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# Cluster nanoplasmas in strong FLASH pulses: Formation, excitation and relaxation

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**Abstract.** Clusters exposed to intense laser radiation will quickly turn into nanoplasmas: short-lived electron plasmas confined by the charged cluster ions on a nanometer scale. Although the cluster will eventually explode, the transient multi-electron dynamics during the pulse is of great interest and largely unexplored. It determines the mechanism of energy absorption and may thus help to understand measured electron and ion spectra, also in other samples like large molecules. Furthermore, an experimental setup with short pulses and access to observables, which becomes possible because of the sample's finite size, offers novel possibilities to investigate non-equilibrium dynamics of plasmas. Here, the formation, excitation and relaxation of nanoplasmas in rare-gas clusters driven by strong pulses from free-electron lasers (FELs) with photon frequencies in the range of about 10 up to 100 eV as currently available at FLASH are discussed. It is the unique combination of brilliant, tunable and short-pulse radiation in this machine and upcoming X-ray FELs which makes such studies feasible.

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## 1. Introduction

Since the very first measurements (Wabnitz et al. 2002) clusters are prominent targets (Bostedt & Möller 2010) for studies with intense vacuum (VUV) and extreme (XUV) ultraviolet radiation as available from the first short-wavelength free-electron laser FLASH (Ackermann et al. 2007). They are prototypes for finite systems with the exclusive feature that their size can be easily changed from a few atoms as in small molecules to a few million atoms as in micro-droplets. Clusters can be made up of atoms or molecules. Here, we restrict ourselves to rare-gas clusters since most experiments are performed with this cluster type. The corresponding inter-atomic distances are a few Ångström just like in molecules. The binding, which is due to van-der-Waals interaction (Haberland 1994), however, is much weaker and hardly changes the electronic structure of the atoms.

The response of such rare-gas clusters to intense pulses at near-infrared (NIR) frequencies has been extensively studied and recently reviewed (Krainov & Smirnov 2002, Saalmann et al. 2006). Experiments in the VUV and XUV regime became feasible by the advent of FLASH (Bostedt et al. 2009) and very recently by the SPring-8 Compact SASE Source (Fukuzawa et al. 2009). First cluster experiments with X-ray pulses are currently under way at the LCLS. In all cases a plasma confined to the cluster volume can be formed. Its characteristics, like density and temperature, depend crucially on the laser radiation and may change strongly on a femtosecond time scale, either due to the absorption of energy from the laser or due to particle and light emission. The observation of fast electrons (Springate et al. 2003), highly-charged ions (Ditmire et al. 1997) or high-energetic photons (McPherson et al. 1994) has been strongly driving the interest in laser-cluster interaction for NIR radiation. FEL sources with shorter wavelengths can induce nanoplasma formation under novel conditions. The possibility to create and drive such finite and “open” plasmas allows to study non-equilibrium multi-electron dynamics, eventually down to a sub-femtosecond time scale (Saalmann et al. 2008).

Firstly, we will present a qualitative picture of clusters in strong laser pulses and introduce relevant quantities that characterize the laser-cluster interaction (sect. 2). Basic processes, like photo-absorption and collisions, occur in strongly excited multi-electron systems which makes a quantitative theoretical description challenging. We will discuss two approaches to this problem (sect. 3). By means of these approaches many theoretical studies have performed in order to understand measurements done at FLASH over the last 8 years. We will report a few of them and discuss the main conclusions (sect. 4). We finish with an outlook on new directions of FEL-cluster experiments and recent theoretical proposal for interesting measurements (sect. 5).

We do not present a review covering all aspects of the theoretical description of atomic clusters exposed to intense radiation from VUV/XUV free-electron lasers like FLASH. We rather discuss the basic mechanisms and present some of the theoretical methods which aim at a quantitative treatment of the induced nanoplasma dynamics.

