosen randomly according to the NIST elastic scattering cross section tables.⁴³

The maximum energy E_{max} is being transferred at $\theta = \pi$ (180°), which corresponds to the central impact case. Since only high angle scattering events may transfer a sufficient amount of energy to displace an atom, a threshold θ_{\min} was introduced. Thereby, the computational

effort is reduced very efficiently, due to the power-law like behaviour of the differential scattering cross section (see Fig. 1b). It is noted that the NIST cross section values are based on scattering by single, free atoms and therefore do not account for effects of bonding and crystallisation in a solid material. However, it has been shown that deviations caused by atom aggregation are only relevant for low electron energies and/or low scattering angles.^{54–57} In the simulation a scattering event is modelled by an additional velocity vector $\vec{v_s} = \frac{\vec{p_n}}{m}$, as illustrated in Fig. 1a. Relativistic effects can be neglected for a nucleus with mass m, because $E_t << mc^2$, which allows the use of classical mechanics to calculate the length of $\vec{v_s}$:

$$|\vec{v_s}| = \sqrt{\frac{2E_t}{m}} \tag{5}$$

From the law of momentum conservation $\vec{p} = \vec{p'} + \vec{p'_n}$ we deduce the following relations:

$$|\vec{p'}| \cdot \sin(\theta) = |\vec{p'_n}| \cdot \sin(\psi) \quad \text{with} \quad \vec{p'} = m_0 \vec{v'} \gamma \text{ and } \vec{p'_n} = m \vec{v_s}$$
(6)

with γ being the Lorentz factor:

$$\gamma = \frac{1}{\sqrt{1 - \left(\frac{|\vec{v'}|}{c}\right)^2}}\tag{7}$$

Finally, the scattering angle ψ of the nucleus is obtained (Eq. (8)).

$$\psi = \arcsin\left(\frac{m_0 v' \gamma}{m v_s} \cdot \sin(\theta)\right) \tag{8}$$

The azimuthal angle φ is generated randomly in the interval $[0, 2\pi]$. Together with ψ and $|\vec{v_s}|$ we now have a complete set of polar coordinates for the velocity vector $\vec{v_s}$ which can finally be converted to Cartesian space (Eq. (9)).

$$\vec{v_s} = -\sqrt{\frac{2E_t}{m}} \cdot \begin{pmatrix} \cos(\varphi)\sin(\psi)\\\sin(\varphi)\sin(\psi)\\\cos(\psi) \end{pmatrix}$$
(9)

During a step of the molecular dynamics run, an atom of the cluster is chosen randomly and its velocity vector is modified according to Eq. (8) and Eq. (9). Note that we intrinsically assume that every electron is scattered only once in the sample, because the mean free path for high scattering angles in a metallic cluster is much larger than its dimensions.

Fig. 2 shows the two algorithms we used within this work. In both a two step displacement detection was used to minimise false positives. After a first positive check another check is performed some ps later. Only if both checks are positive, the thermalisation of the system is continued.



Figure 2: Flow diagrams of the algorithms used for beam damage simulations: Algorithm (a): Calculation of displacement and sputtering rates as a function of the scattering angle. Algorithm (b): Simulation of the cluster evolution during electron beam exposure.

Relation Between Simulations and Experiments

As mentioned before only scattering events above a minimum scattering angle θ_{\min} are considered in the simulations. Therefore, we need to extrapolate to the full angular range, in order to be able to compare the results with experiments. In other words, we have to ex-

trapolate from the number of scattering events which are used in the simulation, to the total dose that must be applied to the system to generate this amount of scattering events. Using Eq. (3) we define a scaling factor F (Eq. (10)), which relates the total elastic scattering cross section $\sigma_{\rm el}$ to the part considered in the simulation $[\theta_{\rm min},\pi]$.

