Electron-ion relaxation in Al nanoplasma: Wave packet molecular dynamics

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Abstract. Interaction of laser pulses with clusters creates non-equilibrium warm dense matter systems. In this work we deploy wave packets molecular dynamics to study initial stage of aluminum cluster relaxation after irradiation with 25–400 fs pulses.

1. Introduction

Recently, interactions of ultrashort laser pulses with plasmonic nanoclusters have become a subject of interest due to efficient laser radiation absorption with an energy capture per atom much higher than for bulk material. The nature of the enhanced absorption determined by plasmon resonance is the topic of many theoretical (e.g. [1–4]) and experimental studies, covering such fields as nanolithography [5], nanocavitation [6], electronics [7] and many others. Off-resonance processes in plasmonic nanoclusters under femtosecond laser irradiation also show an interesting behavior [8, 9]. Interaction of ultrashort laser pulses of fluences $10^{12}$ W/cm$^2$ and higher with nanoclusters allows to obtain plasma with near-solid density—a unique state of matter, so-called warm dense matter (WDM). Processes of electron-ion relaxation and fragmentation in such systems are of significant interest.

Non-equilibrium WDM is a very complicated object for theoretical description. Classical description of electrons and ions (e.g. [3, 4, 10, 11]) has a limited region of validity (in terms of WDM temperature and density). Ab initio methods that describe the system of many electrons taking into account the majority of quantum effects like the density functional theory (DFT), e.g. see [12–14]) are inherently limited in their ability to describe non-equilibrium phenomena [15]. Unlike DFT, the wave packets molecular dynamics (WPMD) methods give a unique possibility to describe non-equilibrium effects in the electron subsystem and non-adiabatic effects of electron-ion interactions. WPMD methods are usually less accurate than DFT because the antisymmetric character of many electron wavefunction is taken into account only approximately. However at the same time WPMD is less computationally demanding. That is why the wave packets approximation is instrumental in bridging the gap between classical and quantum description of WDM.

Al is a promising plasmonic material in the visible and UV parts of the spectrum with a variety of possible applications [16]. Here we use one of the potentials based on the WPMD approach—the eFF [17] potential—to study Al nanocluster evolution after intense laser excitation including its expansion and electron-ion relaxation.
2. Model and calculation method
The eFF potential is based on the WPMD model that provides the combination of particle dynamics for ions with wave packet dynamics representing electrons as floating Gaussians. Unlike the more complex antisymmetrized approximation [18,19], interactions between electrons in the eFF model are restricted to pairwise components only and the total energy of the system is evaluated as in classical force field methods. It means that, despite being delocalized, electrons (or geometrical centers of corresponding wave packets, to be precise) are simulated as classical particles in sense of their equations of motion integration. In such case, unlike Fermi-Dirac statistics, all of the available electron modes are excited uniformly, which brings us to the classical Dulong-Petit heat capacity in the eFF [17].

To accelerate calculations we use the effective core potential (ECP) modification of eFF: every Al atom is represented by a Al$^{3+}$ ion and three valence electrons, while ten core electrons are considered implicitly using pseudo-potential. It allows increasing the integration timestep significantly (from 0.0001 fs in all-electron representation to 0.002 fs for the ECP representation) and reducing the total number of particles in the system. This potential has already been successfully applied for the modeling of warm dense matter [20] and nanocluster explosion [21].

The temperatures of electron and ion subsystems are calculated as the measure of the average kinetic energy of motion in accordance with [20].

Modeling of laser-exited clusters can be divided into two main stages: the cluster external heating, i.e. the stage of laser energy absorption, and the further stage of relaxation, including ionization, expansion and possible subsequent explosion. Molecular dynamics approach should be supplemented with the proper model of the electromagnetic waves (i.e. the solution of Maxwell equations within the simulation cell) in order to describe the energy absorption and scattering. This is not the aim of the present study. In our calculations we focus on the second stage, therefore the model for the heating of the electron subsystem is simplified: during the “laser pulse” stage, we increase electron kinetic energy uniformly in time. It means that in our approach absorption rate is constant as well as the laser fluence. Strictly speaking, it does not correspond to the general case, because due to the cluster expansion and electron heating, parameters of absorption could be shifted. Also, the laser intensity profile is usually of the Gaussian form, but for the ease of analysis we use a step-like shape. Here we study only the consequences of the energy deposition and consider the heating in a simplified way varying only duration and intensity of the laser pulse. Nevertheless, it is shown in this study that the duration of the pulse significantly affects maximum ion temperatures and subsequent relaxation process. The obtained results could be adapted to more specific pulse shapes.

It should be noted that despite MD with the two-temperature model (TTM) could be successfully used to simulate the process of femtosecond laser interaction with bulk Al (see e.g. [22]), it is poorly applicable in the case of the laser heating of nanoclusters, where cluster ionization (which is not described within TTM approach) play a crucial role.

