Ion energetics in electron-rich nanoplasmas

Andreas Heidenreich\textsuperscript{1,2,3}, Ivan Infante\textsuperscript{1} and Jesus M Ugalde\textsuperscript{1}

\textsuperscript{1} Kimika Fakultatea, Eusko Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC), P.K. 1072, 20080 Donostia, Spain
\textsuperscript{2} IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain
E-mail: sckheida@ehu.es

\textit{New Journal of Physics} \textbf{14} (2012) 075017 (23pp)
Received 30 January 2012
Published 20 July 2012
Online at \texttt{http://www.njp.org/}
doi:10.1088/1367-2630/14/7/075017

Abstract. Based on trajectory calculations of xenon clusters up to \(\approx 6000\) atoms irradiated by laser pulses (peak intensities \(I_M = 10^{14} - 10^{16} \text{ W cm}^{-2}\), Gaussian pulse lengths \(\tau = 10-230 \text{ fs}\) and frequency \(0.35 \text{ fs}^{-1}\)), we have analyzed the interrelation between outer ionization and ion kinetic energies. The following three main categories have been identified. (A) For short pulses \((\tau = 10 \text{ fs})\) of higher intensity \(I_M = 10^{16} \text{ W cm}^{-2}\), the outer ionization level leads to a sufficiently high positive cluster charge, which confines the remaining nanoplasma electrons to the cluster center. In this case, ion energies can be reasonably well accounted for by a multi-charge state lychee model, according to which outer ionization is vertical and the nanoplasma can be described by a non-expanding neutral cluster interior, causing a zero-energy component in the ion kinetic energy distribution and an expanding electron-free cluster periphery. (B) For a very low outer ionization level, which is realized for short pulses of low intensity \((I_M = 10^{14} \text{ W cm}^{-2})\) and/or large clusters, a slow gradual evaporation of nanoplasma electrons under laser-free conditions on the picosecond time scale is observed, making the entire outer ionization process highly non-vertical despite the short laser pulse. Accordingly, ions are accelerated only by a gradual buildup of the total cluster charge. (C) For long pulses \((\tau = 230 \text{ fs})\), the cluster expansion during the laser pulse is large and outer ionization is non-vertical. The nanoplasma electrons attain high kinetic energies by resonance heating and are distributed over the entire ion framework without a neutral cluster interior. Consequently, a zero-energy component in the ion energy distribution is missing.

\textsuperscript{3} Author to whom any correspondence should be addressed.
1. Introduction

Rare-gas clusters are experimental and theoretical benchmark systems for investigating the interaction of ultra-intense femtosecond laser pulses with matter [1–3]. Insight into the underlying physical processes was gained, especially from particle trajectory simulations [4–23] and from particle-in-cell simulations [24–28]. For infrared (λ = 800 nm) pulses with peak intensities $I_M \geq 10^{14}$ W cm$^{-2}$ the ionization of cluster atoms is triggered by a small number of tunnel ionizations (TI), followed by classical barrier suppression ionizations (BSI). The stripped electrons together with the ions form a nanoplasma and, driven by the external oscillating laser field, induce an avalanche of electron impact ionizations (EII). Depending on the pulse parameters (intensity and pulse length) and on the cluster size, the nanoplasma electrons are partly or completely removed from the cluster. The removal of nanoplasma electrons from the cluster is termed outer ionization as opposed to inner ionization [5], which subsumes the ionization channels of cluster atoms (TI, BSI and EII in this case).

Subsequently or parallel to the inner and outer ionization processes, Coulomb explosion (CE) sets in, converting the electrostatic repulsion of the cluster excess positive charges into ion kinetic energy up to the MeV region, depending on the cluster size and on the laser parameters. Thereby, the ion energetics and dynamics are strongly determined by the remaining nanoplasma electron population, which screens part of the positive charge in the cluster. In the case when the removal of nanoplasma electrons is complete before the cluster expansion sets in notably (‘vertical complete outer ionization’ [21]), so that the time scales of outer ionization and CE are separable, the description of the ion energetics and dynamics is quite simple and straightforward. Electrostatic models [29–31] are then applicable to the description of the dependence of the nuclear dynamics and energetics of CE on the cluster size, on the inner ionization level (expressed in terms of charge per atom) and on the pulse parameters (which determine the outer ionization level). The complete vertical ionization model will be transcended for larger clusters driven by lower laser intensities ($I_M \leq 10^{16}$ W cm$^{-2}$), when novel features of incomplete outer ionization can be realized [21, 22]. For outer ionization electron dynamics the nuclear motion is not necessarily frozen, as outer ionization of large clusters driven by long (in the range of hundreds of femtoseconds) laser pulses occurs on the time scale of CE, precluding the separation of time scales between electron and nuclear dynamics. The electron-rich nanoplasma produced by incomplete outer ionization will manifest novel features of electron and nuclear dynamics. Under the conditions of incomplete outer ionization, the medium of the nanoplasma electrons is expected to provide a tool for the control of the CE energetics and dynamics, also with respect
to inducing nuclear overrun effects during non-vertical ionization in two-pulse experiments and intracluster nuclear fusion [32].

We have carried out trajectory calculations for Xeₙ clusters 55 ≤ n ≤ 6099 irradiated by infrared Gaussian laser pulses of peak intensities 10^{14} \text{ W cm}^{-2} ≤ I_M ≤ 10^{18} \text{ W cm}^{-2} and pulse lengths 10 fs ≤ t ≤ 230 fs, considerably extending the lower intensity limit of 10^{15} \text{ W cm}^{-2} of our previous simulations [16–18, 21–22] toward lower intensities. For short pulses (t ≤ 30 fs) of low intensity, which is the regime of very electron-rich nanoplasmas, several experimental studies have recently been conducted [33–35]. The ion energetics over the entire considered cluster size and laser parameter ranges will be presented in a forthcoming publication; in this paper, we focus on intensities ≤ 10^{16} \text{ W cm}^{-2} and select three examples for which we discuss the interrelation between outer ionization and ion energetics. Most of the results emerging from our simulations of CE energetics pertain to classification of the effects of outer ionization dynamics and to extension of the electrostatic lychee model [14, 18, 21] to multiple charge states. A mechanistic issue for the ion energetics from an electron-rich nanoplasma pertains to the contribution from CE, which is determined by the conversion of the total potential energy, and from hydrodynamic expansion [36, 37], which is determined by the conversion of the electron kinetic energy into the kinetic energy of the ions.

2. Simulation method

We have previously described [16, 17] the molecular dynamics (MD) simulation scheme for high-energy electron dynamics in a cluster interacting with an electric and a magnetic field of a linearly polarized ultra-intense Gaussian laser pulse, with a photon energy of hν = 1.44 eV, a (cycle-averaged) peak intensity I_M and a temporal length τ of the electric field envelope (the temporal full-width at half-maximum (FWHM) of the intensity profile being τ/√2). The laser electric field was taken as Fₜ(τ) = F_M exp[−4 ln(2)(τ/τ)²] cos(2πvt + ϕ₀) with a phase ϕ₀ = 0 and F_M being the electric field strength corresponding to I_M [17]. In the MD simulations, the electrons are treated non-quantum mechanically but relativistically. This simulation scheme has been modified and extended in two respects.