The total number of elastically scattered electrons $n_{\rm el}$ is then calculated from the number of scattered electrons $n_{\theta_{\min}}$ in an angular range $[\theta_{\min}, \pi]$ by using:

$$n_{el} = \frac{\int_0^{\pi} \frac{\partial \sigma}{\partial \Omega} \cdot \sin \theta \cdot d\theta}{\int_{\theta_{\min}}^{\pi} \frac{\partial \sigma}{\partial \Omega} \cdot \sin \theta \cdot d\theta} \cdot n_{\theta_{\min}} = F \cdot n_{\theta_{\min}}$$
(10)

The total number of incident electrons n_0 is the sum of the total number of elastically scattered electrons $n_{\rm el}$ and the number of unscattered electrons n:

$$n_0 = n + n_{\rm el} \tag{11}$$

Under oversampling conditions the electron dose is independent of pixel size and only depends on the areal density N (in atoms per m^2) in the projection, which means that the pixel size should be smaller than the probe size in a STEM experiment. Assuming such a set-up scattering occurs if an electron strikes a fraction $N \cdot \sigma_{\rm el}$ of the unit area²² and the corresponding number of unscattered electrons n is given by:²²

$$n = n_0 \cdot e^{-\sigma_{\rm el}N} \tag{12}$$

With Eq. (10), Eq. (11) and Eq. (12) we can finally calculate the total number of incident electrons n_0 that corresponds to the number of simulated scattering events $n_{\theta_{\min}}$ for a certain angular range $[\theta_{\min}, \pi]$:

$$n_0 = \frac{n_{\theta_{\min}} \cdot F}{1 - e^{-\sigma_{\rm el}N}} \tag{13}$$

Experimental Details

Cluster Synthesis

The clusters are grown fully inert inside superfluid helium droplets without the use of surfactants. Such species, regularly used in wet-chemical nanoparticle synthesis, would give rise to hydrocarbon contamination and impose a stabilising effect due to immobilisation of surface atoms. Thus, these contaminants would have strong effects on the observable dynamics under electron beam irradiation. Clusters are deposited on a TEM grid (covered by < 3 nm amorphous carbon, Ted Pella, Inc., Prod. No. 01824G) using (superfluid) helium nanodroplets. More details about the cluster synthesis method can be found elsewhere.^{58,59}

Microscopy

Experiments were performed on a probe-corrected FEI Titan³ G2 60-300 microscope, equipped with a Fischione HAADF detector (Model 3000). Clusters were transferred to the microscope in an evacuated vessel, to reduce the exposure time to environmental conditions to $5 \min$ at maximum.

Data Processing

We studied beam induced dynamics of clusters via acquisition of HAADF time-lapse series in the STEM. Such data sets can easily contain several hundred images, which makes the use of automatic image processing routines inevitable. We extracted information about the projected area and intensity image by image with a script written in MathWorks Inc. Matlab (version R2017b). To determine the projected area of the clusters within the series each image was convolved with a 5x5 pixel averaging filter in order to reduce the influence of noise and intensity variations by atomic columns. For automatic particle detection each image pixel was classified using an expectation-maximisation clustering algorithm based on a Gaussian mixture model.⁶⁰ Image pixels that were assigned to the cluster area were then used to calculate an integrated HAADF intensity value. The background intensity was subtracted by using the mean value of the remaining pixels.

For the evaluation of the simulation data we chose a different approach: To obtain projected images of the cluster models we would need to run a multislice simulation for each single displacement, which is computationally highly demanding. Instead, we approximate the HAADF contrast by projections of two-dimensional Gaussian intensity distributions (resembling the probe) to a plane perpendicular to the incident electron beam for each atom in the cluster. This is sufficient to determine their projected area that is needed to calculate the total dose with Eq. (13). For the segmentation of the resulting images we obtain satisfying results by using a simple threshold based approach, using Otsu's method,⁶¹ followed by binary erosion with a disc-shaped structuring element.

Results

Determination Of Displacement And Sputtering Probability

In the following we use simulations to estimate displacement and sputtering probability curves and analyse dependencies on cluster size, species, temperature, and electron energy. With the knowledge of differential elastic scattering cross sections we aim to calculate displacement cross section values by using Eq. (4). Information about these relations help to develop techniques to avoid beam damage and may also be useful to estimate the influence of the beam in *in situ* heating experiments.^{10,62}

Clusters consisting of one of three different species were simulated: Au, Ag and Ni. Following Algorithm 1 (see Fig. 2) initially the cluster geometry has been placed and equilibrated on a substrate, which was considered to be rigid and flat. Used potentials are explained in more detail in the supplementary information.