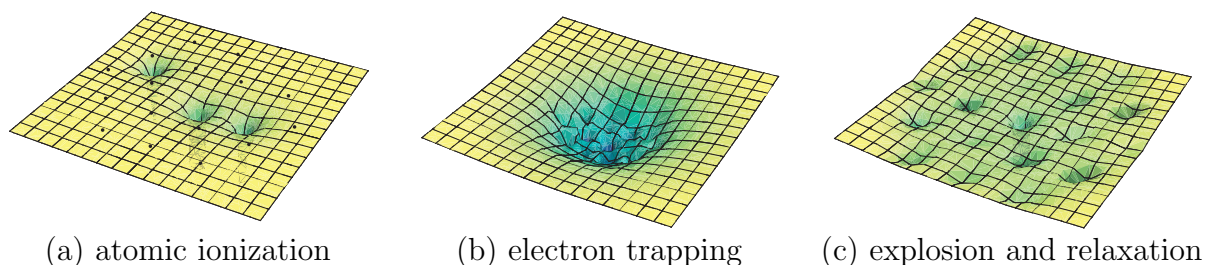
## 2. Clusters in strong laser fields

Before quantifying the laser impact we will briefly outline the general scenario of the cluster dynamics driven by intense laser irradiation. For the moment we consider the laser pulse to be strong, irrespective of its frequency  $\omega$ , if it leads to multiple ionization of the atoms in the cluster. Due to the large number of atoms initially bound in the cluster this ionization may result in a very highly charged system. With  $N$  the number of atoms in the cluster and an average ionic charge  $q$  the cluster charge becomes  $Q = Nq$ , resulting in an extended and strongly attractive potential, cf. Fig. 1 showing its formation. It is this potential which makes the response of clusters to strong laser pulses qualitatively different from that of atoms or small molecules. The two most important implications for the electron dynamics in clusters exposed to short-wavelength radiation, to be discussed below in detail, are

- (i) trapping of electrons which may form a plasma, usually referred to as nanoplasma (Ditmire et al. 1996), which dominates the cluster dynamics,
- (ii) charging of atoms/ions, in particular at the cluster surface, through “field” ionization (Gnodtke et al. 2009).

The plasma formation implies various secondary processes like electron-impact ionization, equilibration through electron-electron collisions and expansion due to hydrodynamic pressure. Note that both effects plasma formation and secondary processes depend on the instantaneous cluster potential which changes in time due to two counteracting processes. On one hand it becomes deeper due to further excitation of bound electrons into the plasma (cf. Fig. 1b). On the other hand the potential expands and becomes shallower because of the expansion of the cluster<sup>‡</sup> (cf. Fig. 1c).

<sup>‡</sup> The expansion dynamics has been measured for NIR frequencies by means of pump-probe experiments (Zweiback et al. 1999) and discussed within a macroscopic model (Ditmire et al. 1996) and microscopic calculations (Saalman & Rost 2003, Saalman 2006). Here, the energy absorption is most efficient when the eigenfrequency of the cluster potential becomes resonant with the laser frequency (Saalman



**Figure 1.** Sketch of the cluster potential as a function of time. For convenience we show a 2D system. (a) The firstly ionized electrons see only single atomic potentials which are not influenced by the other cluster atoms marked by black dots. (b) Further ionization leads to one extended, deep cluster potential in which the electron plasma is trapped. (c) The cluster potential disintegrates due to expansion; inter-atomic barriers are raised.

The expansion dynamics has been hardly investigated in the context of FEL-cluster interaction.

### *Transition from NIR to X-ray frequencies*

The intensity  $I$  of the incoming laser pulse alone is not sufficient in order to quantify its impact on the electrons in the cluster atoms. Rather the frequency  $\omega$  of the laser is another key parameter, which is even relevant for non-resonant processes. It is known from atoms (Faisal 1987) that ionization processes can be treated in perturbation theory as long as the ponderomotive shift

$$E_{\text{pond}} = I/4\omega^2, \quad (1)$$

which occurs mainly for the final (continuum) states, but not for the initial (bound) state, is small compared to the frequency  $\omega$ , i. e., as long as  $E_{\text{pond}} \ll \omega$  or  $I \ll 4\omega^3$  (Joachain et al. 2000). If not specified otherwise we assume atomic units. Clearly, perturbation theory can be used for much higher intensities  $I$  if the frequency  $\omega$  is large. To be specific, for frequencies of  $\hbar\omega = 10$  eV and  $\hbar\omega = 100$  eV perturbation theory applies for  $I \ll 7 \times 10^{15}$  W/cm<sup>2</sup> and  $I \ll 7 \times 10^{18}$  W/cm<sup>2</sup>, respectively. Within this picture electrons are released through the absorption of a single or a few photons. The picture changes qualitatively if the frequency becomes so small that a laser period is long compared to typical times of electron motion. In this case the interaction is strong at maximal electric fields which can be considered as quasi-static. The electron may tunnel through the barrier or, for very high fields, leave the atom/ion above the barrier. The parameter which distinguishes the regimes of single/multi-photon and tunneling ionization was introduced by Keldysh (1965)  $\gamma = \sqrt{E_{\text{bind}}/2E_{\text{pond}}}$ , with  $\gamma < 1$  being an indicator for tunneling ionization. Thus the process by which electrons are excited into the plasma, sometimes referred to as ‘‘inner ionization’’ (Last & Jortner 1999), strongly depends on the laser frequency (Saalman et al. 2006).

