Collision-enhanced plasmonic electron acceleration in small metal clusters

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Abstract. Transient nanoplasmas in laser-excited metal clusters open the route to probing ultrafast collisional and collective laser–plasma processes in a wide and well-tunable range of densities and temperatures. The transition from a fully degenerate to a nearly classical plasma can occur within a few femtoseconds, accompanied by fundamental changes in the relaxation processes driven by electron–electron collisions (EECs). To investigate the resulting implications for laser–metal–cluster interactions, we developed an extended semiclassical Vlasov–Uehling–Uhlenbeck approach where the collision term resolves time-dependent Pauli blocking and local screening effects for arbitrary levels of degeneracy. Our simulation results for resonant dual-pulse excitations of Na_{55} reveal an unexpected synergy effect of EECs and collective laser–plasma processes, i.e. a strongly enhanced electron acceleration via plasmon-assisted rescattering in the presence of EECs.

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1. Introduction

Simple metal clusters provide deep insights into the structure and dynamics of finite Fermi systems [1, 2]. Quantum confinement effects such as electronic shell structure and spectral fragmentation of plasmons can be explored over a wide size range [3, 4]. Almost ideal electronic-level quantization of valence electrons in angular momentum eigenstates has recently been observed on small sodium clusters [5], stunningly justifying the picture of a degenerate nanometer-sized gas of nearly free electrons. The pronounced and spectrally well-confined plasmonic-field enhancement effects resulting from collective electron excitations (Mie plasmons) [6] are relevant for many applications, including nanoantennas for solar cells [7], laser-assisted growth of metallic particles [8, 9] and localized heating of biological tissues [10]. When exposed to intense laser fields, the time-dependent plasmon energy of expanding metal clusters even allows the control of resonance-enhanced laser–cluster interactions for generating energetic electrons or highly charged ions [11–13]. A detailed understanding of the excitation dynamics is thus of both fundamental and practical interest [14].

This study focuses on the impact of electronic degeneracy effects on the response of metal clusters in intense fields. By adjusting laser parameters, the temperature and density of free electrons in laser-driven metal clusters can be varied over a wide range, making them valuable nanoscale laboratories for nonlinear heating and ionization of finite Fermi systems with a tunable level of degeneracy. In a plasma, the latter is typically described by the degeneracy parameter \( \Theta = k_B T_e/\epsilon_F \), where \( T_e \) and \( \epsilon_F = (\hbar^2/2m_e)(3\pi^2n_e)^{2/3} \) are the electron temperature and the Fermi energy respectively (\( n_e \) and \( m_e \) denote the density and mass of electrons). When driven by a strong laser field, heating, electron thermalization and relaxation depend on the level of degeneracy because of two major effects: (i) electron–electron collisions (EECs) obey the Pauli exclusion principle and are thus perfectly blocked in a fully degenerate state (\( \Theta \ll 1 \)), become active at partial degeneracy (\( \Theta \approx 1 \)), and fully contribute in the classical limit (\( \Theta \gg 1 \)); (ii) the level of degeneracy determines the screening properties of the in-medium electron–electron Coulomb interaction and thus the electron–electron scattering cross sections. In the limiting cases, the Thomas–Fermi screening (zero temperature) describes the
fully degenerate quantum state, whereas Debye screening applies in the classical regime. All intermediate partially degenerate states occur transiently in intense laser–cluster interactions and need to be resolved in (i) and (ii) consistently for an in-depth microscopic analysis of the dynamics.

A well-established tool for resolving binary collisions of Fermi particles in time-domain simulations is the semiclassical Vlasov–Uehling–Uhlenbeck (VUU) approach, where a collision term with Pauli blocking factors is added to a Vlasov-type mean-field kinetic transport equation. This strategy has been used successfully for decades in nuclear and cluster physics \[2, 14, 15\]. However, while (i) Pauli blocking effects have been studied for laser–cluster interactions \[16–19\] and dense Coulomb systems \[20\], the impact of (ii) the evolving degeneracy on the response via the cross sections for EECs has not yet been resolved and is the subject of the present analysis.

As the main methodical achievement of this work, we developed an extended VUU-DT code that includes the full density and temperature evolution (as indicated by the additional letters ‘DT’) in the blocking factors and the cross sections simultaneously. The extended VUU-DT scheme utilizes a self-consistent evaluation of the scattering cross sections based on the time-dependent local plasma properties. This concept was originally introduced for collisions in nuclear matter by Alm et al \[21\]. The key idea is to use scattering cross sections for a local screening length that, for our case, depends on the local electron density and temperature in the nanoplasma. An effective Fermi gas model is utilized to evaluate the local screening length self-consistently for arbitrary levels of degeneracy.