Firstly, tunnel ionization (TI) has been incorporated using the Ammosov–Delone–Krainov (ADK) ionization probabilities [38]. The tunnel ionization probability \( w_A \) of atom A per unit time was calculated by (in atomic units)

\[
w_A = \sum_{m=-l}^{l} \left[ f_{nlm} \frac{(q_A + 1)^2}{4\pi n^3} \left( \frac{2e}{n^*} \right)^{2n^*} \left( \frac{2l + 1}{2^{m!}} \frac{(l + |m|)!}{(l - |m|)!} \right) \left( \frac{2(q_A + 1)}{F_A n^3} \right)^{2n^* - |m| - 1} \right] \times \exp \left( -\frac{2(q_A + 1)^3}{3n^3 F_A} \right),
\]

where \( n, l \) and \( m \) are the principal, angular and magnetic quantum numbers of the orbitals of the energetically uppermost electronic shell, \( q_A \) the atomic charge before ionization, \( n^* = (q_A + 1)/\sqrt{2P_q^{(0)}} \) the effective principal quantum number, \( P_q^{(0)} \) the ionization energy of the atomic charge state \( q_A \) in the absence of an electric field and \( F_A \) the instantaneous local electric field at atom A consisting of the laser electric field, all the electrons and all other ions. Following the suggestion of Awasthi et al [39], the contributions of each orbital were multiplied by the corresponding orbital occupation numbers \( f_{nlm} \) (0, 1 or 2). \( w_A \) in equation (1) represents the
non-cycle averaged tunnel ionization probability; \( w_{\mathrm{A}} \cdot \Delta t \) is then the tunnel probability at atom A during the electronic MD time step \( \Delta t \) [40].

Secondly, the formalism of Fennel et al [15] was implemented to describe the enhancement of electron impact ionizations (EII) by the local electric field at each atom. In their treatment [15], the EII cross-sections are calculated by using the simplified Lotz formula [41]

\[
\sigma_{q \rightarrow q+1} = 450 A^2 (\text{eV})^2 \sum_{n,l} \left( f_{nl} \ln \left( \frac{T_{\text{imp}}/P_{nl}}{T_{\text{imp}} P_{nl}} \right) \right),
\]

where \( P_{nl} \) and \( f_{nl} \) are the ionization energies and the occupation numbers of the electronic subshells characterized by the principal and angular quantum numbers \( n \) and \( l \) and \( T_{\text{imp}} \) is the impact kinetic energy of the impinging electron. According to Fennel et al [15], \( P_{nl} \) is taken relative to the electrostatic barrier rather than to the vacuum level. In our simulation scheme, \( P_{nl} \) was obtained by

\[
P_{nl} = P_{nl}^{(0)} + 2q_e \left( \frac{(q_A + 1) F_A}{4\pi \varepsilon_0} \right)^{1/2} + \frac{q_e^2}{P_{nl}^{(0)}} \left( \frac{q_A + 1}{4\pi \varepsilon_0} \right),
\]

with the corresponding ionization energy \( P_{nl}^{(0)} \) in the absence of an electric field, the local electric field strength \( F_A \) at atom A, the atomic charge \( q_A + 1 \) after EII and the electron charge \( q_e \). For each charge state, the lowest ionization energy was taken from Cowan [42], higher ionization energies \( P_{nl}^{(0)} \) were taken from scalar relativistic SCF-MP2 calculations as implemented in the MOLCAS 7.4 package [43], using a triple-zeta basis set contracted to a 7s6p4d2f1g form [44]. \( T_{\text{imp}} \) is taken as the instantaneous electron kinetic energy corrected for the work to move it to the electrostatic barrier defined by the local electric field \( F_A \) and the ion charge \( q_A \) prior to EII

\[
T_{\text{imp}} = T_i - 2q_e \left( \frac{q_A F_A}{4\pi \varepsilon_0} \right)^{1/2} + \frac{q_e q_A}{4\pi \varepsilon_0 \vec{r}_i} - q_e F_A \cdot \vec{r}_i,
\]

where \( \vec{r}_i \) is the instantaneous position vector of the impinging electron with respect to the target atom.

The treatment of EII adapted from the work of Fennel et al [15] differs considerably from our previous work [16, 17], where we used experimental EII cross-sections that were fitted to the three-parameter Lotz formula [12, 41], but disregarded the enhancement of the EII cross-sections by the electric field. Although the Lotz formula in the form of equation (2) takes into account only the channel of direct EII, disregarding the excitation-autoionization and recombination-autoionization channels, which for some charge states can increase the EII cross-sections by one order of magnitude [45], the Lotz formula in the form of equation (2) has the advantage that cross-sections can be calculated for all charge states, whereas experimental EII cross-sections are available only until Xe\(^{11+}\) (as well as for some selected higher charge states). While in the previous simulations EII had to be disregarded for charge states higher than Xe\(^{11+}\), the inclusion of higher charge states is essential, because it is otherwise not possible to reproduce the ion charges as high as Xe\(^{20+}\)–Xe\(^{23+}\) experimentally found already for intensities \( 10^{15} \)–\( 10^{16} \) W cm\(^{-2}\) [46, 47]. We considered a combined approach, taking experimental cross-sections for charge states up to Xe\(^{11+}\) and Lotz cross-sections in the form of equation (2) for higher charge states, but did not pursue it, because it is not known how the contributions from the excitation-autoionization and recombination-autoionization channels change under the influence of an electric field; the Lotz cross-sections, equation (2), are therefore considered

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a safe conservative choice. Although our simulations lead now for the Xe$_{6099}$ cluster, $I_M = 10^{15}$ W cm$^{-2}$, $\tau = 230$ fs, to a maximum ion charge of 21, it is expected that the current treatment of EII still leads to too low charge states [15].

At every electronic time step, the local electric field at each atom is recalculated, consisting of the external laser electric field and the contributions from all the other ions and electrons, and each atom is checked for the occurrence of inner ionization in the hierarchy BSI $>$ EII $>$ TI, allowing only for one ionization per atom per time step. In this way, it is ensured, for instance, that tunnel ionization is applied only when the particular atom is not in the BSI regime where the ADK formula should not be applied [48]. Although the contribution of TI to the total number of inner ionizations is far below 1%, TI is essential for triggering the ionization avalanche at laser intensities below the BSI regime.

As the standard procedure, electrons farther away from the cluster center than ten cluster radii were removed permanently from the simulation. The initial MD setup consists of an fcc cluster structure of neutral atoms. We chose an electronic time step $\Delta t$ between $10^{-4}$ and $10^{-3}$ fs; the nuclear time step was $20\Delta t$.

3. Results and discussion

3.1. Simulation results

For three examples involving different cluster sizes and laser parameters, figure 1 shows time-resolved key quantities of the ionization process: the average ion charge $q_{av}$, the number $n_p$ of nanoplasma electrons per atom inside the cluster, the relative cluster radius $R/R_0$ of the expanding cluster (taken as the distance of the most distant ion from the cluster center-of-mass, with $R_0$ being the initial cluster radius) and, for a comparison of time scales, the oscillating laser electric field. The three examples represent three categories of incomplete outer ionization:

(A) Vertical moderate outer ionization for short pulses, Xe$_{1061}$, $I_M = 10^{16}$ W cm$^{-2}$, $\tau = 10$ fs (figure 1(a)). The nanoplasma electron population is in the range 1/2–3/4 of the average ion charge ($n_p/q_{av} = 0.73$ in this example), and the cluster does not expand appreciably during the laser pulse. Depending on the cluster size, this category is found for moderate laser intensities $10^{15}$–$10^{17}$ W cm$^{-2}$.

(B) Non-vertical low outer ionization for short weak pulses, Xe$_{1061}$, $I_M = 10^{14}$ W cm$^{-2}$, $\tau = 10$ fs (figure 1(b)). Outer ionization is very low, only a few per cent of the average ion charge. Despite the negligible cluster expansion during the laser pulse, outer ionization is non-vertical, which will become apparent in the next section of this paper.

(C) Non-vertical moderate to high outer ionization for long weak pulses, Xe$_{6099}$, $I_M = 5 \times 10^{14}$ W cm$^{-2}$, $\tau = 230$ fs (figure 1(c)). The cluster expansion during the laser pulse is large; at the end of the laser pulse, $t \approx \tau$, the cluster radius is increased by a factor of 10. For the long pulse of $\tau = 230$ fs, outer ionization is very efficient via resonance heating [3, 49]. In this example, the cluster size and laser intensity were chosen such that the outer ionization level $n_p/q_{av} = 0.69$ at the end of the trajectory is comparable to case (A). (As a general rule, outer ionization increases with increasing laser intensity and with decreasing cluster size.)