Correspondingly, ‘‘outer ionization’’, which refers to the loss of electrons from the nanoplasma, differs for NIR and VUV/XUV frequencies. In order to quantify the importance of the laser one may use the quiver amplitude

$$x_{\text{quiv}} = \sqrt{I}/\omega^2, \quad (2)$$

characterizing the amplitude of free electron motion in an oscillating field defined by  $I$  and  $\omega$ . This length has to be compared to the cluster size. Quiver amplitudes for a typical intensity of  $I = 10^{14}$  W/cm<sup>2</sup> and the two frequencies  $\omega$  considered above are about 0.2 Å and 0.002 Å, respectively, and thus much smaller than the clusters

& Rost 2003). For quasi-neutral clusters this frequency coincides with the frequency of a spherical plasma  $\omega_{\text{pl}} = \sqrt{4\pi\rho_{\text{el}}/3}$  (Ditmire et al. 1996). This resonant collective absorption makes clusters extremely reactive for certain delays between pump and probe pulse; almost 100 % absorption of the incoming light has been measured (Zweiback et al. 1999). Of course, the absolute value depends also on target size and target density.

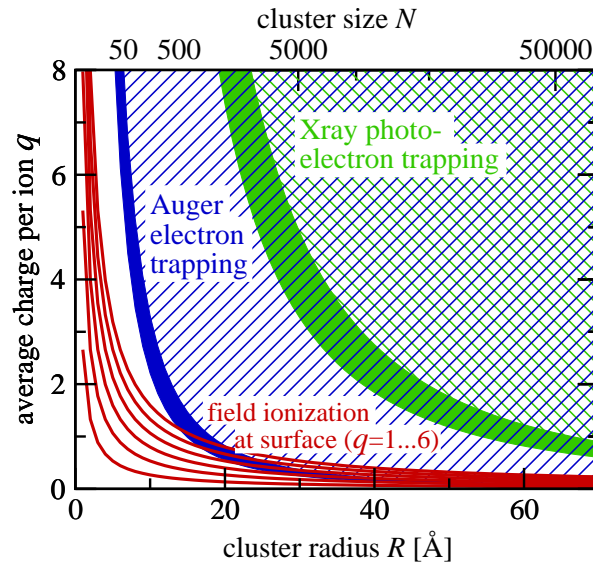
with diameters of a few nanometer§. Therefore, energy absorption occurs “locally” at individual atoms/ions. The two relevant processes are discussed in paragraph “Energy absorption” of Sect. 4.

### *Electron trapping in the cluster potential*

Electrons released early in the pulse from their “mother” atom leave the cluster (cf. Fig. 1a) directly. They could loose energy due to inelastic scattering on the way out. Nevertheless, recent experiments (Bostedt et al. 2008, Bostedt et al. 2010) clearly show a peak at the energy  $E_{\text{excess}}$  expected for the ionization of single atoms. This observation agrees with the fact that in rare-gas clusters, which are bound by vander-Waals interaction, the electronic structure is only slightly modified during cluster formation. Furthermore it indicates that inelastic scattering is less important that one would expect from the large cross sections, probably due to the small sizes of the cluster and the large fraction of atoms being at the cluster surface.

The emitted electrons leave a positively charged background behind, which eventually further electrons cannot escape from since they do not have sufficient energy;

§ For NIR frequencies the quiver amplitude and the cluster size are of the same order. The electron plasma is driven through the whole cluster and absorption occurs mainly “globally” (Ditmire et al. 1996, Saalman & Rost 2003), which is sometimes referred to as collisionless absorption.