After initial equilibration scattering events are generated from a uniform angular distribution between 0 and π . After another equilibration step the geometry is checked for displaced atoms and the cluster geometry is reset to the initial equilibrated configuration with new velocity vectors for each atom, generated from a Boltzmann distribution for the given temperature. This procedure is repeated until the desired maximum number of sampling electrons is reached ($n_{\text{max}} = 25000-50000$).

Displacements

First we explore the dependence of the displacement probability $P(\theta)$ (Eq. (4)) on different experimental parameters such as cluster sizes, temperatures, materials, and electron energies. Results are summarised in Fig. 3.

It follows directly from Eq. (2) that the probability for an atom to be displaced by an electron with energy E, which was scattered to an angle θ , increases with decreasing mass of the nucleus. This relation is also reflected in our results. It is remarkable, however, that no well defined sharp onset can be found for the displacement threshold energy, especially for Au clusters. On the one hand this fact can be explained with varying energy thresholds for different jump mechanisms. For surface atoms of Au clusters, threshold energy values were found in literature to be between 0.1 and $0.4 \,\mathrm{eV}$, 45,63 depending on their lattice sites. On the other hand also the thermal movement of atoms contributes. Vibrations of an atom affect its own displacement, which means that the atom gains more energy if it is displaced, while it moves parallel to the electron beam compared to the static case.³⁴

Values for the threshold energy can roughly be estimated from the displacement probability plots and Eq. (2). For this Au_{55} cluster a value of approximately 0.5 eV was obtained which complies with previously found values given above.

We also explored the influence of the cluster size on the displacement probability. A comparison of four different Ag cluster sizes is given in Figure 3b. The probability for a displacement increases with decreasing cluster size, except for the largest clusters comprised of 490 atoms. Interestingly, clusters of this size show a higher displacement probability over the full range of scattering angles compared to clusters with 309 atoms. The difference in displacement



Figure 3: (a) Displacement probability of cluster atoms, comprised of 55 atoms of 3 different species over the scattering angle of the scattered electron for an energy of E = 200 keV. (b) Displacement probability for different Ag cluster sizes over the scattering angle of the scattered electron; E = 300 keV. (c) Displacement probability for different electron energies over the scattering angle of the scattered electron for a cluster comprised of 55 Au atoms. Corresponding displacement cross sections σ_D are included for comparison. (d) Displacement probability for different cluster temperatures over the scattering angle of the scattered electron for a cluster comprised of 55 Au atoms.

probability between 116 and 55 atoms also appears to be remarkably small. This behaviour was observed in every simulation run and for Ag as well as for Au clusters. We explain these results with the existence of stability plateaus for certain cluster sizes (magic numbers). While clusters containing 55 or 309 atoms have a fully filled outer shell, clusters with 116 or 490 atoms have only a partially filled shell.⁶⁴ These non-closed shell clusters exhibit a higher number of weakly bound surface and edge atoms, which increases the overall displacement probability. Although these stability criteria are valid for unsupported clusters, this finding suggests that support interactions do not have a big influence on the magic numbers in our case.

The displacement probability is also highly dependent on the primary electron energy as shown in Figure 3c. Here, Au₅₅ clusters were illuminated with either 100, 200 or 300 keV electrons. It can clearly be seen that the displacement rate is significantly reduced by lowering the electron energy, which comes as no surprise. The mean displacement cross section σ_D of an atom in a supported Au₅₅ cluster can be calculated, by numerical integration of Eq. (4) over the full angular range. The resulting values are included in Fig. 3c for comparison. Interestingly, we find that reducing the electron energy from 300 keV to 200 keV has only little influence on σ_D in this certain case, because the increase of $P(\theta)$ with electron energy is almost completely compensated by the decrease of σ .

With the knowledge of the current density j and the cross section σ , the mean time period between two scattering events τ can be calculated:

$$\tau = \frac{1}{j \cdot \sigma} \tag{14}$$

With a typical current density in STEM of the order of $10^8 e^{-} nm^{-2} s^{-1}$ and the cross section for 300 keV we find that on average every few ms a displacement occurs in such a cluster under electron irradiation, which explains the high dynamics of small clusters under the electron beam in experiment (see Fig. 6).