To investigate the effects of the extended treatment of collisions, we analyze the response of small sodium clusters for pump–probe excitations with intense near-infrared femtosecond laser pulses. The considered laser intensity corresponds to the regime where internal plasmonic fields are equally strong or even stronger than the laser field, such that pronounced plasmonic effects are expected. Results are compared for different levels of refinement, i.e. for (i) the fully EEC-free case (Vlasov), (ii) conventional EECs with blocking and fixed velocity-dependent cross sections (VUU) and (iii) self-consistent density- and temperature-dependent EEC cross sections (VUU-DT). We find that the full treatment within the VUU-DT approach always leads to a moderate increase of plasma heating when compared with the Vlasov and VUU calculations, whilst the evolution of global observables such as absorption or net ionization remains qualitatively unchanged. In contrast, strong changes are found in the energy- and angular-resolved electron emission, where collisions lead to exponential but still highly anisotropic spectra. Most importantly, we find that collisions support the electron acceleration via surface-plasmon-enhanced rescattering of electrons \[13\], demonstrating a surprising synergy effect of collisional and collective plasma processes.

The rest of this paper is organized as follows. In section 2, we briefly review key aspects of the semiclassical Vlasov and VUU approaches and describe the extended treatment of electron–electron scattering in the VUU-DT scheme. The details of evaluating the self-consistent local screening length for arbitrary degeneracy are the subject of section 2.3. Section 3 contains the numerical results on resonant dual-pulse excitations of Na\(_5\), with a detailed discussion of the evolution of global observables (section 3.1), the analysis of angular- and energy-resolved electron spectra (section 3.2) and a time-resolved trajectory analysis of the plasmon-enhanced electron acceleration mechanisms (section 3.3). The conclusions drawn are presented in section 4.
2. Methods

2.1. The Vlasov and Vlasov–Uehling–Uhlenbeck equations

The starting point for the semiclassical description of the electron dynamics is the VUU equation

$$\frac{\partial}{\partial t} f + \frac{\mathbf{p}}{m_e} \cdot \nabla_r f - \nabla_p f \cdot \nabla_t V_{mf}(\mathbf{r}, t) = I_{UU}. \quad (1)$$

The left-hand side of (1) contains the kinetic transport terms (the Vlasov equation) for the one-body electron phase-space distribution $f(\mathbf{r}, \mathbf{p}, t)$ and describes the collective electron dynamics in semiclassical mean-field approximation ($\hbar \to 0$) [2, 14, 15, 19]. Here $V_{mf}$ denotes the self-consistent electron mean-field potential. The collision term $I_{UU}$ on the right-hand side describes binary EECs emerging from short-range interactions that are missing in the pure mean-field treatment. The Uehling–Uhlenbeck (UU) collision term [22] for interacting fermions reads

$$I_{UU}(\mathbf{r}, \mathbf{p}) = \int \int \frac{\left| \mathbf{p} - \mathbf{p}_1 \right|}{m} \frac{d\sigma^{(1)}(\theta, \left| \mathbf{p} - \mathbf{p}_1 \right|/m_e)}{d\Omega} \times \left[ f_p f_{p_1}(1 - \tilde{f}_p)(1 - \tilde{f}_{p_1}) - f_p f_{p_1}(1 - \tilde{f}_p)(1 - \tilde{f}_{p_1}) \right] d\Omega d\mathbf{p}_1. \quad (2)$$

The Markovian UU collision term represents a local gain–loss balance for elastic electron–electron scattering $(\mathbf{p}, \mathbf{p}_1) \leftrightarrow (\mathbf{p}, \mathbf{p}_1')$, with the velocity-dependent differential cross section $d\sigma^{(1)}(\theta, \mathbf{v}_{el})/d\Omega$ in the center-of-mass frame of the colliding electrons, the local phase-space densities $f_p = f(\mathbf{r}, \mathbf{p})$ and the Pauli blocking factors in parentheses as functions of the relative phase-space occupation for paired spins $\tilde{f}_p = \frac{(2\pi\hbar)^3}{2} f_p$. The integration over $\Omega$ runs over all deflection angles $(\mathbf{p} \to \mathbf{p}')$ in the center-of-mass frame, fixing the remaining momentum $\mathbf{p}_1'$ via the constraint of momentum conservation of the colliding electrons.