**Figure 2.** Electron trapping and strong-field effects of homogeneously charged neon clusters with an average charge  $q$  per ion and a cluster radius  $R$ . Trapping of electrons detached by 12 keV photons (region above and including green/light-grey shaded band) and Auger decays (region above and including blue/dark-grey shaded band). The thick lower borders take into account that electrons are released from any position in the cluster. Red/solid lines: Ionization of surface ions at various charge states ( $q = 1 \dots 6$ ) due to the internal radial field of the charged cluster estimated by the Bethe rule. Figure from Gnodtke et al. (2009).

the electrons are trapped. Such trapping reduces the overall charging (Saalman & Rost 2002). This build up of the trapping potential has recently been measured by photo-electron spectroscopy with argon clusters (Bostedt et al. 2008). The onset of trapping depends on the cluster size  $N$  and the laser frequency  $\omega$ . For simplicity one may assume a spherical, homogeneously charged cluster of charge  $Q$  and radius  $R$ . The corresponding potential reads

$$V(r) = \begin{cases} -Q/R [3/2 - (r/R)^2/2] & \text{for } r \leq R, \\ -Q/r & \text{for } R \leq r. \end{cases} \quad (3)$$

This potential increases the binding energy  $E_{\text{bind}}$  of an electron in an atom having a distance  $r$  to the cluster center by  $V(r)$ . Accordingly the excess or final energy is reduced  $E_{\text{excess}} = [E_{\text{bind}} + V(r)] + \hbar\omega$  and can eventually become negative; the electrons are trapped. This occurs earlier for atoms at the cluster center ( $r=0$ ) than at its surface ( $r=R$ ). Figure 2 shows an overview for neon clusters at which radii  $R$  and average charge  $q = Q/N$  trapping starts to occur. The atom type fixes the clusters atomic density as well as the binding energy  $E_{\text{bind}}$ . The frequency of  $\hbar\omega = 12 \text{ keV}$  used in this figure (Gnodtke et al. 2009) is the high-end frequency of the upcoming European XFEL. At these high photon energies trapping occurs only for large and highly charged clusters (green area in Fig. 2). Auger electrons, which in the case of Neon have excess energies of about 900 eV, are trapped for much smaller and more weakly charged systems (blue area in Fig. 2). Obviously, at FLASH with even smaller photon energies of  $\hbar\omega = 10 \dots 100 \text{ eV}$ , trapping of electrons is a very important process.

### Field ionization and electron migration

From the expression for the cluster potential in Eq. (3) it becomes clear that there is a radial electric field  $\mathcal{E}(r) = d/dr V(r)$ , which is maximal at the cluster surface  $r \approx R$ . This applies also to situations where electrons tend to screen the ionic charge, since the screening modifies the potential|| only for small  $r < R$ . The absolute value of the electric field at the surface reads

$$\mathcal{E}(R) = Q/R^2 = \sqrt[3]{N} q/r_s^2, \quad (4)$$

with the Wigner-Seitz radius  $r_s = \sqrt[3]{3/4\pi\rho_{\text{at}}}$  for an atomic density  $\rho_{\text{at}}$ . Obviously the field increases for larger cluster sizes  $N$ . It can easily become strong enough in order to ionize atoms at the cluster's surface. To estimate this effect one may compare the electric field (4) with the critical fields necessary for above-the-barrier ionization according to

|| Of course, the potential depends on the instantaneous electron density. We assume that it is spherical and fully neutralizes the ion background from the center up to radius  $R_{\text{el}}$ . This requires an electron charge of  $Q_{\text{el}} = (R_{\text{el}}/R)^3 Q_{\text{ion}}$  and the clusters net charge becomes  $Q = Q_{\text{ion}} - Q_{\text{el}}$ . Then the potential reads

$$V(r) = \begin{cases} -(Q/R) [3/2 - (R_{\text{el}}/R)^2/2] & \text{for } r \leq R_{\text{el}}, \\ -(Q/R) [3/2 - (r/R)^2/2] & \text{for } R_{\text{el}} \leq r \leq R, \\ -Q/r & \text{for } R \leq r. \end{cases}$$

i. e., it is constant for  $r < R_{\text{el}}$ , becomes harmonic up to  $r = R$ , and finally Coulombic for  $r > R$ .

the so-called Bethe rule (Bethe & Salpeter 1957). Using these critical fields, which are given for the ionic charge  $q$  by  $\mathcal{E}_q = E_{\text{bind},q}^2/(4q)$ , one sees from the red lines for  $q = 1 \dots 6$  in Fig. 2 that this ionization process cannot be neglected. As it is similar to ionization with a static electric field, the process is termed field ionization. Note, however, that electrons released from the surface atoms in this way are always trapped in the cluster potential and become part of the nanoplasma. They will migrate to the cluster center in order to screen the positive cluster charge (Gnodtke et al. 2009).