This finding has important consequences on STEM analysis of such small clusters. Typically

several pixels are needed to represent an atomic column in a STEM data set (oversampling conditions). Considering a pixel time of several μ s for image acquisition or even several ms for spectrum image acquisition, the acquired intensity that is assignable to a single column is likely to vary while it is sampled by the electron beam. Accordingly, if beam induced displacements are too frequent, significant blurring is observed and single atomic columns may not be resolved any more. Such blurring effects can often be observed especially in the surface regions of clusters, where atoms are more likely to be displaced than in the centre. Furthermore, we studied the temperature dependency of displacement and sputtering, which is of special interest in the rapidly growing field of *in situ* TEM. The influence of the temperature is examined in Fig. 3d. Here a cluster consisting of 55 Au atoms has been equilibrated once and then used in every run (50000 electrons each), to eliminate the influence of slightly different geometries. The cluster was thermalised at three temperatures, 77 K, 300 K and 500 K, before the beam damage simulations were started. We see that the displacement probabil-

ity increases while the displacement threshold energy decreases with increasing temperature. Remarkably, however, we find that heat has only little influence on the displacement probability for temperatures less than 500 K. Cooling to liquid nitrogen temperatures ($\approx 77 \text{ K}$) also does not significantly reduce knock-on damage effects.

Although general trends remain valid, it has to be noted that the absolute values for displacement probabilities and cross sections greatly vary with the cluster geometry and can therefore only be directly compared with each other for a certain geometry.

Sputtering

Similar to the displacement probabilities determined in the previous section, we calculate the probability that an atom is permanently removed from the cluster after displacement. To determine whether an atom is sputtered we calculate the coordination number for each atom at the end of an equilibration run. If one or more atoms are found with a coordination number of zero they are considered as sputtered. An atom is also considered as sputtered if it leaves the proximity of the cluster during the equilibration step. Since sputtering events are much less likely than displacement events, it is difficult to give values for the sputtering probability as a function of the scattering angle as it was done in the previous section (Fig. 3). The computational effort would be very large to obtain sufficient statistics, especially for large clusters and heavy elements. Instead we only give general trends in this section. For Au clusters almost no sputtering is observed, even at the highest electron energy (300 keV) and the smallest clusters size (55 atoms). With these settings and 50000 simulated scattering events, only approximately 50 led to the loss of an atom, out of 18847 detected displacements. The minimum transferred energy for a sputter event was 3.6 eV. Similar to the displacement probability we found almost no difference for temperatures below 500 K, which leads us to the conclusion that the influence of thermal movement of atoms on the sputtering cross section is generally negligible in this temperature range. This finding seems to be reasonable, considering the large threshold energy for sputtering in comparison to thermal energies in the range of meV.

For Ag clusters on the contrary, sputtering is much more likely. For a size of 55 atoms and a beam energy of 300 keV, about 17% of all displacement events led to sputtering of an atom (4341 out of 25622 displacements). The threshold energy was found at 2.7 eV. This trend continues for Ni clusters, where for 25000 displacements about 9000 sputtering events are observed (36%). Here, the sputtering threshold energy was found at approximately 4 eV.

Evolution Of Clusters During Electron Beam Exposure

Simulations of the cluster evolution during electron beam exposure was performed using Algorithm 2 in Fig. 2. After each detection of a displacement the new configuration is equilibrated, instead of resetting the geometry after each displacement as done in Algorithm 1. During equilibration the temperature is increased from room temperature to 500 K to speed up the process. The new configuration is then used as a starting point for the next scattering event. Thereby, one possible evolution of the structure over time is simulated.