Before analyzing the ion kinetic energies, it is instructive to consider the total energy of electron-rich nanoplasmas. Figure 2 exhibits for the examples (A) and (B) the time-resolved
Figure 1. Time-resolved key quantities of the cluster ionization: the time-resolved average ion charge $q_{av}$ (closed line), the number $n_p$ of nanoplasma electrons per atom (dashed line) and the relative cluster radius $R/R_0$ with the initial cluster radius $R_0$ (dotted line). The oscillating laser electric field (thin closed line) is given in arbitrary units. (a) Xe$_{1061}$, $I_M = 10^{16}$ W cm$^{-2}$, $\tau = 10$ fs; (b) Xe$_{1061}$, $I_M = 10^{14}$ W cm$^{-2}$, $\tau = 10$ fs; and (c) Xe$_{6099}$, $I_M = 5 \times 10^{14}$ W cm$^{-2}$, $\tau = 230$ fs. The examples given in panels (a)–(c) constitute outer ionization categories (A)–(C) discussed in this paper.

total energy $E_{tot}$ of the entire system consisting of $n$ ions and the total number $n \cdot n_e$ of electrons inside and outside the ionic framework ($n_e = n_p + n_{oi}$, with $n_{oi}$ being the number of electrons per atom outside the ion framework). Shown also is the partition of $E_{tot}$, $E_{tot} = T_n + T_e + V_{tot}$, with $T_n$ and $T_e$ being the ion and electron kinetic energy, respectively, and $V_{tot}$ the total potential energy as the sum of ion repulsion, electron repulsion and ion–electron attraction. In both trajectory calculations all electrons were included; the standard procedure of removing distant electrons > 10$R$ (see section 2) was not applied. $E_{tot}$ is measured with respect to a total decomposition of the nanoplasma into single particles. $E_{tot}$ is not constant after the termination of the laser pulse due to the continued formation of ion charges and nanoplasma electrons by EII, as the expended ionization energy is not counted in this balance of $E_{tot}$.

In the case (A) (figure 2(a)) $E_{tot}$ is positive, allowing in principle for a total decomposition of the plasma into single ions and electrons. The largest contribution to $E_{tot}$ at long times

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Figure 2. The time-dependent total energy $E_{\text{tot}}$ of the system consisting of $n$ ions and $n \cdot n_e$ electrons inside and outside the ion framework, with respect to total decomposition of the nanoplasma into single particles, for outer ionization categories (A) and (B). Included are the total ion kinetic energy $T_n$, the total electron kinetic energy $T_e$ as well as the total potential energy $V_{\text{tot}}$: $E_{\text{tot}} = T_n + T_e + V_{\text{tot}}$, with $V_{\text{tot}} = V_{\text{nn}} + V_{\text{ee}} + V_{\text{ne}}$ being the sum of the ion repulsion $V_{\text{nn}}$, electron repulsion $V_{\text{ee}}$ and ion–electron attraction energy $V_{\text{ne}}$ of the full ion charges and total number $n \cdot n_e$ of electrons. $V''_{\text{tot}} = V''_{\text{nn}} + V''_{\text{ee}} + V''_{\text{ne}}$ is the corresponding potential energy of the effective ion charges and the remaining $n n_e^{(\text{free})}$ free electrons. $V_{\text{ions}}$ and $V''_{\text{ions}}$ represent the sum of ion repulsion and attraction by the nanoplasma electrons, for the full ion charges and full number $n \cdot n_p$ nanoplasma electrons, and for the effective ion charges and the number $n n_p^{(\text{free})}$ of free nanoplasma electrons, respectively. $V''_{\text{ions}}$ is the potential energy available for the ion acceleration. The inset in panel (a) shows $V_{\text{tot}}$, $V''_{\text{tot}}$, $V_{\text{ions}}$ and $V''_{\text{ions}}$ with a better energy resolution and for longer times.

is the ion kinetic energy $T_n$. Another large part of $E_{\text{tot}}$ is carried away in terms of electron kinetic energy; more than 96% of the long-time $T_e$ value is attributed to electrons that were stripped by outer ionization. The total potential energy $V_{\text{tot}}$ converges to a negative value despite the ongoing cluster expansion, indicating ion–electron trapping. Further analysis showed that 40% of all nanoplasma electrons remain trapped by ions at long times, orbiting the ions at distances $r_{\text{cut}} < 2 \, \text{Å}$. Considering only the effective ion charges $q_i^{(\text{eff})}$, i.e. the bare ion charges $q_i$ reduced by the number of trapped electrons, and the remaining $n \cdot n_p^{(\text{free})}$ free electrons, the resulting potential energy $V''_{\text{tot}}$ (dotted line in figure 2) becomes positive and converges to zero at long times. (Regarding notation, we shall distinguish energies, which were calculated from effective ion charges and free electrons, by a prime.) Of particular interest is the potential energy $V''_{\text{ions}}$ which is available for the conversion into ion kinetic energy $T_n$. When the spatial charge
distribution is spherical and the nanoplasma sufficiently diluted, $V'_{\text{ions}}$ is approximately given by (in atomic units)

$$V'_{\text{ions}} \approx \sum_{i} \sum_{j (r_{ij} < r_{r})} \left( q^{(\text{eff})}_{i} / r_{ij} \right) - \sum_{i} \sum_{k (r_{ik} < r_{r})} \left( q^{(\text{eff})}_{i} / r_{ik} \right),$$

(5)

where $k$ in the second double sum runs over all $n \cdot n_{p}^{(\text{free})}$ free nanoplasma electrons. For comparison, $V_{\text{ions}}$ is also included in figure 2, i.e. the corresponding quantity with the full ion charges $q_{i}$ and $n \cdot n_{p}$ nanoplasma electrons. While the long-time value of $V_{\text{ions}}$ is negative, $V'_{\text{ions}}$ assumes a small positive value and goes to zero at long times, driving the ion acceleration.

In the case (B) (figure 2(b)) $E_{\text{tot}}$ converges to a negative value at long times; total decomposition of the nanoplasma into single particles is therefore precluded. Some 70% of the nanoplasma electrons were found to be trapped. $V'_{\text{tot}}$ and $V'_{\text{ions}}$ assume small positive values.

Another interesting issue of the energy analysis pertains to the question of the dominant driving force of the cluster expansion, CE or hydrodynamic expansion (HE), being attributed to the conversion of total potential energy and electron kinetic energy, respectively, into ion kinetic energy [36]. Under the condition that the total energy $E_{\text{tot}}$ of the system is constant in the course of the trajectory, the CE part is given by the difference $\Delta V_{\text{tot}} = V_{\text{tot}} (t_{L}) - V_{\text{tot}} (t_{I})$ of the total potential energy of the system and the HE part by the difference $\Delta T_{e} = T_{e} (t_{L}) - T_{e} (t_{I})$ of the electron kinetic energy, $t_{I}$ and $t_{L}$ being instants close to the beginning and at the end of the trajectory. In the ideal case, $t_{I}$ is chosen at a time when the inner ionization and energy absorption of the electrons has terminated and $E_{\text{tot}}$ has reached its final constant value. On the other hand, the kinetic energy attained by the ions at $t < t_{I}$ cannot be assigned to CE and HE, so that $t_{I}$ should be chosen as close as possible to the beginning of the trajectory. In practice, $t_{I}$ is a trade-off between both requirements. For the same reason, the energy analysis is not meaningful for long pulses (case C).

