Abstract. We investigate the electron emission from clean monotonically flat crystalline aluminum surfaces due to the impact of rare gas atoms at the surface under grazing angles of incidence. Recent improvements of experimental methods allowed for the first time the measurement of electron yields as small as $\gamma \approx 0.01$ electrons/projectile. Using these methods kinetic electron emission (KE) was found for projectile velocities well below the classical threshold $v_{th}$ for KE, the minimum velocity a projectile has to have in order to transfer in a binary collision enough momentum to an electron at the Fermi edge (with $k = k_F$) to overcome the surface potential. Quantum mechanical effects smear out the Fermi edge creating electrons with momenta above $k_F$. We present a calculation of $\gamma$ in the below threshold region within the framework of a classical trajectory Monte Carlo simulation in which special emphasis is put on the description of the projectile trajectory and on an accurate determination of the momentum distribution, i.e. the Compton profile of the surface electronic structure. We employ different methods for calculating the electronic structure and study its influence on. We find that realistic momentum distributions can account for kinetic electron emission in the below threshold region.

1. Introduction
Impact of atoms or ions on surfaces leads to a number of processes depending on the projectile type and energy transfer channels (kinetic and potential). For specific choices of the experimental parameters many of these channels are closed which allows for detailed investigation of selected processes. We study the emission of electrons from aluminum surfaces due to the impact of slow atomic projectiles. In general, electron emission processes can be divided by the “type” of energy transferred from the projectile to the electron. This is either potential or kinetic energy leading to potential (PE) or kinetic emission (KE), respectively. The use of rare gas atoms in their ground state as projectiles eliminates contributions of PE to the so-called secondary emission coefficient $\gamma$. For slow projectiles the two most important contributions to KE are quasi-molecular promotion (QMP) and direct collisions between projectile and target electrons, i.e. excitation of electron-hole pairs in the conduction band of the surface material by binary collisions. Electron emission by QMP occurs upon close contact of projectile and target atoms, when electronic levels are shifted giving rise to electronic excitations at avoided crossings or promotion of occupied states above the vacuum level. In recent experiments Winter et al. scattered rare gas atoms with kinetic energies between 2 and 28 keV off atomically flat aluminum surfaces (terrace lengths $\sim 2000$ a.u.) under a grazing angle of incidence [1]. Within this setup projectile atoms move along well defined trajectories and are reflected from the surface with distances of closest approach large enough to exclude QMP. Therefore, binary collisions between...
projectiles and target electrons above the surface provide the most significant contribution to $\gamma$ [2]. Fig. 1 shows a schematic picture of a projectile trajectory in the experiments performed by Winter et al.

Kinetic emission (KE) of target electrons induced by projectile atoms was already explored in the late 1970s. In 1979 Baragiola calculated the projectile velocity threshold $v_{th}$ for KE due to collisions of projectile atoms with target electrons [3]. He considered a projectile entering a solid with a free electron gas of density $n_e$ in which the highest available electron momentum is the Fermi momentum $k_F$. From these target properties a threshold for the onset of KE was derived treating a head-on collision within the binary-encounter approximation. As $n_e$ is smaller above the surface (“spill-out”) an even higher velocity threshold was expected due to a “local” Fermi momentum [4]. Measurements of Winter et al. (fig. 2) show, however, electron emission even below the threshold for bulk $k_F$. Since Winter and Winter derived a $\gamma \propto (v - v_{th})^2$ proportionality in the threshold region [5], $\sqrt{\gamma}$ is plotted versus the projectile velocity $v_p$.

Although several processes have been proposed to explain below threshold KE [5–8], definitive conclusions as to the origin of KE near the threshold were still outstanding. Our model is based on the notion that in difference to the free electron gas model (sharp Fermi edge) the momentum distribution of metal electrons is not bounded from above by $k_F$ but, instead, contains off-shell components with $k > k_F$ due to correlation (interaction with other metal electrons) and corrugation (influence of the crystal structure) effects. Different methods of calculating such momentum distributions within the framework of density functional theory (DFT) are presented in section 3.