Evolution of Supported Au and Ag Clusters

To simulate the dynamics of electron irradiated clusters we chose Au and Ag as cluster material, because of their highly different sputtering probabilities. The clusters were generated randomly and equilibrated with a Metropolis Monte Carlo code. Then the clusters were placed on a randomly generated amorphous carbon substrate. The substrate interaction is calculated with a Lennard-Jones potential with corresponding parameter sets for Au-C and Ag-C.^{65,66} The dimensions of the substrate are 4x4x0.4 nm with a target density of $2000 \,\mathrm{kg}\,\mathrm{m}^{-1}$, which corresponds to approximately 650 carbon atoms. The primary electron energy was set to 300 keV. The minimum scattering angle was chosen under consideration of the sputtering probabilities obtained in the previous section. We chose a minimum scattering angle θ_{\min} in a way that the minimum energy $E_{t,\min}$ transferred to an atom was 0.4 eV for Ag and 1.0 eV (after Eq. (2)). Although, this choice of $E_{t,min}$ appears high compared to activation energies of surface diffusion it seems reasonable since we are mainly interested in the change in cluster size. No direct sputtering is expected below this energy for both Ag and Au, as shown in the previous section. We have to note, however, that we miss sputtering events where an atom is first displaced by a lower angle scattering event to a low-coordination site and subsequently sputtered by a second scattering event, which would result in an increased sputter rate compared to the experiment. This mechanism, however, appears to have only little influence on the sputter rate as demonstrated in the supplementary information (SFig. 2).

Figure 4 shows the evolution of a Au cluster, initially comprised of 350 atoms, under electron irradiation. The simulation included 61121 scattering events, which led to 6572 displacements, including 9 sputtering events. Despite the low sputter rate, the Au cluster exhibits significant morphological changes during the simulation, which complies with ex-



Figure 4: Transient evolution of a Au cluster initially consisting of 350 atoms under 300 keV electron irradiation, together with the corresponding Gaussian projection images and automatically determined contours. n is the number of electron scattering events in the simulation; n_0 is the corresponding no. of incident electrons, calculated with Eq. (13); scale bar is 2 nm.

perimental results.⁴ Significant dynamics of surface atoms is observed and a more flattened structure is formed.

Figure 5 shows the evolution of a Ag cluster initially consisting of 350 atoms for comparison. In this case the cluster shows significant sputtering effects and shrinks very rapidly. Initially the cluster shape becomes more flattened, resulting in an increased projected area (also visible in Fig. 7). It loses about 140 atoms within the first 6×10^4 simulated scattering events and completely dissociates after about 1.2×10^5 . The remaining nine atoms are detached from the substrate at once during the final scattering event.

Determining the projected areas and utilising Eq. (13) results in a total dose of 1.7×10^9 electrons applied to the cluster until it vanishes completely.



Figure 5: Transient evolution of a Ag cluster initially consisting of 350 atoms under 300 keV electron irradiation, together with the corresponding Gaussian projection images and automatically determined contours. n corresponds to the number of electron scattering events in the simulation; n_0 is the corresponding no. of incident electrons, calculated with Eq. (13); scale bar is 2 nm

Comparison with Experiments

orientation.

In order to compare simulation results with experimental data, we observe the dynamics of Ag and Au clusters under electron beam irradiation. We realised this via STEM HAADF time-lapse series of single, carbon supported clusters. The experiments were conducted with 300 keV primary electrons. Although, in experiment it is difficult to track single displacement events due to their high dynamics, we observe sputtering via the mass loss and accompanying decrease in cluster size and HAADF intensity.⁵ Data evaluation is done automatically with procedures described in the method section.

From our experiments we chose two image series, one from a Ag cluster and one from a Au cluster, consisting of 299 and 423 images, respectively. The beam current was measured by using the drift tube of our EELS spectrometer as a Faraday cup. Obtained values were 110 pA for Au and 78 pA for Ag. Pixel times of 2.4 µs and 3 µs were used for Au and Ag, respectively. With the probe current, the pixel time and the projected area of the cluster we can calculate the number of incident electrons on the clusters projected area during image acquisition. Integrated over the number of images we obtain the total dose that was applied to the clusters. Figure 6b shows the progression of HAADF intensity, extracted from each image and normalised to the maximum value in each series $I_{\rm max}$, as a function of the total dose. Note that because of this definition of the total applied dose, this quantity does not change linearly with the observation time if the projected area decreases due to mass loss. The Au cluster exhibits only little sputtering effects. The integrated intensity is reduced by about 20% within the observed time span. The cluster clearly changes its orientation with regard to the electron beam several times during data acquisition. The cluster rotation is obvious especially between image 98 and image 269, where it changes from [100] to [111]