Table 1 contains the results of the analysis for examples (A) and (B). For the example (A) we chose $t_{I} = \tau = 10$ fs, when the nanoplasma build-up is nearly complete and the variation of the total energy in the course of the trajectory, $E_{\text{tot}} (t_{L}) - E_{\text{tot}} (t_{I}) = 93$ keV, is small compared to the final ion kinetic energy, $T_{a} (t_{L}) = 2079$ keV. Also, at $t = 10$ fs the non-assignable part of the ion kinetic energy is still relatively small, $T_{a} (t_{I}) = 155$ keV. With this choice of $t_{I}$ and $t_{L}$, $\Delta V_{\text{tot}} = 1702$ keV and $\Delta T_{e} = 317$ keV, so that the relative contributions of CE and HE to the sum $\Delta V_{\text{tot}} + \Delta T_{e} + T_{a} (t_{I})$ are 78 and 15%, respectively. The close agreement of the sum $\Delta V_{\text{tot}} + \Delta T_{e} + T_{a} (t_{I}) = 2174$ keV with $T_{a} (t_{L}) = 2079$ keV reflects the good accuracy of the energy partitioning. Clearly, example (A) pertains to the CE regime.

The analysis of example (B) is fraught with much larger inaccuracies. Until $t = \tau$, only 73% of the inner ionizations occur. We therefore chose $t_{I} = 112$ fs; when $T_{e}$ becomes maximal, $E_{\text{tot}} (t_{L}) - E_{\text{tot}} (t_{I})$ drops to 20 keV and $T_{a} (t_{I}) = 2.6$ keV is still relatively small. With this choice of $t_{I}$ one obtains $\Delta V_{\text{tot}} = 30$ keV and $\Delta T_{e} = 36.3$ keV, corresponding to contributions of 44% and 53% CE and HE, respectively. Although $\Delta V_{\text{tot}} + \Delta T_{e} + T_{a} (t_{I})$ differs from $T_{a} (t_{L})$ by 20 keV and $E_{\text{tot}} (t_{L}) - E_{\text{tot}} (t_{I}) = 20$ keV, indicating a large error of the energy partitioning which is 40% of $T_{a} (t_{L})$, the trend is visible that a large, if not a major part of the cluster expansion, stems from HE.

Proceeding from an analysis of the total energy of the system to the individual ions, their long-time kinetic energies can, in principle, be obtained directly from a trajectory calculation. In practice, because of computational workload, trajectories are mostly not long enough, so that
A pairwise interaction formula based on $V'_{\text{ions}}$, equation (5). The corrected energy $T_i^{(\text{corr})}$ of ion $i$ is given by its instantaneous kinetic energy $T_i$ and the sum over all Coulomb interactions with the effective ion charges $q_j^{(\text{eff})}$ and free nanoplasma electrons $k$ closer to the cluster center than ion $i$:

$$T_i^{(\text{corr})} = T_i + q_i^{(\text{eff})} \sum_{j(r_{ij} < r_i)} \left( \frac{q_j^{(\text{eff})}}{r_{ij}} \right) - q_i^{(\text{eff})} \sum_{k(r_{ik} < r_i)} \left( \frac{1}{r_{ik}} \right).$$

(6)

(1) A pairwise interaction formula with effective ion charges. The energy correction for ion $i$ is a single pairwise Coulomb term of the effective charge $q_i^{(\text{eff})}$ and a charge $Q_i$ in the cluster center, which is the sum of all the ion and electron charges closer to the cluster center than ion $i$:

$$T_i^{(\text{corr})} = T_i + \frac{Q_i q_i^{(\text{eff})}}{r_i},$$

(7)

$$Q_i = \sum_{j(r_j < r_i)} (q_j) - \sum_{k(r_k < r_i)} (1).$$

(8)

(3) The pairwise interaction formula, equation (6), with the full ion charges $q_i$ and the full number $n \cdot n_p$ of nanoplasma electrons $k$:

$$T_i^{(\text{corr})} = T_i + q_i \sum_{j(r_{ij} < r_i)} \left( \frac{q_j}{r_{ij}} \right) - q_i \sum_{k(r_{ik} < r_i)} \left( \frac{1}{r_{ik}} \right).$$

(9)
The energy correction corresponds to the potential energy $V_{\text{ion}}$ and was used in the previous work [21] where electron trapping was mostly insignificant.

Each of the three energy corrections presumes a spherical charge distribution inside the nanoplasma. In practical calculations, smoothed Coulomb potentials for the ion–electron and electron–electron interactions were used in equations (5), (6) and (9), in accordance with the trajectory calculations [9, 16–18, 21, 22].

The Xe$_{1061}$ cluster is still small enough to check the three energy correction formulae against long-time ion kinetic energies, where $T_{i}(\text{corr}) \approx T_{i}$. For the outer ionization case (A), figure 3(a) shows the maximum corrected and uncorrected ion energy, $E_{M}$ and $T_{M}$, respectively, as a function of time. The three correction formulae lead to nearly identical results and are nearly converged to the long-time $T_{M}$ value already at $t = 200$ fs. For the average ion energy (figure 3(b)), the values corrected by the pairwise interaction formula with effective ion charges and by the central charge formula are identical, converged already at $t = 20$ fs and in close agreement with the long-time $\langle T \rangle$ value. In contrast, the pairwise interaction formula without trapping gives too low values. The reason is that using bare ion charges in the energy correction formula (equation (9)) does not take into account the Coulomb repulsion between trapped electrons and other electrons which are closer to the cluster center. As the trapped electrons form a subsystem together with their host ion, the energy correction must involve all interactions of the subsystem with other ions and electrons. When the interparticle distances are large compared to the distances inside the ion-trapped electron subsystem, it suffices to reduce the ion charges rather than considering the repulsion of the subsystem electrons with other nanoplasma electrons explicitly. For the maximum ion energy (figure 3(a)), the pairwise interaction formula with bare ion charges and the full number of nanoplasma electrons (equation (9)) works well, because the maximum energy stems from an ion near the cluster surface, where trapping does not play a role for these laser parameters.

In all calculations an ion–electron cutoff distance of 2 Å was used; the ion energies turned out to be insensitive to the particular choice of the cutoff distance. The residence times of the trapped electrons increase with the dilution of the nanoplasma. A cursory analysis revealed that for the Xe$_{1061}$ cluster irradiated by a pulse of $I_{M} = 10^{16}$ W cm$^{-2}$, $\tau = 10$ fs, the average residence time is of the order of 300–400 fs at $t = 1$ ps.