3. Results and discussions
We examined the evolution of laser-heated spherical Al clusters containing 490 and 1048 atoms (diameters approximately 12 and 16 Å). The total energy of every pulse was $E_{\text{imp}} = 1.85$ eV per electron (at values higher than $E_{\text{imp}} = 2.5$ eV cluster explosion was observed), the power was varied in compliance with the pulse duration (25, 100 or 400 fs). This value approximately corresponds to the level of pulse energy $W \approx 7.5$ mJ/cm$^2$ (considering 100% energy absorption) and intensities in range $3 \times 10^{10} - 5 \times 10^{11}$ W/cm$^2$. Temperatures for the ion and electron subsystems were calculated separately (figures 1 and 2). Temperature relaxation takes place on the timescale of few picoseconds. Figure 3 displays its exponential type:

$$\frac{\Delta T}{T_{\text{eq}}} \sim \exp \left(-\frac{t}{\tau_e}\right),$$  \hspace{1cm} (1)
where $T_{eq}$ is the equilibrium temperature of the relaxed system. Linear approximation for both Al$_{490}$ and Al$_{1048}$ gives $\tau_e$ in the range 0.9–1.1 ps with larger values for longer pulses. This result is in excellent agreement with the ab initio data for aluminum [23]. Taking from [23] electron heat capacity $C_e \approx 3.5 \times 10^5$ $\text{Jm}^{-3}\text{K}^{-1}$ and electron-phonon coupling factor $G \approx 3.4 \times 10^{17}$ $\text{Wm}^{-3}\text{K}^{-1}$ at $T_e = 4000$ K in accordance with [24] we obtain:

$$\tau_e \approx \frac{C_e}{G} = 1.03 \text{ ps}. \quad (2)$$

The behavior of ion temperature shows an interesting peculiarity: for short pulses (25 and 100 fs) there are significant peaks in the ion temperatures at approximately 100 and 120 fs for 25 and 100 fs impulses (the effect is much weaker for the 400 fs pulse).

The sharp increase in the kinetic energy of ions during and right after the pulse (figures 1 and 2) corresponds to the spherically symmetrical expansion of the cluster. The longer is the pulse, the larger interval is required for the cluster to reach its asymptotic size.

As seen from figure 4 the expansion is non-monotonic with fading oscillations. Such oscillations are expected to have acoustic nature as was experimentally observed in [26].
Figure 2. Relaxation of the electron and ion temperatures for Al\textsubscript{1048} cluster. Dashed red curves correspond to the 100 fs impulse length, solid green—400 fs. For the ease of comparison, black dotted curves show the ion temperatures for Al\textsubscript{490} (figure 1).

Figure 3. Temperature relaxation log(\(\Delta T/T_{eq}\)) on time. The linear approximation corresponds to the coefficient \(\tau_e = 1.1\) ps.

asymptotic size is determined by the total value of deposited energy (figure 5) and does not have a visible dependence on the pulse duration (figure 4). Figure 6 shows the evolution of the radial electron density profile of Al\textsubscript{1048} after the onset of 100 fs pulse. At \(t = 0\), it reproduces
Figure 4. Evolution of the cluster radius $R_{\text{cluster}}$ with time. Two curves at the top correspond to Al$_{1048}$ cluster (the 100 fs pulse—red, the 400 fs pulse—green), three lower—Al$_{490}$ (the 25 fs pulse—blue, the 100 fs pulse—red, the 400 fs pulse—green).

Figure 5. Evolution of the cluster radius $R_{\text{cluster}}$ with time for Al$_{490}$ after the 25 fs pulse with different total energies: 50% (red dashed), 75% (green dotted) and 100% (blue solid) of initial $E_{\text{imp}}=1.85$ eV per electron.
rather accurately the radial distribution function of the unperturbed Al crystal lattice. During the expansion phase (from $t = 200$ to $t = 600$ fs) the electron (and ion—not shown) density in the inner part of the cluster is decreasing. It returns to the mean values at $t = 1000$ fs, when the cluster slightly shrinks. Therefore, as seen from figures 4 and 6, the oscillations of the cluster size are accompanied by the spherically symmetric oscillations of the electron density. The magnitude of this effect depends on the duration of the energy deposition and the cluster size. For larger nanoclusters at higher levels of laser intensity, this fast expansion could lead to the disruption of the outer layers of ions from the surface. But the main influence of the effect should result in the optical parameters change, e.g. the plasmonic resonance shifting that will affect the intensity of energy absorption.

4. Conclusions
In summary, we have performed MD simulations of the laser exited Al nanocluster with explicit electron and ion dynamics. The electron-ion temperature relaxation showed the exponential behavior with $\tau_e$ in the range 0.9–1.1 ps, which is in the excellent agreement with ab initio data [23]. An interesting feature of the early stages of relaxation—the spherically symmetrical oscillations of the mass density in cluster—has been observed.

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Figure 6. Evolution of the radial electron density profile for Al$_{1048}$ cluster after the onset of the 100 fs pulse.
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