A subtle but important aspect arises from the fact that collisions between indistinguishable particles are considered. The cross section $\frac{d\sigma^{(1)}}{d\Omega}$ must be defined in a certain way to ensure the formal correctness of the collision term, i.e. as a cross section for the particle loss in one of the incident channels (therefore the superscript in the cross section). The importance of this requirement, which is discussed thoroughly in [23], has frequently been overlooked. Considering the flux due to the second term in square brackets in (2), the cross section has to quantify the loss rate only in the incoming scattering channel $f_p$, and not the total loss rate in both incoming channels (which is twice as high). Equivalently, when focusing on the gain due to the first term in square brackets in (2), the gain rate in the outgoing scattering channel $f_{p_1}$ has to be equal to the loss in one of the incoming channels, e.g. for $f_{p'}$. The total flux of particles scattered into the element of solid angle $d\Omega$, which is the usual meaning of differential cross sections for identical particles, would be twice as high. We return to the different meanings of both pictures in section 2.2.

Coming back to the general features of the dynamics described by equations (1) and (2), the Vlasov description is recovered asymptotically in the limit of weak excitations as the collision integral vanishes in the ground state at zero temperature, due to full Pauli blocking. This can be seen by noting that $\tilde{f}$ is unity (fully occupied phase space) in at least one of the outgoing phase-space channels for the gain as well as the loss term, which therefore both vanish. The pure Vlasov dynamics follows from setting the collision term to zero at all times.

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For both the Vlasov and the VUU case, we consider a self-consistent mean-field potential of the form

$$V_{\text{mf}}(r) = \sum_i V_{\text{ion}}(r - R_i) + V_{\text{Har}}[n_e] + V_{\text{xc}}[n_e] + e E(t) \cdot r,$$

containing the sum over the ion potentials for the present configuration $R_i$, the electron Hartree potential $V_{\text{Har}}$, the exchange-correlation potential $V_{\text{xc}}$ in local-density approximation (we use the parameterization of [24]) and the laser field in dipole approximation via the last term. Note that $e$ is the elementary charge unit. The Hartree term and the exchange-correlation potential are functionals of the actual total electron density $n_e(r, t) = \int d^3p \, f(r, p, t)$. To avoid the numerically expensive propagation of strongly localized states, only valence electrons are treated explicitly in the model, while the interaction with nuclei and core electrons is described by a local pseudopotential. Note that electron–ion collisions are accounted for via the inclusion of the ionic structure in the effective potential.

For the present study on sodium clusters we use the pseudopotential from [25]. Furthermore classical motion is assumed for the ions. The initial ion geometry, and the corresponding electron phase-space distribution, is determined using the self-consistent Thomas–Fermi ground state with paired spins at zero temperature [14, 17]. The mean-field part of the dynamics is solved by the well-known pseudoparticle method (for details see [19, 25]), employing the particle-mesh technique in combination with a parallelized iterative multigrid Poisson-solver. The combination of these methods yields a linear scaling of the numerical load with system size.

2.2. Scattering cross sections for a screened Coulomb interaction

To determine EEC cross sections, the short-range in-medium interaction between two electrons in the cluster is modeled by a statically screened Coulomb potential

$$V_{\text{sc}}(r) = \frac{e^2}{4\pi \varepsilon_0} \frac{\exp(-r/r_0)}{r},$$

where $r_0$ denotes the screening length. The determination of the latter is described in section 2.3. To obtain the electron scattering cross sections we solve the stationary Schrödinger equation $[\Delta + k^2 - \frac{2\mu}{\hbar^2} V_{\text{sc}}(r)] \psi(r) = 0$ in the electron center-of-mass frame with the standard ansatz $\psi(r) = \exp(ikz) + f(\theta) \exp(ikr)/r$, where $k$ is the asymptotic wavenumber and $\mu$ is the reduced mass. We employ the amplitude-phase method [26, 27] to determine the complex scattering amplitude $f(\theta)$ for given values of $k$ and $r_0$. Note that the differential cross sections for singlet (S) and triplet (T) configurations (symmetric and antisymmetric spatial wave functions) follow as

$$\frac{d\sigma_{S,T}(\theta)}{d\Omega} = |f(\theta) \pm f(\pi - \theta)|^2.$$  

Viewed in the center-of-mass frame of the colliding particles, this specifies the total flux of scattered particles into the element of solid angle $d\Omega$ for a given spin configuration. The cross section for unpolarized spins follows as the average over such configurations as

$$\frac{d\sigma(\theta)}{d\Omega} = \frac{1}{4} \frac{d\sigma_S}{d\Omega} + \frac{3}{4} \frac{d\sigma_T}{d\Omega}.$$
Figure 1. Total scattering cross section $\sigma_{\text{tot}}$ for elastic EECs (spin averaged for unpolarized spins) as a function of the relative velocity for different screening lengths $r_0$: full numerical solution (solid) and the first Born approximation (dashed).