Figures 3(c) and (d) exhibit the maximum and the average ion energy for outer ionization category (B), the Xe$_{1061}$ cluster irradiated by a laser pulse of $I_{M} = 10^{14}$ W cm$^{-2}$, $\tau = 10$ fs. The pairwise interaction formula with trapping (equation (6)) and the central charge formula (equations (7) and (8)) give nearly identical results for $E_{M}$, whereas the pairwise interaction formula without trapping (equation (9)) results in unphysical fluctuations of $E_{M}$ (figure 3(c)). As equation (9) sums ion–electron interactions $r_{k} < r_{i}$, the number of summands oscillates with the instantaneous coordinates of the trapped electrons orbiting their host ion, indicating that for short weak pulses electron trapping plays a role also for surface ions. For the average ion energies (figure 3(d)), the pairwise interaction formula with trapping and the central charge formula converge to the same final value. The pairwise interaction formula without trapping (equation (9)) fails completely and gives negative average ion energies. Comparing the ion energetics of cases (A) and (B), not only the average and maximum ion energies are much lower in case (B). Rather, the striking difference lies in the slow convergence of ion energies, in particular of the average ion energy, in case (B). Whereas in case (A) the average ion energy is converged already at 20 fs after the temporal peak of the laser envelope function, in case (B)
Figure 3. The time-dependent corrected and uncorrected maximum and average ion kinetic energies obtained from trajectory calculations. (a), (b) $\text{Xe}_{1061}$, $I_M = 10^{16}$ W cm$^{-2}$, $\tau = 10$ fs (outer ionization category (A)). The three energy correction formulae, equations (6), (7) and (9), lead to undistinguishable curves $E_M$, with the uncorrected maximum ion kinetic energy $T_M$ converging to the long-time corrected value $E_M^{(L)}$ (panel (a)). For the average corrected ion energy $\langle E \rangle$ (panel (b)), the central charge formula and the pairwise interaction formula with trapping yield nearly identical results, with the uncorrected average kinetic energy $\langle T \rangle$ converging to their long-time value $\langle E \rangle^{(L)}$, whereas the pairwise interaction formula without trapping gives too low values. (c), (d) $\text{Xe}_{1061}$, $I_M = 10^{14}$ W cm$^{-2}$, $\tau = 10$ fs (outer ionization category (B)). The pairwise interaction formula and the central charge formula lead to nearly identical results for $E_M$ and $\langle E \rangle$. $T_M$ and $\langle T \rangle$ approach the long-time corrected values $E_M^{(L)}$ and $\langle E \rangle^{(L)}$ but are not converged until the end of the 15 ps trajectory. The pairwise interaction formula without trapping leads to unphysical fluctuations for $E_M$ (panel (c)) and to negative values for $\langle E \rangle$ (not shown in panel (d)). (e), (f) $\text{Xe}_{6099}$, $I_M = 5 \times 10^{14}$ W cm$^{-2}$, $\tau = 230$ fs (outer ionization category C). The three energy correction formulae give nearly identical results for $E_M$ and $\langle E \rangle$.

convergence is achieved only after $\approx 5$ ps. This point will be analyzed in section 3.2 utilizing the lychee model.

In figures 3(e) and (f), the time-dependent maximum and average ion energies are presented for the example (C), the $\text{Xe}_{6099}$ cluster irradiated by a 230 fs pulse at $I_M = 5 \times 10^{14}$ W cm$^{-2}$. 

New Journal of Physics 14 (2012) 075017 (http://www.njp.org/)
The energies obtained by the pairwise interaction formula with and without trapping (equations (6) and (9)) and by the central charge formula (equations (7) and (8)) are nearly identical, as trapping is prevented by the high electron kinetic energies attained during resonance heating. The corrected average and maximum ion energies, $\langle E \rangle$ and $E_M$, pass a maximum during the resonance of the nanoplasma electrons with the laser field ($t = 140–180$ fs). During the resonance, the electron population within the ion framework is lowered (cf figure 1(c)), so that the energy correction formulae overestimate the ion energies. After the resonance situation, the electrons are decelerated by the laser field and partly return from the vicinity of the cluster ($<10R$) into the ion framework. The ion energies are nearly converged at $t \approx \tau$, when the laser electric field has abated.

Our calculated single-trajectory results are in reasonably good agreement with the results of Holkundkar et al [23]. Their maximum ion energies for 25 fs infrared laser pulses are 7 keV for Xe$_{2171}$ at $I_M = 10^{15}$ W cm$^{-2}$ and 77 keV for Xe$_{6100}$ at $2 \times 10^{16}$ W cm$^{-2}$; our results are 5.2 and 76 keV, respectively. For the Xe$_{6100}$ cluster irradiated by a 125 fs pulse at $I_M = 10^{16}$ W cm$^{-2}$, Holkundkar et al [23] obtained $\langle E \rangle = 58$ keV and $E_M = 100$ keV; our results are $\langle E \rangle = 56$ keV and $E_M = 121$ keV. For a Xe$_{6140}$ cluster irradiated by a 100 fs pulse at $I_M = 10^{16}$ W cm$^{-2}$, Petrov and Davis [13] have simulated an average ion energy of 68 keV, which is considerably higher than our value of 38 keV obtained for the Xe$_{6099}$ cluster.

Erk et al [50] have recently published experimentally obtained ion kinetic energy distributions (KEDs) for xenon and argon clusters. To make contact with their experimental results, the simulated single-trajectory KEDs must be doubly averaged over the cluster size distribution and over the laser intensity profile [22]. For the cluster sizes we assume a log-normal distribution with an FWHM equal to the modal cluster size [51]. For the laser intensity we take a Gaussian beam intensity profile [52]

$$I_M(r, z) = I_M^{\text{max}} \frac{2r^2}{z_R^2 + z^2} \exp \left[ - \frac{(2r^2)}{w_0^2} \left( \frac{z^2}{z_R^2 + z^2} \right) \right],$$

where $I_M^{\text{max}}$ is the spatially and temporarily overall peak intensity at the center of the focus volume, $w_0$ the beam waist radius and $z_R = \pi w_0^2/\lambda$ is the Rayleigh length, with $\lambda = 800$ nm being the laser wavelength. The cluster beam, with a radius $r_B$, is directed along the $r$-axis, which is perpendicular to the focus offset axis $z$. The relation between $r_B$ and $z_R$ determines which part of the intensity profile is relevant for intensity averaging. For $r_B \gg z_R$, the averaging over the entire three-dimensional (3D) laser focus volume has to be carried out; for $z_R < r_B$, only a slice of the laser intensity profile around $z = 0$ is involved, so that equation (10) reduces to a 2D intensity profile

$$I_M(r) = I_M^{\text{max}} \exp \left( - \frac{2r^2}{w_0^2} \right).$$

Compared to the 3D profile, in the 2D case the relative weight of low intensities is considerably lower. In the paper by Erk et al [50], $r_B = 0.75$ mm, but $z_R$ is not specified. However, from experience $z_R$ can be assumed to be $\approx 2.5$ mm [53], nearly realizing the 2D scenario of equation (11). The KEDs in the experiment of Erk et al were obtained for $I_M^{\text{max}} = 5 \times 10^{15}$ W cm$^{-2}$ and $\tau = 35$ fs. For the double averaging in [22], we used ion energies from trajectories in the cluster size range $55 \leq n \leq 4093$ and intensities $10^{14}$ W cm$^{-2} \leq I_M \leq 5 \times 10^{15}$ W cm$^{-2}$. Erk et al give KEDs for two average xenon cluster sizes, $(n) = 200$ and 700, which are in our simulated cluster size range. The experimental maximum ion energy for
\( \langle n \rangle = 200 \) is about 22 keV and for \( \langle n \rangle = 700 \) 27 keV. Applying the same definition of the maximum ion energy as in the experiment, that is, when the KED drops to the given fraction of its maximum value \((2 \times 10^{-4}) \) for \( \langle n \rangle = 200 \) and \(4 \times 10^{-5}\) for \( \langle n \rangle = 700\), the simulated maximum ion energies on the basis of a 2D intensity profile are 11 keV for \( \langle n \rangle = 200 \) and 18 keV for \( \langle n \rangle = 700 \). The corresponding maximum ion energies on the basis of the 3D intensity profile are much lower, 7 keV for \( \langle n \rangle = 200 \) and 12 keV for \( \langle n \rangle = 700 \). That is to say, all simulated values are considerably lower than the experimental values, but better agreement with the experiment is obtained for the 2D scenario. A more detailed analysis of the experimental KEDs will be given in a forthcoming paper. Trying to assess our simulation results for the ion energetics, one may expect in general that our trajectory simulation model tends to underestimate ion energies, since the neglect of the excitation-autoionization and recombination-autoionization EII channels (see section 2) causes too low ion charges. For \( \langle n \rangle = 700 \), Erk et al observed a maximum charge state \( q_M = 19 \), whereas our simulations give values \( q_M = 13 \) for Xe\(_{106}\) and \( q_M = 14 \) for Xe\(_{217}\) \((I_M = 5 \times 10^{15} \text{ W cm}^{-2}, \tau = 35 \text{ fs})\). The deviations between simulation and experiment may be partly due to the uncertainties of the experimental cluster size and laser intensity distributions. As pointed out by Schultze et al \([54]\), the assumption of a Gaussian beam intensity profile is a significant oversimplification.