Finally, we stress again that, although not specified in Eq. (3), the trapping potential and the induced radial electric field change in time since charge  $Q$  and radius  $R$  are time-dependent, cf. Fig. 1 which shows the disintegration of the cluster potential. The respective time scales of charging and expansion depend sensitively on the combination of cluster type and FEL radiation.

### 3. Theoretical methods

The very first experiments of clusters irradiated with VUV-FEL radiation by the Hamburg group (Wabnitz et al. 2002) lead to a variety of theoretical investigations last but not least because of the surprisingly high ionic charge states detected. From these observations it became clear that atoms in the clusters are multiply charged and thus a nanoplasma has been formed. The interaction of a finite plasma with intense radiation at these frequencies had never been investigated before. Since a first-principle description of the complex ultrafast dynamics is not possible, theoretical models, which incorporate the essential physical processes in forming and exciting the plasma, have been proposed. One may classify the approaches into those based on molecular dynamics (Siedschlag & Rost 2004, Jungreuthmayer et al. 2005, Georgescu et al. 2007b) and those using rate equations (Santra & Greene 2003, Walters et al. 2006, Ziaja et al. 2008).

In the first group of models classical equations of motion for (interacting) electrons and ions in the field of the oscillating laser field are solved. The numerical propagation is trivial for small systems but requires hierarchical schemes like tree-codes (Barnes & Hut 1986) or fast-multipole methods (Greengard & Rokhlin 1987, Dachsel 2009) for large particle numbers  $n$ , i. e.,  $n \gtrsim 10^4$ . The laser becomes less important for larger frequencies since ponderomotive energy and quiver amplitude decreases, cf. Eqs. (1) and (2) and their discussion. The Coulomb interaction of electrons and ions, however, can never be neglected since ion charges, electron densities, charge imbalances etc. may change strongly during the FEL pulse. Besides that, the calculation of electron or ion spectra requires large propagation times because of the long range of the Coulomb interaction. Similar to methods applied for clusters in NIR pulses (Saalman et al. 2006) only *non-bound* electrons are propagated. These electrons are sometimes referred to as quasi-free or plasma electrons since, although released from the mother atom/ion (“inner ionization”), they may be bound to the cluster as a whole, cf. Sect. 2. Eventually, these electrons may be emitted from the cluster (“outer ionization”). Energy absorption, collisions with other electrons and ions, and transient or permanent recombination of



these electrons as well as ionic expansion are fully contained in the molecular dynamics calculation (Saalman et al. 2006, Jungreuthmayer et al. 2005). The transition from bound to plasma electrons is treated by means of a Monte Carlo sampling (Georgescu et al. 2007b) and requires rates to be discussed below.

In the second group of models the various physical processes, like photoionization, inverse-bremsstrahlung heating, collisional ionization and recombination, are treated independently using rates. These rates are adopted from known atomic cross sections, e.g. Lotz formulas for electron-impact ionization (Lotz 1968), or calculated in single-active-electron approaches, e.g. for inverse bremsstrahlung (Walters et al. 2006). However, neighboring ions may strongly perturb the nearby environment of the considered atom/ion, which is usually neglected for the rate calculation. Furthermore, photo-absorption and collision processes are considered as independent events in both time and space (Walters et al. 2006). Plasma effects, however, are taken into account by artificially shifting ionization thresholds (Ziaja et al. 2008), by considering Debye screening (Santra & Greene 2003) and as input for electron-impact ionization. Density and temperature of the electron plasma are obtained by solving Boltzmann equations for electron and ion density distribution functions (Ziaja et al. 2008) or by globally calculating them for the cluster (Walters et al. 2006). The advantage of such approaches is its applicability to large cluster sizes, e.g.  $N = 9 \times 10^4$  (Ziaja et al. 2009b), which are inaccessible to molecular dynamics calculations.

There has been a number of implementations for both approaches. In particular the calculations based on the rate approach differ in whether and how certain processes are taken into account. In order to validate theoretical approaches often ion charge distributions are calculated and compared to measured data (Siedschlag & Rost 2004, Jungreuthmayer et al. 2005, Ziaja et al. 2009b). Instead of presenting such comparisons we will concentrate in the following on the underlying physical mechanisms.