As the distance of closest approach strongly influences the expected KE yield ($\gamma \propto n(z) \propto n_{\text{bulk}} \cdot e^{-\alpha z}$), another prerequisite for the determination of $\gamma$ at different projectile velocities is an accurate description of the projectile trajectory. Our method to determine projectile-surface potentials governing these trajectories is described in section 2. Finally, a classical trajectory Monte Carlo (CTMC) simulation of KE due to binary collisions of projectile atoms with target electrons including electron transport from the point of excitation to the detector is explained in section 4 with its results presented and discussed in section 5.
Figure 2. Results of a KE measurement for Ar atoms scattered off an Al(111) surface. The arrow indicates Baragiola’s threshold. The line is a best fit to experimental data for larger projectile velocities according to a quasi-classical estimate [5].

2. The projectile surface potential
An appropriate test for the reliability of the projectile-surface potential is the comparison of classical trajectory simulations with rainbow scattering experiments. In these experiments projectiles are directed at the surface under a grazing angle of incidence and along a low indexed crystal direction. The small incidence angles lead to widely disparate kinetic energies parallel \( E_\parallel \) and normal \( E_\perp \) to the surface. The fast motion along low indexed crystal directions makes the projectile experience an effective two-dimensional atomic string potential of approximately sinusoidal shape. This shape leads to characteristic intensity distributions in the reflected atomic beam. Fig. 3 shows the schematic experimental setup with the measured intensity distribution of an 18 keV Ar beam directed onto an Al(111) surface \( (E_\perp \approx 10 \text{ eV}) \) along the \( \langle 1\overline{1}0 \rangle \) direction. The two intensity maxima at the edge of the distribution represent the rainbow peaks located at the rainbow angle \( \theta_{rb} \). For inert gas atoms \( \theta_{rb} \) depends solely on the projectile’s kinetic energy perpendicular to the surface. This dependence is very sensitive to the potential landscape above the aluminum surface and, hence, a good benchmark for the quality of projectile-surface potentials. We calculated the projectile-surface potential by considering the static limit of the collision complex consisting of the projectile and the target surface [9]. To this end we performed DFT slab calculations with periodic boundary conditions using the Abinit program package [10].

From classical trajectory simulations we determined the rainbow angles for Ar projectiles directed onto an Al(111) surface. Fig. 4(b) shows the near-perfect agreement of simulated and experimental results for \( \theta_{rb}(E_\perp) \). Especially in the low energy region, i.e. at large distances from the surface, there is a considerable improvement to earlier calculations in which the projectile-surface potential was approximated by a sum over two-body potentials, see fig. 4(a) [11].

In the kinetic electron emission experiments the inert gas projectiles are directed at the surface along a “random” (high indexed) direction. The projectiles experience a planar averaged surface potential, solely depending on the distance parallel to the surface normal. For our KE simulations we used the planar averaged DFT projectile-surface potentials.
Figure 3. Schematic picture of the scattering geometry. The 2D intensity distribution on the
detector plane arises from scattering of 10 keV Ar atoms from Al(111) along the \langle 1\bar{1}0 \rangle
direction at an angle of incidence $\phi_{\text{in}} = 2.35^\circ$. This corresponds to an energy perpendicular to the surface
of $E_\perp \approx 16.81$ eV.

Figure 4. Rainbow angles as function of normal component of kinetic energy for Ar atoms
scattered from Al(111) along low indexed directions. Symbols: experimental data for different
total kinetic energies [11]. Curves: results from trajectory simulations based on (a) the O’Conner
Biersack (OCB) potential [12] and (b) on Ar-Al(111) potentials from ab-initio DFT slab-
calculations [9].
Figure 5. Lateral cut through the momentum distribution $\rho(\vec{k}_{||}, z)$ at a distance of $z = 1$ a.u. in front of the topmost atomic layer of an Al(111) surface (logarithmic color code).