3.2. The multi-charge state lychee model

Insight into the ion energetics can be gained by using the electrostatic lychee model \([14, 21]\). The model presumes that (i) inner and outer ionizations are vertical, (ii) all nanoplasma electrons are confined to the cluster interior and form, together with the ions, a neutral sphere where the sum of ion and electron charges is equal, so that (iii) only ions in the electron-free cluster periphery participate in the Coulomb explosion. Knowing the initial radius \( R_0 \) and the homogeneous initial density \( \rho \) of a spherical cluster, the lychee model gives analytical expressions for the central charge \( Q(r) \) as a function of the distance \( r \) from the cluster center, for the radius \( R_p \) of the neutral interior cluster sphere, for the ion energies \( E(r) \), for the average and maximum ion energies \( \langle E \rangle \) and \( E_M \) and for the ion kinetic energy distribution (KED) \( P(E) \) \([21]\). While in previous work \([21]\) the lychee model was expressed for an average ion charge \( q_{\text{av}} \), an obvious improvement is extension to a charge distribution, in particular since \( E_M \) and therefore the width of \( P(E) \) are determined by the maximum ion charge \( q_M \) at the cluster surface. The extension to a multiple-charge state lychee model is straightforward, for simplicity presuming that the ions of each charge state are homogeneously distributed over the cluster with a density

\[
\rho_q = \rho \frac{n_q}{n}, \tag{12}
\]

where \( n_q \) is the number of ions of charge \( q \) and \( n \) is the total number of ions. The resulting expressions for \( R_p \), \( Q(r) \) and \( \langle E \rangle \) are identical with those of the single-charge state lychee model (all energies in the equations are given in atomic units)

\[
R_p = R_0 \left( \frac{n_p}{q_{\text{av}}} \right)^{1/3}, \tag{13}
\]

\[
Q(r) = \frac{4\pi}{3} \left( r^3 - R_p^3 \right) \rho q_{\text{av}} \quad (r \geq R_p), \tag{14}
\]

\[
\langle E \rangle = \frac{4\pi}{5} \rho q_{\text{av}}^2 R_0^2 \left[ 1 - \frac{5}{2} \frac{n_p}{q_{\text{av}}} + \frac{3}{2} \left( \frac{n_p}{q_{\text{av}}} \right)^{5/3} \right]. \tag{15}
\]
For the energy \( E_q(r) \) of an ion of charge \( q \) at a distance \( r \) from the cluster center, one obtains
\[
E_q(r) = \frac{Q(r)q}{r},
\]
and for the maximum ion energy
\[
E_M = \frac{Q(R_0)q_M}{R_0}. \tag{17}
\]

The energy distribution function \( P(E) \) is the superposition of the partial distribution functions \( P_q(E) \) of each charge state
\[
P(E) = \sum_q \left( \frac{\rho_q}{\rho} P_q(E) \right),
\]
with
\[
P_q(E) = \frac{3}{E_{M,q}} \frac{r^2}{R_0^2} \left( 1 - \frac{R_0^3}{r^3} \right),
\]
where \( E_{M,q} = E_q(R_0) \) is the maximum ion energy for charge state \( q \); cf equations (16) and (17). The \( P_q(E) \) and, consequently, also \( P(E) \) are normalized to \( 1 - n_p/q_{av} \)
\[
\int_0^{E_{M,q}} P_q(E) \, dE = 1 - \frac{n_p}{q_{av}},
\]
excluding the neutral lychee core, which is consistent with the average ion energy \( \langle E \rangle \), equation (15). Reasonably, one applies equations (12)–(20) to the effective ion charges and the free nanoplasma electron population rather than to the full ion charges and total nanoplasma electron population.

Applying the lychee model to the analysis of the slow convergence of the average ion energy in case (B), we note that the expression for \( \langle E \rangle \), equation (15), contains powers of \( n_p/q_{av} \) and \( q_{av}^2 \) in the prefactor. With \( x = n_p/q_{av} \) and the average net charge per atom, \( q_{net} = q_{av} - n_p \), equation (15) can be recast:
\[
E = \frac{4\pi}{5} \rho R_0^3 q_{net} \frac{1 - \frac{5}{2}x + \frac{3}{2}x^{5/3}}{(1-x)^2}.
\]

To find out to what extent \( \langle E \rangle \) is dependent on \( x = n_p/q_{av} \), in figure 4 the fractional polynomial in equation (21), which is equivalent to the relative average ion energy \( \langle E \rangle(x)/\langle E \rangle(0) \) for constant \( q_{net} \),
\[
1 - \left( \frac{\frac{5}{2}x + \frac{3}{2}x^{5/3}}{(1-x)^2} \right)^{5/3} = \frac{E(x)}{E(0)},
\]
is plotted against \( n_p/q_{av} \). Note that \( \langle E \rangle(0) \) is the average ion energy for the lower limit \( n_p/q_{av} = 0 \), when all nanoplasma electrons are trapped. The upper limit, \( n_p/q_{av} = 1 \), where the total cluster charge is zero and \( \langle E \rangle(n_p/q_{av})/\langle E \rangle(0) = 5/6 \), is approached by outer ionization category (B). Large clusters can come arbitrarily close to this limit. As shown by figure 4, the
fractional polynomial, equation (22), varies at most by 17% over the entire \( n_p/q_{av} \) range, so that \( \langle E \rangle \) depends mainly on \( q_{\text{net}} \). Since \( q_{\text{net}} \) is directly related to the total cluster charge \( Q(R_0) \)

\[
Q(R_0) = \frac{4\pi}{3} \rho R_0^3 \left( q_{av} - n_p \right),
\]

we conclude that the average ion energy depends mainly on the total cluster charge rather than on the charge distribution inside the cluster, and \( Q \) may be a key parameter for understanding the convergence behavior of the ion energetics and the underlying physical processes.

For the Xe\(_{1061}\) cluster, \( I_M = 10^{16} \text{ W cm}^{-2} \), \( \tau = 10 \text{ fs} \) (outer ionization category (A)), in figure 5 the central charge \( Q(i) \) (equation (8)) experienced by each ion \( i \) is plotted against the ion number \( i \), where the ions are ordered according to their distance from the cluster center. In this way, figure 5 contains information on the charge distribution inside the cluster as well as on the total cluster charge; \( Q(1061) \) represents the central charge experienced by a surface ion. \( Q(i) \) is given for \( t = 0.02, 0.5 \) and 3.5 ps. For all the considered times, \( Q(i) \) reflects a typical spatial lychee charge distribution, low \( Q \) values in the cluster interior and a steep rise toward the cluster periphery. \( Q(1061) \) is practically converged at \( t = 0.5 \) ps. At \( t = 20 \) fs, when \( \langle E \rangle \) is already converged but \( E_M \) still by 1.5 keV above its final value of 16.5 keV (figure 3(a)), \( Q(1061) \) exceeds its final value by 20%. Apparently, the lowering of \( Q(1061) \) for \( t > 20 \) fs is due to the rapid expansion of the cluster periphery into the surrounding electron cloud.