The resulting total cross section is defined by

$$\sigma_{\text{tot}} = \int d\sigma(\theta) d\Omega,$$

quantifying the total rate of scattered indistinguishable particles, or equivalently, the rate of deflected incoming particles. As a consequence, both of the colliding electrons are counted in this form. For the evaluation of the UU collision term, however, we require a cross section $d\sigma^{(1)}(\theta)/d\Omega$ for the loss in only one of the incident channels. According to [23], this is achieved by rescaling the total and differential cross sections as

$$\sigma^{(1)}_{\text{tot}} = \frac{1}{2} \sigma_{\text{tot}} \quad \text{and} \quad \frac{d\sigma^{(1)}(\theta)}{d\Omega} = \frac{1}{2} \frac{d\sigma(\theta)}{d\Omega}. \quad (8)$$

Figure 1 displays the total scattering cross sections ($\sigma_{\text{tot}}$ without rescaling) as a function of the relative electron velocity for selected values of the screening length $r_0$. Note that the cross sections increase strongly with the increasing screening length, are nearly constant at small velocities and begin to decrease substantially for electron velocities beyond 10 Å fs$^{-1}$. At high velocities, the results agree well with the predictions of the first Born approximation (see dashed lines).

2.3. Density- and temperature-dependent local screening length

The next step towards utilizing the extended treatment of collisions is the determination of the local screening length in (4). To this end, we assume local thermal equilibrium of the electronic system, and determine the electron density $n_e(r, t)$ and the drift-corrected local mean electron kinetic energy $\tilde{u}_k(r, t)$ from the phase-space distribution $f(r, p, t)$ in each time step of the
simulation. The mean local electron kinetic energy is determined in the local rest frame of electrons via

$$\tilde{u}_k(r, t) = \frac{1}{n_e(r, t)} \int d^3p \ f(r, p, t) \frac{|p - \langle p(r, t) \rangle|^2}{2m_e},$$

(9)

with the mean local momentum

$$\langle p \rangle = \frac{1}{n_e} \int d^3p \ f(r, p, t) \ p.$$

(10)

The removal of the drift motion via subtraction of the mean momentum $\langle p \rangle$ is particularly important for strong collective motion of a cold electron cloud. Neglecting the correction would lead to artificial oscillations of the predicted temperature.

From $n_e$ and $\tilde{u}_k$ the local temperature and finally the local screening length $r_0(r, t)$ are found by applying ideal Fermi gas theory from equilibrium quantum statistics. This concept has proved useful for investigating heavy-ion reactions in nuclear physics [21] and is applied here for the first time to the plasma dynamics in metal clusters. The local Fermi gas model is fully consistent with the Thomas–Fermi description of the initial electronic ground state of the cluster.

Within ideal Fermi gas theory [28], all important properties can be expressed by Fermi integrals

$$I_n(\mu/k_B T) = \frac{1}{\Gamma(n+1)} \int_0^\infty ds \ \frac{s^n}{\exp(s - \mu/k_B T) + 1},$$

(11)

where $\mu$ is the chemical potential, $k_B$ is the Boltzmann constant and $\Gamma$ is the Gamma function. In particular, the electron density $n_e$ and the mean kinetic energy per electron $u_k$ are defined by

$$n_e = \frac{2}{\Lambda^3} I_{1/2}(\mu/k_B T),$$

(12)

and

$$u_k = \frac{3k_B T}{n_e \Lambda^3} I_{3/2}(\mu/k_B T),$$

(13)

where $\Lambda = \sqrt{2\pi \hbar^2 / m_e k_B T}$ is the thermal wave length.

For a given set of $n_e$ and $u_k$, the local temperature $T$ and the chemical potential $\mu$ are uniquely defined and can be determined by iterative numerical inversion of equations (12) and (13). For the non-interacting Fermi gas with arbitrary degeneracy, linear screening theory yields the screening length

$$r_0 = \left[ \frac{e^2}{\varepsilon_0 k_B T \Lambda^3} I_{-1/2}(\mu/k_B T) \right]^{-1/2},$$

(14)

as shown in figure 2 for selected values in the density–temperature plane (blue solid curves).