In contrast, the Ag cluster is completely dissolved after a dose of approximately 5.6×10^9 incident electrons. Note that, while atomic columns can clearly be resolved for the Au cluster, we hardly see any contrast variations caused by the lattice in case of Ag, especially close



Figure 6: (a) Images chosen from HAADF time-lapse series for a Ag and Au cluster, respectively. The full series can be found in the Supporting Information. (b) Comparison of the integrated HAADF intensities in units of the maximum value, for each image in the time-lapse series over the total number of electrons applied to the cluster area. The orange rectangle starting at 4.4×10^9 electrons) marks the dose range that approximately corresponds to the simulated range (see Fig. 7 for comparison).

to the cluster surface. We explain this with the higher displacement rate for Ag compared to Au, as found in the simulations section. Nevertheless, single atoms are also visible occasionally for the Ag cluster (see yellow marks in Fig. 6).

Fig. 7 depicts a comparison of the change of the projected area in the experiment and in the simulation as a function of the dose. The experimental data is extracted from the region marked with a box in Fig. 6b. The direct comparison of experiment and simulation shows



Figure 7: Ag sputtering: Comparison of the projected areas of simulation and experiment; every 100th point is plotted from the simulation data for better visibility (11415 displacements in total). Experimental data is taken from the image series shown in Fig. 6. The dose off-set for the experimental series has been determined by an estimation of the clusters number of atoms, based on comparison with the size dependent areal density extracted from simulation data (see supplementary information for more details).

good qualitative agreement and also reasonable quantitative accordance. While in the simulation a dose of approximately 1.7×10^9 electrons is needed to dissolve a cluster comprised of 350 atoms, it takes 1.1×10^9 electrons for the same process in the experiment in this case. Overall the simulation tends to underestimate the sputter rate found in the experiment. The resulting discrepancy between simulation and experiment might have several origins:

• The substrate is considered as rigid in our simulations, which neglects dynamic interactions with the substrate and the effect of displacements of substrate atoms.

- Different surface configurations and the roughness of the substrate in the experiment likely influence its interactions with the cluster.⁵³ Such variations could give rise to enhanced two-step sputtering effects with lower activation energies, where atoms are first displaced to the substrate and subsequently sputtered to the vacuum. A similar mechanism has also been observed experimentally by Jones et al.⁵
- It has also been shown that jumps to metastable sites can be reversible on a time scale exceeding the equilibration time used in our MD simulations. Such jumps would introduce a dose rate dependency at low dose rates, violating our assumption of temporal independence of single scattering events.³¹
- The empirical potentials used to model interatomic forces in molecular dynamics are originally not designed for highly non-equilibrium processes like the ballistic motion of energetic atoms. Therefore, calculated forces might be less accurate at close interatomic distances.²⁶
- We extrapolate from the number of electrons that were simulated to the total amount of electrons, which also introduces some uncertainty.
- Due to dynamic scattering events (channelling) the displacement probability might vary for each atom in an atomic column.
- The automatic area determination in the experimental HAADF images introduces some uncertainty, especially for very small clusters due to their weak contrast and high noise levels. The blurred cluster edges, caused by the high mobility of surface atoms, further impede this procedure.
- The choice of the minimum scattering angle θ_{\min} also influences the sputter rate to some extend, as discussed previously. However, our findings suggest that other influences have a higher impact on sputtering. See the supporting information for details on this aspect.

Speed improvements of the code would help to enhance the quality of the simulation results because it would allow to consider larger angular ranges by lowering θ_{\min} and to fully include the dynamics of the substrate atoms. We therefore intend to include highly optimised MD codes in future versions of our code (eg. LAMMPS⁶⁷). Furthermore, it would also be advantageous to modify the used potentials in order to better account for close atomic distances²⁶ or to use *ab initio* MD codes if possible.

The largely different sputtering behaviour of Ag compared to Au is also reflected in selective removal of Ag in AgAu nanoalloys in experiments. See the supplementary information for a dataset demonstrating selective sputtering of Ag atoms in an AuAg Janus particle (SFig. 1). The supplementary information also contains the sources code that was used for the present work, written in Julia language.⁶⁸ Updated versions of the code are available upon request.