3. Momentum distributions above Al surfaces

Experiments showed that electron emission induced by projectile electron collisions occur well below Baragiola’s threshold velocity for the projectile $v_{th}$. In his estimate for $v_{th}$ he assumed the highest available electron momentum to be $k_{max} = k_{F}^{bulk}$. We conclude that the free-electron gas approximation is not sufficient to explain so-called sub threshold kinetic electron emission and suggest the use of more realistic momentum distributions taking into account many-particle effects (correlation) and a structured crystal potential featuring off-shell momentum components $k > k_{F}^{bulk}$. The momentum distributions above the Al(111) surface, i.e. the Compton profiles, are extracted from Kohn-Sham (KS) wave functions of ab-initio DFT slab calculations by corresponding Fourier-transforms [13]. In general, the KS pseudo-wave functions are not to be identified with the true wave functions and, therefore, it is a priori not obvious that the electron density $n_e(\vec{r})$ and the momentum density $\rho(\vec{k})$ are Fourier transforms of each other. In the following we postulate the applicability of the KS pseudo-wave functions which can be justified for the homogeneous electron gas. Its extension to realistic DFT calculation for surfaces can be viewed as an analogue of the local-density approximation to the exchange-correlation potential. Performing Fourier transforms of the KS wave function only for the coordinates parallel ($x, y$) to the surface yields the distance-dependent partial momentum distribution $\rho(\vec{k}_{||}, z)$. Fig. 5 shows a lateral cut through $\rho(\vec{k}_{||}, z)$ at a distance of $z = 1$ a.u. The hexagonal structure of the surface unit cell results in six humps at wave numbers of about $k_{||} = 2\pi/a_{nn}$ with $a_{nn} \approx 5.4$ a.u., the nearest neighbor distance for the Al(111) surface.

$\rho(\vec{k}_{||}, z)$ features small but finite momentum components above the surface larger than the Fermi momentum of bulk aluminum $k_{F}^{bulk} \sim 0.9$ a.u. Due to Heisenberg’s uncertainty principle information about the $z$-dependence comes at the price of giving up any knowledge about the momentum component $k_z$. Since for grazingly incident particle beams high momentum components parallel to the surface are expected to be responsible for sub-threshold KE in head-on collisions with maximum momentum transfer $\rho(\vec{k}_{||}, z)$ should be well suited to account for the onset of KE.
We also parameterized the momentum distribution above the surface by a $z$-dependent spherically symmetric Fermi distributions at high temperatures $\rho_{\mu,T}(\vec{k}, z)$. High temperatures lead to smearing of the Fermi edge and, therefore, to momentum components $k > k_F^{\text{bulk}}$. The $z$-dependence is introduced via an effective local temperature $T_{\text{eff}}(z)$ and an effective local chemical potential $\mu_{\text{eff}}(z)$. Note that $T_{\text{eff}}(z)$ and $\mu_{\text{eff}}(z)$ are not to be seen as physical temperature or chemical potential, respectively. They are fit parameters. In this sense $T_{\text{eff}}(z)$ can be interpreted as a measure for corrugation and correlation effects and $\mu_{\text{eff}}(z)$ plays the role of a $z$-dependent or local Fermi energy [5]. Both parameters are chosen such that $\rho_{\mu,T}(k||, z) = \int \rho_{\mu,T}(\vec{k}, z)d\vec{k}d\varphi_k$ fits best to the partial momentum distribution $\rho(k||, z) = \int \rho(\vec{k}, z)d\varphi_k$, where $\varphi_k$ is the azimuthal angle in momentum space.

As a third variant for the description of a locally varying momentum distribution we use the Husimi function $\rho_{H}^z(\vec{k}, z)$ [14], the closest analog to the classical phase space distribution consistent with Heisenberg’s uncertainty principle. It is calculated by averaging the Wigner function [15] over a Gaussian wave packet with minimum uncertainty.