In the highly degenerate quantum regime, i.e. at low degeneracy parameters (low temperature, high density), the screening length depends only on the density and converges to the Thomas–Fermi screening length

$$r_{TF} = \sqrt{\frac{\hbar^2 \varepsilon_0}{e^2 m_e}} \left( \frac{\pi^4}{3n_e} \right)^{1/6}$$

(15)
in the limit \( \Theta \to 0 \) (see dotted violet lines in figure 2). In contrast, the screening length becomes density- and temperature-dependent in the partially degenerate regime (\( \Theta \approx 1 \)) and converges to the Debye length

\[
r_D = \sqrt{\frac{k_B T e_0}{e^2 n_e}}
\]

for weak degeneracy (\( \Theta \gg 1 \)) (see dashed violet lines in figure 2). Note that strong deviations from both asymptotic behaviors and a transition between them are found in the regime of partial degeneracy, making the use of the full Fermi gas theory indispensable.

To indicate the screening-length range relevant for the present study, figure 2 displays a typical trace of the electron density and temperature for a dual-pulse laser excitation of a small metal cluster (Na\(_{55}\)), as calculated with the extended semiclassical VUU-DT approach. Departing from \( \Theta \approx 0 \) and the ground-state density, the non-resonant first pulse (photon energy well below the Mie plasmon resonance) heats the electron system to a state with partial degeneracy of \( \Theta \approx 1 \). Subsequent ionic expansion lowers the electron density and allows...
resonant plasmon heating by the second pulse, driving the system into the classical regime of $\Theta \gg 1$. The nanoplasma undergoes rapid transitions between the quantum and classical plasma regimes during the interaction process, demonstrating the requirement of applying the screening length from the Fermi gas expression in (14).

2.4. Implementation of the collision term

To implement the above concepts in the simulation, the electron density $n_e$ and local drift-corrected mean electron kinetic energy $\tilde{u}_k$ are sampled from the swarm of test particles on a grid. In this study, we used a mesh size of $\Delta x = 1 \, \text{Å}$ and a cubic simulation volume with $N_{\text{grid}} = 257^3$ cells. The local temperature distribution $T(r, t)$ is found by interpolation using a look-up table for $T(n_e, \tilde{u}_k)$ to avoid the tedious inversion of equations (12) and (13) for each cell. We further define a global temperature as a density-weighted average of the temperature profile via

$$T_{\text{glob}}(t) = \frac{1}{N_e} \int d^3r \, n_e(r, t) T(r, t).$$

(17)

A second look-up table $r_0(n_e, T)$ is used to find the local screening length. Finally, the velocity-dependent total and differential scattering cross sections are stored in a third large look-up table for the relevant screening length range. It should be emphasized that the use of this series of look-up tables is crucial for an efficient implementation of the extended collision scheme.

In each time step, neighboring test particle pairs are identified using the cell-index method [29]. A test particle pair is tested for a potential collision event, if the time of closest approach lies within the current time step. In this case, the distance of closest approach $b_{\text{min}}$ is determined and the total single-channel cross section $\sigma_{\text{tot}}^{(1)}$ is sampled for the respective relative electron velocity and local screening length from the look-up tables. A collision event is considered if

$$b_{\text{min}} \leq \sqrt{\frac{\sigma_{\text{tot}}^{(1)}}{\pi N_s}}.$$  

(18)

Note that the cross section has to be rescaled by the test-particle sampling factor $N_s$. Here we use $N_s = 10^4$. This rescaling is of central importance to the feasibility of the method, as a high test-particle sampling reduces the maximum impact parameter and therefore ensures the effective locality of the collisions via the resulting cutoff radius, within which test-particle pairs need to be tested.

In the next step, each collision event still under consideration is counted as kinematically possible and the deflection angle is determined via Monte Carlo sampling from the differential scattering cross section. The final step is a Monte Carlo-based decision of the acceptance of the collision event, according to the acceptance probability given by the blocking factors for the outgoing momenta of the colliding test particles (see (2)). The energy blocking scheme from [17] is utilized to determine global single-particle energy-averaged blocking factors.

3. Results and discussion

To investigate the effects of the extended EEC treatment, we consider the nonlinear dual-pulse excitation (pump–probe) of small sodium clusters (Na$_{35}$) by intense femtosecond laser...
pulses at 800 nm with $\tau = 25$ fs pulse duration (intensity FWHM) and peak intensity $I_0 = 8 \times 10^{12}$ W cm$^{-2}$. In the ground state the cluster has a Mie plasmon energy of about 3 eV. Within such a dual-pulse scenario, the pump pulse utilizes a non-resonant excitation of the cold cluster, while the second pulse probes the transient response properties of the pre-excited expanding cluster, with the possibility of resonant plasmon excitation for an appropriate pulse delay due to the expansion-induced red-shift of the Mie plasmon.