For the outer ionization category (B), the spatial dependence and time evolution of \( Q(i) \) are very different from that of category (A). In figure 6(a), the \( Q(i) \) function is given for \( t = 0.02, 0.2, 1, 5, 10 \) and 15 ps. \( Q(i) \) assumes much lower values than in case (A) and is not converged until at least \( t = 10 \) ps. To elucidate the different roles of ions and electrons, in figure 6(b) \( Q(i) \) is calculated from the reduced ion charges only, i.e. excluding the free nanoplasma electrons. When the free nanoplasma electrons are excluded, not only are the \( Q(i) \) values much higher, as expected, but \( Q(i) \) also converges much faster. This provides additional evidence that the slow

**Figure 4.** The fractional polynomial, equation (22), in the range \( 0 \leq x \leq 1 \), \( x = n_p/q_{av} \).
convergence of the total $Q(i)$ function (figure 6(a)) is caused by a gradual loss of nanoplasma electrons, a continuous evaporation of nanoplasma electrons from the ion framework on the picosecond time scale. The consequence of the slow electron evaporation on the ion energetics is that the ions are accelerated by a variable central charge $Q$, precluding a meaningful estimate of the ion potential energy residues from short trajectories. The electron evaporation causes the outer ionization to be highly non-vertical, despite a negligible cluster expansion during the short laser pulse. A comparison of figures 3(d) and 6(a) shows that $\langle E \rangle$ is earlier converged (around $t = 5$ ps) than $Q$ (not before $t = 10–15$ ps), reflecting that the effect of the electron evaporation on the ion energetics fades away at a late stage of the cluster expansion.

For a quantitative comparison of the KEDs from the trajectory calculations and those of the lychee model, it must be taken into account that in the trajectory calculations, $P(E)$ is approximated by a histogram $h_k$ of ion energies of finite-energy intervals $\Delta E$

$$P \left( \left( k + \frac{1}{2} \right) \Delta E \right) \approx \frac{h_k}{\Delta E}; \quad k \cdot \Delta E \leq E < (k + 1) \cdot \Delta E. \quad (24)$$

Figure 5. The central charge $Q(i)$, equation (8), experienced by the ions of the Xe$_{1061}$ cluster irradiated by a laser pulse of $I_M = 10^{16}$ W cm$^{-2}$, $\tau = 10$ fs (outer ionization category (A)), calculated from trajectory data. The 1061 ions $i$ defining the abscissa are ordered by their distance from the cluster center, so that $Q(i)$ reflects the spatial charge distribution in the cluster; $Q(1061)$ is the central charge experienced by a surface ion. $Q(i)$ is given at times $t = 0.02$, 0.5 and 3.5 ps.
Figure 6. The central charge $Q(i)$ experienced by the ions of the Xe$_{1061}$ cluster irradiated by a laser pulse of $I_M = 10^{14}$ W cm$^{-2}$, $\tau = 10$ fs (outer ionization category (B)), at times $t = 0.02, 0.2, 1, 5, 10$ and $15$ ps, calculated from trajectory data. (a) $Q(i)$ calculated from ion and electron charges; (b) $Q(i)$ calculated from effective ion charges without the contribution of the free nanoplasma electrons.

Unlike in the lychee model, in the trajectory calculations $P(E)$ is normalized to 1, as well as the ions in the nearly neutral lychee core participate in the cluster expansion and contribute to the $h_k$ of the lowest-energy interval. Therefore, to be comparable with the KED of the trajectory calculation, the constant term $n_p^{\text{free}}/q_{av}^{\text{eff}} \delta_k$ has to be added to $h_0$ of the lychee model

$$h_k = \frac{1}{\Delta E} \left[ \int_{E-\Delta E}^{E+\Delta E} P_{\text{lychee}}(E') \, dE' + \frac{n_p^{\text{free}}}{q_{av}^{\text{free}}} \delta_k + \frac{n_0}{n} \left( 1 - \frac{n_p^{\text{free}}}{q_{av}^{\text{eff}}} \right) \delta_k \right]. \quad (25)$$

The last term in equation (25), $n_0/n \left( 1 - \frac{n_p^{\text{free}}}{q_{av}^{\text{eff}}} \right) \cdot \delta_k$, accounts for ions that have reached charge neutrality by trapping the corresponding number of electrons, with $n_0$ and $n$ being the number of neutral atoms and the total number of atoms in the cluster, respectively.

For a numerical application of equation (25), with $P_{\text{lychee}}(E)$ from equations (18) and (19), $n_p^{\text{free}}$ and the ion charge state abundances $\{n_q^{\text{eff}}\}$ are taken from trajectory calculations. The question arises then at which instant of the trajectory, $n_p^{\text{free}}$ and $\{n_q^{\text{eff}}\}$ should be taken, as the charge build-up in the cluster is not completely vertical even for outer ionization case (A). One possible choice is at a comparatively long time $t_L$ of the trajectory, when the ion energies are converged. A better alternative seems to be the charge distribution, which is dominant for the cluster expansion; we therefore take $n_p^{\text{free}}$ and $\{n_q^{\text{eff}}\}$ at the instant $t_{acc}$ when the average ion acceleration reaches its maximum, $t_{acc} = 20, 200$ and $110$ fs for examples (A)–(C), respectively. For the example (A) the instant $t = 20$ fs practically coincides with the termination of outer ionization. In case (B), the delay of $t_{acc}$ to $200$ fs, which is long after the termination of the laser pulse, reflects the slow charge build-up in the cluster by electron evaporation. In case (C), the instant of maximum ion acceleration coincides roughly with the enhanced outer ionization at the nanoplasma electron resonance.
The relative ion charge state abundances for the examples (A)–(C). Symbols ■ and □ are the effective ion charge state abundances \( n_q^{\text{eff}}/n \) at \( t = t_{\text{acc}} \) and \( t = t_L \), respectively; • and ○ are the full ion charge state abundances \( n_q/n \) at \( t = t_{\text{acc}} \) and \( t = t_L \), respectively. For the examples (A)–(C), the times \( t_{\text{acc}} \) are at 20, 200 and 110 fs (times when the average ion acceleration assumes a maximum), and the times \( t_L \) are 3.5, 15 and 0.6 ps, respectively.

Figure 7 shows the distributions of effective and bare ion charges at the maximum ion acceleration times \( t_{\text{acc}} \). For comparison, the corresponding ion charge distributions at long times \( t_L \) have been included. Using the abundances of effective ion charges and free nanoplasma electron populations at \( t_{\text{acc}} \), the KEDs calculated by the lychee model are shown in figure 8, together with the corresponding results of the trajectory calculations.

In case (A) (figure 8(a)), the KEDs of the trajectory calculation and of the lychee model are in overall good agreement and the average ion energy is in perfect agreement. The overestimate of \( E_M \) by the lychee model by 3 keV is a non-vertical effect, as the cluster expansion sets in before the charge build-up is complete. The low-energy component \( h_0 \), which constitutes the maximum of the KED, is reproduced by the lychee model within 35%.

The underlying effective ion charge abundances of case (A) (figure 7(a)), at \( t_{\text{acc}} = 20 \) fs and \( t_L = 3.5 \) ps, differ mainly for the low ion charges 0–4, whereas the highest ion charge \( q = 13 \), which defines the width of the KED, is practically unaffected. Effective ion charges of 0 and 1 are a consequence of the high electron density in the practically unexpanded lychee core at...
Figure 8. The KEDs for the examples (A)–(C), approximated by the histogram values $h_k/\Delta E$ for finite-energy intervals $\Delta E$. The KEDs obtained from the trajectory calculations are represented by histograms. The lychee model results were obtained from equation (25), using the effective ion charges and populations of free nanoplasma electrons at $t = t_{\text{acc}}$. The trajectory and lychee model results for $\langle E \rangle$ and $E_M$ are given inside the panels.