#### 4. Clusters exposed to FLASH pulses

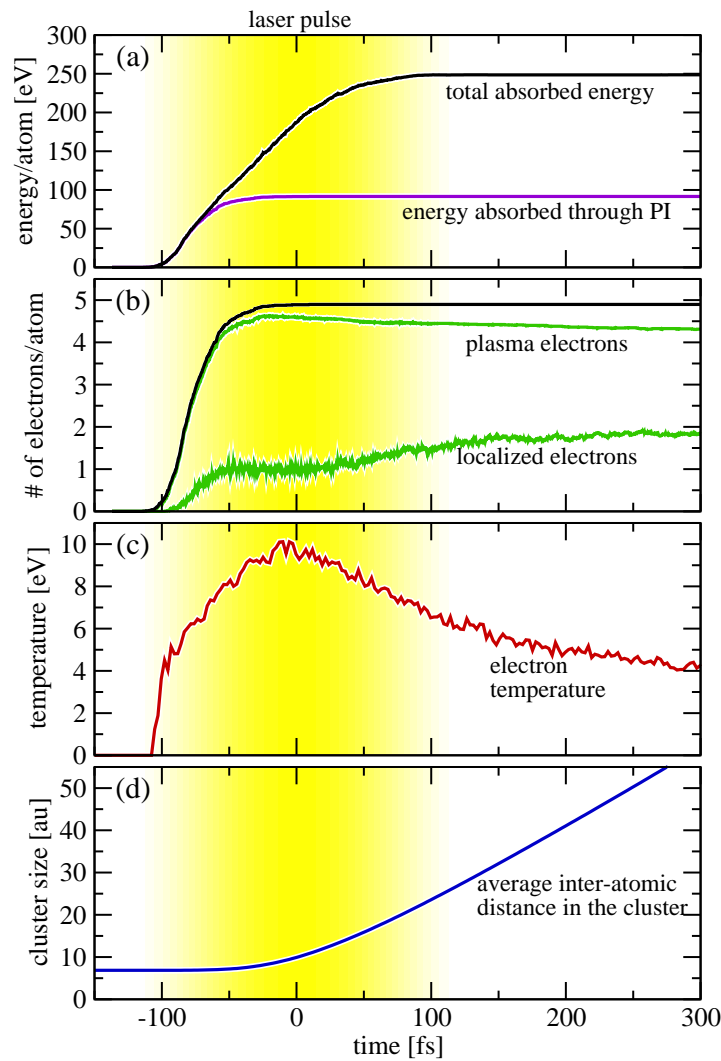
We will discuss the nanoplasma dynamics in clusters related to experiments performed at FLASH which covered frequencies from  $\hbar\omega \approx 12$  eV (early experiments) to  $\hbar\omega \approx 90$  eV (recent experiments). A detailed description of these experiments is given in this issue (Bostedt & Möller 2010). These two frequencies induce very different processes and are characteristic for the VUV and XUV regime, respectively.

##### *Energy absorption*

At the very first measurements at the Hamburg FEL (Wabnitz et al. 2002) the laser frequency was  $\hbar\omega = 12.7$  eV. This is slightly larger than the first ionization potential of xenon  $E_{Xe} = 12.1$  eV, but smaller than the ionization potentials of higher charge states, e.g.  $E_{Xe^+} = 21.0$  eV and  $E_{Xe^{2+}} = 32.1$  eV (Lide 2010). Despite these large ionization

potentials time-of-flight spectra have clearly shown charge states as high as  $\text{Xe}^{8+}$  for large clusters  $\text{Xe}_N$  with  $\langle N \rangle \approx 3 \times 10^4$ . Since smaller cluster with  $\langle N \rangle \approx 20 \dots 80$  did not produce such highly charged ions it was clear that a “cluster effect” has to be responsible for the particular efficient absorption of energy from the VUV laser pulse.