3.1. Global observables

To analyze the impact of EECs, we compare three different levels of approximation: (i) the Vlasov model as a fully EEC-free reference case, (ii) a conventional VUU treatment with fixed screening length determined for the ground-state density at zero temperature (i.e. only velocity-dependent cross sections) and (iii) the new VUU-DT approach with a fully self-consistent evaluation of the screening length based on the local density and temperature. The resulting dynamical evolutions for a typical scenario are displayed in figure 3.

Focusing on the dynamics induced by the non-resonant pump pulse, all three methods predict similar evolutions of the dipole moment, energy absorption and ionization (figures 3(a)–(c)). Note that the excitation creates an unstable system (see atomization threshold of the model in figure 3(b)) with nearly zero total energy. Within VUU and VUU-DT, absorption and ionization are slightly enhanced due to the presence of EECs. Two effects can be observed from the evolution of the collision frequencies in figure 3(d). Firstly, in the rising edge of the pump pulse up to about $t = 40$ fs, collisions are strongly limited due to Pauli blocking. Laser heating leads to a substantial reduction of Pauli blocking, while the EEC cross sections remain mostly constant (compare kinematically possible and finally accepted collisions, i.e. after Pauli blocking). When approaching the peak of the pump pulse, Pauli blocking rejects about 50% of the collision events, reflecting the partial degeneracy in the valence electron cloud. At this time the degeneracy parameter is near unity and the thermal electron energy is of the order of the Fermi energy (for sodium, about 3 eV $\approx 35000$ K) (see figure 3(e)). Secondly, near the pulse peak the temperature dependence of the cross sections gains relevance and becomes even more important than Pauli blocking. This can be understood by recalling the strong increase of the screening length and the resulting total cross sections with temperature in the regime of partial degeneracy (see figures 1 and 2, respectively). Hence, the EECs become cross-section limited, underlining the importance of resolving their full density and temperature dependence. The resulting higher impact of thermal electron evaporation within VUU-DT is reflected in a stronger ionization rate after the pump pulse.

The collision-induced increase of absorption and ionization from the pump pulse leads to slightly faster cluster expansion (see the rms cluster radius in figure 3(b)), but does not change the general response behavior. For the selected scenario with a pulse delay of $\Delta t = 150$ fs, all runs show resonant excitation of the expanding cluster by the probe pulse, with much stronger absorption and ionization when compared with the pump scenario. Note that the dipole signal shows a pronounced resonance enhancement. In the presence of collisions, especially in the VUU-DT case, ionization is somewhat stronger as in the Vlasov case, but mostly due to slow thermal evaporation after the probe pulse (see figure 3(c)). A very pronounced effect of the extended treatment of collisions is seen in the evolution of the collision frequency occurs during the probe pulse. In the VUU result, the decrease of the total EEC cross sections with increasing electron velocity (see figure 1) leads to a significant reduction of the collision...
Figure 3. Dual pulse excitation of Na$_{55}$ with nearly optimal delay for resonant plasmon excitation $\Delta t = 150$ fs as predicted by the Vlasov, standard VUU and VUU-DT approaches (identical pulses with $\tau = 25$ fs FWHM, $\lambda = 800$ nm, $I_0 = 8 \times 10^{12}$ W cm$^{-2}$): (a) pulse envelopes and dipole moments, (b) total energies (valence electrons and pseudo-ions only) and ion rms radii, (c) emitted electrons, (d) collision frequency (rate of collision events per electron) with (solid line) and without (dashed line) Pauli blocking and (e) electron temperatures and degeneracy parameters $\theta$.

frequency (see figure 3(c)). The reverse trend is found in the VUU-DT results, i.e. an increase of the collision frequency occurs during the probe pulse. This trend highlights the strong effect of the temperature dependence of the cross sections, which overcompensates for the reduction resulting from the velocity dependence in the partially and weakly degenerate regime.

Despite deviations in absorption and ionization in the models, the results do not indicate any qualitative change of the dynamical cluster response. This is supported by the systematic
comparison of the pump–probe dynamics of absorption and ionization in figure 4, showing that
the optimal delay for resonant excitation is only weakly modified in the presence of collisions.
Comparing the peak values at the respective optimal delays, absorption and ionization are
of the order of 10% higher in VUU-DT when compared with Vlasov. Hence, the collisions have
only minor effects on the general evolution of global observables such as absorption, ionization
and expansion.

3.2. Signatures in photoelectron spectra

A much stronger impact of the collisions is found in the detailed spectra of emitted electrons. Figure 5(a) compares the final electron energy spectra predicted by the three model variants for
two cases: (i) pump-only excitation and (ii) pump–probe excitation with the nearly resonance-
optimized delay ($\Delta t = 150$ fs).