Conclusion and Outlook

We developed a scheme to simulate electron beam induced dynamics in metallic, nanoscaled systems and we applied our method to determine displacement and sputter rates for Ni, Ag and Au clusters. We also performed simulations of beam induced dynamics in Ag and Au clusters on an amorphous carbon support. Comparison with sputter experiments in the STEM showed good qualitative agreement and, to some extent, even quantitative information could be extracted. Simulations can also help to control the dosage in cluster experiments such as to avoid damage to the studied structures. Furthermore, electron-solid interactions are not intrinsic to the application of STEM on metallic clusters, the presented methodology could also be applied to other applications. However, further improvements in terms of the used potentials and calculation speed are necessary to be able to study beam induced dynamics in larger systems, such as surfaces, interfaces, amorphous materials, ⁶⁹ grain boundaries, or single atom diffusion on arbitrary surfaces.¹⁸ Further experiments applying HAADF quantification techniques might also provide more detailed experimental insight into

beam driven surface diffusion and sputtering processes.⁵

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Supplementary Information: Modelling electron beam induced dynamics in metallic nanoclusters

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Interatomic Potentials

In classical molecular dynamics, the force each atom exerts on its neighbours is modelled via empirical potentials. By choosing an appropriate model a trade-off between the computational effort and the proximity to reality has to be made. To model the interaction between metal atoms in our simulations, the semi-empirical Sutton-Chen many-body potential was chosen, since it is widely used for fcc-metals.¹ A modified parameter set was used, which accounts for effects in nanoscaled systems.²

To model the interaction of cluster atoms with the amorphous carbon (aC) support is a challenging task since the exact configuration of the substrate is not known. Local variations of morphology, adsorbed species and dangling bonds influence the interaction with the adsorbed metal atoms. Similarities in electronic structure between aC and graphite were reported in literature,^{3,4} which allows the assumption that sp² hybridisation is prevailing and that adsorption energies of metal atoms on aC are comparable to graphite rather than to diamond. Two different substrate models were used within this work.

For the simulation of displacement and sputter probabilities the substrate is modelled as rigid and flat. The force exerted by the substrate on each cluster atom is described using a one-dimensional potential, depending only on the distance z from the metal atom to the substrate's surface. For the interaction of Au atoms a modified Lennard-Jones potential was used, as suggested by Werner et al.⁴ (Eq. (1)).

$$U(z) = V_0 \left(\frac{297}{\left(\frac{z}{r_0} - 1.2\right)^{12}} - \frac{34.5}{\left(\frac{z}{r_0} - 1.2\right)^6} \right)$$
(1)

with $V_0 = 0.34 \,\text{eV}$ and $r_0 = 2.885 \,\text{Å}$.

To our knowledge there are no such parametrised potentials available in literature for other metals. Therefore, the interaction of Ag and Ni atoms with the carbon substrate was modelled using a Morse potential of the form given in Eq.(2).

$$U(z) = D_M \cdot \left(e^{-2 \cdot a_M(z - R_M)} - 2 \cdot e^{-a_M(z - R_M)} \right)$$
(2)

 R_M determines the position of the potentials minimum. The parameters D_M and a_M representing adsorption energies and potential widths were extracted from previous work.⁵⁻⁸ At the same time we ensured that the obtained cluster morphologies comply with experimental results.⁹⁻¹¹

For the calculation of cluster dynamics the substrate was modelled as a random arrangement of carbon atoms confined in a box with a given density of $2000 \,\mathrm{kg}\,\mathrm{m}^{-3}$.⁴ Although, in this model the substrate interaction is calculated separately for each pair of substrate and cluster atom, the positions of the substrate atoms were kept constant to reduce the computational load. Here, the forces between carbon atoms and metal atoms are modelled with a classical Lennard-Jones-(12,6)-potential:

$$U(r) = 4\epsilon \left[\left(\frac{R}{r}\right)^{12} - \left(\frac{R}{r}\right)^6 \right]$$
(3)

with ϵ being the depth of the potential in units of energy and R the position of the zero in units of length. For C-Ni, C-Ag and C-Au interactions these parameters are found in literature.¹²⁻¹⁴

Selective sputtering of Ag in AgAu Janus particle

The significantly increased sputtering cross section for Ag compared to Au leads to selective sputtering phenomena, as shown in SFig. 1. This figure shows an HAADF time-lapse series of a AgAu Janus particle. Under electron beam illumination with 300 keV electrons the Ag part shrinks rapidly while the Au part remains almost unchanged within the observed time span.