4. **Kinetic electron emission simulation**

In the CTMC simulations scattering events between projectiles and surface electrons are treated within the binary-encounter approximation by neglecting, for the time of the collision, the influence of surrounding particles. This is justified in our simulation due to the large distance between single electrons. The Wigner-Seitz radius at a distance of $z = 1$ a.u. above the surface is $r_s \approx 2.3$ a.u. Initial electron momenta $k$ are selected randomly from the Compton profiles discussed in sec. 3 and the scattering angle $\vartheta$ is randomly chosen from the differential elastic scattering cross section $\frac{d\sigma^{el}}{d\vartheta_0}(\vartheta, E)$.

Electrons excited by the scattering event to energies above the vacuum level propagate close to the surface and may eventually leave the target. Within an electron propagation calculation [16] the trajectories of these particles are modeled individually to determine whether they leave the aluminum crystal or deposit their excess energy within the solid. We find that only a minor fraction (25%) of electrons excited to energies above the vacuum level leave the surface and contribute to the measured KE yield.

Note that all distribution in sec. 3 feature initial electron momenta with kinetic energies (but not total energies) above the vacuum level. This is not a surprise since even in a classical picture electrons may reach high velocities close to the nucleus but remain bound. A well-known quantum mechanical example is the electron momentum distribution $\rho(p) \propto (1 + p^2)^{-4}$ of the hydrogen atom with very large momenta which can be made visible (“put on shell”) in ionization experiments [17]. Due to Heisenberg’s uncertainty relation it is only possible to calculate partial, i.e. planar averaged (in real space), momentum distributions from KS wave functions. This, however, leaves high $k$-components in our distributions which are not balanced by the local potential $V_{el}(\vec{r})$ or its planar averaged version $V_{el}(z)$ which in turn leads to “auto-emission” (i.e. spontaneous emission in the absence of interactions) for electrons with initial energies above the vacuum level. In order to estimate the effect of “auto-emission” we performed calculations for the limiting cases in which electrons with initial energies above the vacuum level are fully taken into account or are completely neglected.

5. **Results and Discussion**

Fig. 6 show experimental data of $\sqrt{\tau}$ as a function of the projectile velocity for argon atoms impinging on an aluminum (111) surface under an angle of incidence of $\phi_{\text{in}} = 2.2^\circ$ and results of KE simulations in which the three momentum distributions of section 3 are used. In each figure two lines are plotted corresponding to the limiting cases in which “auto-emission” is allowed or suppressed.
Figure 6. Lines: Secondary kinetic electron emission yields with respect to the projectile velocity calculated with the momentum distributions (a) $\rho(\vec{k} ||, z)$, (b) $\rho_{\mu,T}(\vec{k}, z)$, and (c) $\rho_H^\sigma(\vec{k}, z)$. Points: experimental data. Dashed vertical lines at $v_p \approx 0.08$ a.u. indicate the classical threshold for KE.

Due to the high $k$-tails, all distributions feature sub threshold kinetic electron emission caused by binary-encounter processes with atomic projectiles. However, without a more elaborate method to treat electrons with initial energies above the vacuum level a quantitative analysis of sub threshold KE remains an open problem.

At low velocities $v_p < 0.12$ a.u. calculated yields compare well with experimental results when discriminating against auto-emission. At high velocities $v_p > 0.12$ a.u. the distributions lead to a quadratic rise of the yield $\gamma = \alpha v_p^2$ similar to experimental values. The proportionality $\alpha$, however, differs by up to a factor 4. Tests showed that in the high velocity region even a $z$-independent momentum distribution equal to the bulk Fermi distribution cannot account for the increase of $\gamma$. The difference between measured and calculated yields has, therefore to be related to electron emission channels not treated in this work.

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