In general, all models show significantly higher electron energies for the resonant
pump–probe excitation, supporting a resonance-enhanced emission and acceleration of
electrons. Furthermore, for both the pump-only and the pump–probe case the inclusion of
collisions produces a more exponential shape of the electron energy spectra. The difference
between VUU and VUU-DT is smaller in the pump-only case, as the impact of the density- and
temperature-dependent cross sections is less pronounced. However, in the resonant pump–probe
case, the VUU-DT treatment results in substantially higher electron energies than the Vlasov
and VUU models and predicts an almost perfect exponential energy spectrum.

The exponential shape of the electron spectra with the inclusion of fully density- and
temperature-dependent EECs could be interpreted as a signature of strong thermal evaporation
from a resonantly heated nanoplasma. This picture, however, would be in sharp contrast to
the results of an earlier work on metal clusters [13], where a rescattering mechanism in the
enhanced plasmonic field on the cluster was identified as the major mechanism for enhanced
electron emission and acceleration in the regime of moderate laser intensities. The main idea
of this surface plasmon-enhanced rescattering in clusters (SPARC) is the acceleration of highly
Figure 5. Final electron spectra from Na$_{55}$ as predicted by the Vlasov, VUU and VUU-DT simulations in figure 3; (a) electron energy spectra for pump-only excitation and resonant pump–probe excitation with $\Delta t = 150$ fs (as indicated). (b) Final angle- and energy-resolved electron spectra for pump–probe excitation. The emission angle is measured to the laser polarization axis. Note that the double-differential emission cross section is shown on a logarithmic scale. The colorbar shown in the top panel applies to all three cases.

excited electrons via the resonance-enhanced plasmonic polarization field, during a final transit through the cluster. It should be noted that this earlier analysis was based on calculations on the standard VUU level without density- and temperature-dependent collisions and did not predict such highly exponential spectra as the new VUU-DT results. The corresponding experimental data in [13], however, showed exponential electron spectra and are thus in good qualitative agreement with the new VUU-DT treatment. It should be noted that single exponential shapes of the electron spectra are typical for moderate laser intensity, while two-temperature or double-exponential behavior has been observed in the domain of higher ($\gtrsim 10^{15}$ W cm$^{-2}$) intensity [30, 31]. Furthermore, an alternative explanation for high electron energies at resonance is purely laser-field-driven acceleration in the quasistatic space-charge potential of the cluster [32]. This mechanism is known to be particularly important at high laser intensity. Hence, the clarification of the main emission processes for the moderate intensities with strong plasmonic effects as studied here are a key issue and our main subject for the rest of the paper.

For a closer analysis of the emission process, we first inspect the angular-resolved electron energy spectra for the resonant pump–probe case. The comparison of the spectra in figure 5(b) shows anisotropic emission with preferential electron ejection along the polarization axis for all three model variants. Interestingly, not only the maximum electron energies but also the anisotropy increases when going from the Vlasov over the VUU to the VUU-DT results. Surprisingly, even the high-energy tail in the VUU-DT data shows a clear enhancement for
emission along the polarization axis. This signature supports the picture of a directly laser-driven or polarization field-induced acceleration process over thermal evaporation from the heated nanoplasma. Further insights can only be gained from a detailed trajectory analysis, as discussed in the following.

3.3. Time-resolved trajectory analysis

In the next step, we focus on the detailed microscopic dynamics to identify the effect of collisions on the mechanism of energetic electron emission along the polarization axis. Therefore, we track the trajectories of all electron test particles and record the final transit time \( t_{\text{trans}} \) through the \( x = 0 \) plane (the plane perpendicular to the laser polarization vector). Compared with the evolution of the laser and cluster polarization fields, this transit time provides a characteristic marker for the sub-cycle timing of the acceleration process. The final electron energies for forward and backward emission (emission in a cone with 90° full opening angle) are shown as a function of the transit times in figures 6(a)–(c).

The cycle-spaced cam-like modulation of the signal in the time–energy correlation map found for all models indicates electron rescattering in the cluster. Note that a possibly important thermal evaporation process should be particularly pronounced in the VUU-DT results, with a featureless or weakly quiver-modulated signal in the time–energy map. Because of the pronounced periodicity of the final transit times for high-energy electrons even in the VUU-DT case, pure thermal evaporation can be excluded as an important mechanism for high-energy electron emission.