Influence of Choice of the minimum transferred energy in the dynamic simulation

SFig. 2 illustrates the influence of the choice of the minimum scattering angle θ_{\min} in the simulation, which directly determines the minimum transferred energy $E_{t,\min}$ in a scattering event (see Eq. (2)). The value in the main paper $E_{t,\min} = 0.4$ eV is compared with a higher value $E_{t,\min} = 1.0$ eV, that is fairly over the energy threshold for surface diffusion for a 350 atom Ag cluster at 300 keV electron energy. It can be seen that over the full range the sputter rate is slightly increased by lowering $E_{t,\min}$, which is explained with the increased



SFig. 1: HAADF time-lapse series of a AuAg Janus particle on an amporphous carbon support, demonstrating the selective sputtering of Ag with 300 keV electrons (302 images, 512x512 pixels, probe current: 53 pA, pixel time: 2.4 µs) with the corresponding integrated HAADF intensity curve

sputter probability for atoms that were displaced to lower-coordinated surface sites by a previous displacement event, caused by an energy transfer in the interval [0.4 eV,1 eV].

The dose that is needed to completely dissolve the cluster decreases from 1.8×10^9 electrons for $E_{t,min} = 1.0$ eV to 1.7×10^9 electrons for $E_{t,min} = 0.4$ eV, which is closer to the experimental determined value of 1.1×10^9 electrons in the paper.

Estimation of the cluster size from projected areas

Supported clusters exhibt a flattened geometry, which can be described by a truncated Wulffshape.¹⁵ The amount of flattening, however, depends on the cluster size and the strength of the support interaction and is in general not known. To be able to extract volumetric information from the projected images we, therefore, compare the areal density of similar sized, equilibrated clusters in the molecular dynamics simulation. Fig. 3 shows a plot of the number of cluster atoms as function of the corresponding projected areas, based on the simulation series of the dynamics of a Ag cluster, initially comprised of 350 atoms.

Assuming a spherical symmetry we would expect that the number of atoms is proportional to area^{3/2}. By fitting a power law $y = a \cdot x^b$ to the data we found that the atom number changes with area^{1.4} with a proportionality constant a = 35 in the simulation. This information was used to roughly estimate the number of cluster atoms in the HAADF image series by their projected area. Fig. 4 illustrates the mass loss of a Ag cluster under 300 keV electron irradiation in experiment and simulation, based on the projected area (as in Fig. 7 in the paper) and number of atoms in comparison.

Parameters for Cluster Synthesis

For cluster synthesis high purity helium (99.9999%) is expanded trough a 5 µm nozzle, which is cooled below 8 K. Evaporative cooling leads to droplet temperatures of $0.37 \, \text{K}$.¹⁰ Further collimation by a 400 µm skimmer results in the formation of a He nano-droplet beam. The



SFig. 2: Comparison of sputtering dynamics with different choices of the minimum transferred energy $E_{t,min}$ considered in the simulation. (a) Simulation with $E_{t,min} = 1.0$ eV. (b) The same simulation with $E_{t,min} = 0.4$ eV, that was used in the main paper. (c) Comparison of both sputtering simulations showing the number of cluster atoms as a function of the dose.



SFig. 3: Number of Ag atoms in the cluster in the sputter simulation as a function of the determined projected areas, with a power law fit $(y = a \cdot x^b)$

droplets pick up metal atoms as they pass a pick-up cell, where the desired metal is thermally evaporated. The metal atoms agglomerate inside the droplet forming clusters.



SFig. 4: Ag cluster sputtering: Comparison of simulation and experiment based on the projected area (top) and number of atoms

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