$t_{\text{acc}} = 20$ fs; under these conditions, electrons are only formally assigned to ions according to their ion–electron cutoff distance (2 Å) rather than actually trapped. (Ions that formally acquire negative charges by close encounters with electrons are counted as neutral atoms; the resulting excess electrons are counted as free nanoplasma electrons.) Using the ion charge abundances at $t_L = 3.5$ ps, where the effective ion charges of 0 and 1 are missing, the lychee model gives nearly identical results, $\langle E \rangle = 1.92$ keV and $E_M = 19.6$ keV, and a very similar KED (not shown in figure 8(a) for $t = t_L$), provided that the number of nanoplasma electrons is chosen such that $Q(1061)$ is adjusted to the same value as that at $t = t_{\text{acc}}$. Note that $Q(1061)$ at $t = t_L$ is lower by almost 500 charge units than that at $t = t_{\text{acc}}$ (figure 5) due to the rapid expansion of the cluster periphery into the surrounding dilute electron cloud. While the reentry of the electrons into the expanded cluster periphery has a relatively small effect on the ion energetics of the trajectory, the 500 charge units make a considerable difference to $n_p^{\text{(free)}}$ as one of the key input parameters of the lychee model; the inclusion of the 500 electrons lowers $\langle E \rangle$ and $E_M$ to 1.25 and 15.9 keV, respectively. In conclusion, the lychee model results for $\langle E \rangle$ and $E_M$ are insensitive to the abundances of low ion charges, as long as the total cluster charge and the highest ion charge remain unaffected, reflecting the essence of equations (17) and (21).

The ion charges are not homogeneously distributed over the entire cluster as presumed by the lychee model. Rather, higher ion charges are enriched toward the cluster periphery. The presumption of a spatially homogeneous distribution of ion charges does not affect $E_M$ but is expected to influence the shape of the KED. In particular, the larger number of higher charge states in the cluster periphery will enhance the high-energy tail of the KED.
Proceeding to case (B) (figure 8(b)), the deviations of the lychee model results manifest extreme non-vertical effects. With the abundances of reduced ion charges and the number of free nanoplasma electrons taken at $t_{acc} = 200$ fs, the lychee model underestimates $\langle E \rangle$ by a factor of 5. To reproduce the trajectory calculation result of $\langle E \rangle = 53$ eV, the lychee model requires a central charge value $Q(1061) \approx 420$, which is approached only at $t \approx 4–5$ ps (cf figure 6(a)), when $\langle E \rangle$ of the trajectory calculation also converges. In view of this slow charge build-up, it is therefore at first surprising that the lychee model overestimates $E_M$. Taking the maximum effective ion charge $q_{M}^{(eff)} = 4$ (figure 7(b)), the lychee model yields $E_M = 0.44$ keV as compared to $E_M = 0.33$ keV from the trajectory calculation. However, a closer inspection of the trajectory reveals that although the maximum effective ion charge of 4 is reached already at an early stage of the trajectory, it is not constantly attributed to the same ions. Short-time averaging shows that the maximum ion charge fluctuates between 2 and 4, reaching its final constant value of 4 only at $t \approx 0.5$ ps. The shape of the KED calculated by the lychee model is dominated by the low-energy component $h_0$, which is by one order of magnitude higher than that of the trajectory calculation. In the trajectory calculation, the sharp $h_0$ peak is spread over a larger number of low-energy intervals, reflecting the large departure of the spatial charge distribution (figure 6(a)) from that of a lychee structure.

In case (C) (figure 8(c)), the $E_M$ value calculated by the lychee model is 201 keV, being too high by almost a factor of 3, as a consequence of the neglect of the large cluster expansion until $t_{acc}$, $R(t_{acc}) = 8R_0$ (figure 1(c)). Furthermore, the lychee model predicts a large low-energy component $h_0$ of the KED, since the lychee model presumes all nanoplasma electrons to be located in the lychee core due to the neglect of electron dynamics. A neutral cluster core is not found in the trajectory calculation, as the electrons are nearly equally distributed over the entire ion framework by resonance heating.

For carrying out trajectory calculations, it is of practical interest to define some guidelines on what is the temporal length of a trajectory that is necessary for achieving convergence of the ion energies. From the foregoing discussion one can infer that a sufficient criterion for the convergence of the corrected ion energies is the convergence of the charge distribution inside the cluster and of the total cluster charge. This includes the absence of nuclear overrun subsequent to the truncation of the trajectory, as nuclear overrun can lead to an exchange of ion energies. However, as examples (A) and (B) have shown, the effect of the remaining variations of the charge distribution on ion energies fades out at a late stage of the cluster expansion, so that the criterion of a converged charge distribution is sufficient but not necessary. As an empirical rule of thumb, we found that the corrected ion energies are sufficiently converged when $\langle T \rangle/\langle E \rangle \geq 0.85$.

4. Conclusions

The inclusion of tunnel ionization and of the enhancement of EII by the electric field [15] in the simulation formalism allowed us to consider laser peak intensities down to $I_M = 10^{14}$ W cm$^{-2}$, one order of magnitude lower than that in our previous simulations [21, 22]. A presentation of the ion energetics over the entire pulse parameter range considered, $I_M = 10^{14}–10^{18}$ W cm$^{-2}$, $\tau = 10–230$ fs, and a comparison with our previous simulation results and with experimental results will be given in a forthcoming paper. From these results, we mention here only that we did not find anomalous anisotropy of the ion energies recently reported by Skopolová et al [33] and Mathur et al [34, 35], according to which higher ion energies have been found.
experimentally perpendicular to the laser polarization direction. In our simulations we found higher ion energies in the laser polarization direction. With decreasing the laser intensity and with decreasing the pulse length, the average ion energy becomes increasingly isotropic except from some fluctuations.

In this paper, we have selected three examples to discuss the dependence of the ion energetics on outer ionization. These three examples represent three categories of incomplete outer ionization, resulting in electron-rich nanoplastmas: (A) vertical incomplete outer ionization for short \( \tau = 10 \) fs intense \( I_M = 10^{16} \) W cm\(^{-2} \) pulses; (B) non-vertical incomplete outer ionization for short \( \tau = 10 \) fs weak \( I_M = 10^{14} \) W cm\(^{-2} \) pulses; and (C) non-vertical incomplete outer ionization for long \( \tau = 230 \) fs weak \( 5 \times 10^{14} \) W cm\(^{-2} \) pulses. While cases (A) and (C) have already been identified in previous work \[21\], case (B) is new. In case (C), the non-verticality of outer ionization is caused by the large cluster expansion during the long laser pulse; the cluster charge build-up ends with the termination of the laser pulse. In contrast, in case (B) the cluster expansion during the short laser pulse is negligible, but the cluster charge build-up continues by electron evaporation under laser-free conditions for a long time.

The example representing outer ionization category (A) differs from example (B) only by the higher laser intensity and consequently by a higher outer ionization level, better confining the remaining nanoplasma electrons to the cluster interior and prohibiting electron evaporation. Likewise, one may expect that increasing the cluster size causes a transition from outer ionization category (A) to (B), due to a decreasing outer ionization level for larger clusters. A quantification of the cluster size and intensity dependence of the vertical to non-vertical transition will be of interest.

To improve the description of the ion KED function by the electrostatic lychee model, we have extended the model to multi-charge states. In the case of vertical outer ionization (example (A)), the model reproduces the energy distribution function semiquantitatively. The characteristic signature of a lychee core is its intense low-energy peak in the ion kinetic energy distribution. Such low-energy peaks are exhibited in the ion kinetic energy distributions of Erk \textit{et al} \[50\], which deserve further analysis. In case of non-vertical outer ionization by short pulses (example (B)), the lychee model shows very poor numerical agreement with the simulation results but was very useful in interpreting and characterizing the underlying physical processes. In the case of non-vertical outer ionizations by long pulses (example (C)) the lychee model fails completely due to the total neglect of the electron dynamics. Clearly, a further improvement of the lychee model requires a smooth rather than an abrupt transition between the neutral lychee core and the electron-free cluster periphery via the electron kinetic energy governing the spatial electron distribution inside the ion framework.

**Acknowledgments**

We are grateful to Professor Uzi Even for discussions of the laser-intensity profiles. Computation time, technical and manpower support of the computation center IZO-SGI SDIker of the University of the Basque Country (UPV/EHU), provided by the Spanish Ministry of Science and Education (MICINN), by the Basque Government (GV/EJ) and by the European Social Fund (ESF) are gratefully acknowledged. This research was partially supported by the Saiotek Program (GV/EJ).
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