Next, focusing on the detailed timing, all models show a clear correlation between the final transit times and the dipole signal. In particular, electrons emitted with high energy in the positive direction show a final passage through the cluster center at maximum positive polarization, i.e. when the main electron cloud has maximum negative deflection. This shows that the accelerated electrons traverse the cluster with a phase shift to the resonantly driven collective electron motion, as suggested by the plasmon-assisted rescattering picture [14]. It should be noted that the dipole polarization itself exhibits a transient behavior, with a phase lag below \( \pi/2 \) in the rising edge of the pulse, a \( \pi/2 \) crossing near the center of the pulse and a phase lag of more than \( \pi/2 \) at the end of the pulse. This phase dynamics reflects the passage of the expanding cluster through the Mie resonance. Since the transit times remain temporally linked to the polarization field, the plasmon-assisted acceleration can be identified to be dominant over pure laser-driven acceleration in the cluster-space charge potential for the present scenario. If dominant, the direct laser acceleration would lead to a temporal locking of the final transits in a given direction to times with maximum electric field pointing in the opposite direction. Combining these arguments, electron rescattering in the plasmonic polarization field (SPARC) can be identified as the main origin of the energetic electrons in the resonant clusters with strong plasmonic response when compared with the laser field. In turn, direct laser acceleration will become important as soon as the laser field exceeds the magnitude of the achievable internal plasmonic fields in the clusters.

A detailed comparison of the time–energy maps further shows that the neglect of EECs in the Vlasov model leads to the cleanest confinement of final transits to the relevant half-cycle of the polarization field. Within the VUU and VUU-DT results, weak additional contributions appear in between the cam structure (note the logarithmic scaling). This shows that the randomization effect of collisions slightly disturbs the high selectivity but does not destroy
the plasmon-assisted rescattering effect. More importantly, in the presence of collisions the maximum energies are substantially higher. In particular, the energy cutoff is about a factor of two higher in VUU-DT when compared with pure Vlasov treatment. This effect is attributed to collisional momentum redistribution of electrons in phase space. In the Vlasov picture, the SPARC process depopulates the electron phase space near the continuum level, i.e. it efficiently removes highly excited electrons from the cluster potential. In the presence of collisions, thermalization results in a repopulation of the near threshold states, which are then available for efficient SPARC acceleration.

Figure 6. Transit-time analysis of emitted electrons and evolution of cluster polarization (dipole moment) and laser field during the probe pulse for excitation of Na$_{55}$ with $\Delta t = 150$ fs. The simulation data correspond to the runs shown in figure 3. Color-coded time–energy maps display the final energy distribution of electrons as a function of their final transit times $n(E, t_{\text{trans}}) = dN/dt_{\text{trans}} dE$ (double differential). The transit time indicates the final transit through the $x = 0$ plane (laser polarized along the $x$-axis). Positive and negative energies reflect emission in the forward and backward directions with respect to the laser polarization vector into a cone with 90° opening angle. The colorbar in panel (b) is valid for all time–energy maps. For convenience, the dipole moment and laser field have been rescaled by a constant factor, respectively.

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The collisional repopulation of the phase space near the threshold, as a local correlation effect, and the plasmon-assisted rescattering, as a collective mean-field process, therefore operate together in a synergetic manner to produce high-energy electrons. This cooperative action of correlation and collective effects demonstrates that collisions can play an important role in understanding plasmonic enhancement effects in laser–matter interactions that goes far beyond mere dephasing and damping. The combined impact of polarization fields and collisional effects is expected to diminish as soon as the laser field strength begins to exceed the achievable plasmonic fields in the cluster. This has been demonstrated previously for small rare-gas clusters [33].

4. Conclusions

We have developed an extended VUU model to include EECs in time-resolved semiclassical real space simulations for arbitrary levels of degeneracy. The inclusion of density- and temperature-dependent collisions could be efficiently implemented in a grid-based code by using cell-indexing and parallel iterative multigrid methods, resulting in linear scaling of the numerical effort with system size. The effect of the collisions has been studied for nonlinear laser excitation of Na$_{55}$ in a pump–probe scenario. Our analysis demonstrates that global observables such as absorption, cluster expansion and ionization are only weakly affected by the treatment of collisions, while strong systematic changes can be found in the final electron emission spectra. For resonant pump–probe excitation at moderate laser intensity, we identify plasmon-assisted rescattering as the main mechanism for energetic electron emission and observe that collisions even support the high-energy electron generation by phase-space repopulation.

Our scheme provides a versatile tool for investigating the laser-induced heating and ionization dynamics of finite systems such as clusters. We expect it to be also suitable for studies of collisional effects in the laser-driven electron emission from metallic nanotips [34]. Moreover, the microscopic resolution of the sub-femtosecond electron dynamics is relevant for the description of laser machining of metallic surfaces. Our next steps include the systematic analysis of larger systems and the impact of collisions on the phase-dependent electron dynamics, e.g. for excitation with phase-controlled few-cycle laser fields [35].

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