Highly charged ions (also with even higher charges) from laser-irradiated clusters have been observed before in experiments with intense NIR pulses (Ditmire et al. 1997). There, resonant collective absorption of the nanoplasma dominates all other processes by far (Ditmire et al. 1996, Saalmann 2006). The whole plasma is periodically driven in the background trapping potential and absorbs energy when the clusters eigenfrequency is resonant with the laser frequency. As individual collisions with ions are not relevant



**Figure 3.** Typical scenario of VUV–cluster interaction. Dynamics of  $\text{Ar}_{147}$  exposed to a 20 eV FEL pulse with intensity  $I = 7 \times 10^{13} \text{ W/cm}^2$  and duration  $T = 100 \text{ fs}$ , which is marked by the yellow-shaded area. From top to bottom: a) total absorbed energy and energy absorbed through photo-ionization, b) total electron number and number of plasma and transiently localized electrons, c) electron temperature, d) cluster size. Data from Georgescu et al. (2007b).

for the mechanism to work it is sometimes referred to as collisionless absorption. At VUV or higher frequencies, however, resonant collective absorption of the nanoplasma can be ruled out, since the plasma eigenfrequencies are typically a few eV only and thus much smaller. Besides, the quiver amplitude in the VUV field is much smaller than typical cluster radii, cf. Eq. (2) and its discussion. Therefore it was surprising, that, despite the absence of the most important absorption mechanism of laser-cluster interaction, highly charged ions were detected. These surprising observations sparked immediately theoretical studies (Santra & Greene 2003, Siedschlag & Rost 2004, Rusek & Orłowski 2005, Jungreuthmayer et al. 2005) aiming at understanding the underlying mechanism.

There are basically two process by which clusters can *absorb* photons and thus energy: photo-ionization (PI) and inverse bremsstrahlung (IBS). In photoionization a bound electron is promoted to a continuum state by absorption of a photon. Correspondingly, IBS describes photo-absorption of a free electron (Kroll & Watson 1973) which becomes possible only during collision with an ion. Cross sections for both processes can in principle be calculated in first order with transition matrix elements between initial ( $\psi_i$ ) and final ( $\psi_f$ ) states as

$$\sigma = 4\pi^2\alpha/\omega^3 \left| \langle \psi_f | \partial V(r)/\partial z | \psi_i \rangle \right|^2, \quad (5)$$

with  $V(r)$  denoting the spherical atomic/ionic potential. The acceleration form used in Eq. (5), reveals that a steep slope of the potential  $V$  leads to large cross sections for PI and IBS. For first-order processes the energy of initial and final states differ by the energy of one photon:  $E_f = E_i + \hbar\omega$ . The cross sections (5) are determined, beside the shape of the potential, by initial and final states. For PI the initial state  $\psi_i$  is a bound state; for IBS both states are continuum states of free electrons and one has to sum over all possible states, i. e., with different angular momenta (Walters et al. 2006). The challenge in calculating the cross sections and hence the corresponding rates consist in finding a reasonable approximation for the involved states. This is particularly difficult due to strongly perturbing neighboring ions, which may modify ionization potentials as well as orbitals considerably.

At VUV frequencies electrons are removed from the atoms/ions “outside-in” like shells of an onion because the ionization of inner-shell electrons would require multiphoton processes which are unlikely at the applied laser intensities. That, nevertheless, ionization can occur for charged ions, with  $\hbar\omega < E_{Xe^{q+}}$ , is due to a modified “continuum” in the cluster (Siedschlag & Rost 2004). The neighboring ions lower the ionization potentials, whereby it turned out that in any charge step the resulting barriers are sufficiently low to allow for single-photon ionization into the quasi-continuum. In the original proposal (Siedschlag & Rost 2004) the influence of the electron plasma has been completely neglected. Its consideration, which has been achieved through coarse-graining the ultra-fast electron dynamics in time in order to calculate transient ion charge states (Georgescu et al. 2007b), only slightly changes this picture. Since typical temperatures of the electron plasma are about 10 eV or less (Ziaja et al. 2009a), cf. also

Fig. 3c, many electrons are (temporarily) localized at the ionic cores and screen them. A careful analysis of this electron localization, combined with calculations of PI cross sections for equivalent electronic configurations, revealed that single-photon ionization is possible for the complete upper shell of the atoms (Georgescu et al. 2007b). The resulting high electron density in the plasma (Fig. 3b) leads to an efficient heating by IBS, which explains the large amount of energy absorbed by the clusters. Figure 3a shows the IBS contribution as the difference between total absorbed energy and energy absorbed by PI. Note, that in the case of  $\hbar\omega = 13\text{ eV}$  (Siedschlag & Rost 2004) this contribution is much larger.

Alternatively, it has been proposed that the absorbed energy is not due to the high electron density but due to a particular efficient IBS (Santra & Greene 2003, Walters et al. 2006). Instead of applying a simple Coulomb potential as usually done in plasma physics (Shima & Yatom 1975), a modified potential  $V(r)$  was used for the calculation of IBS according to Eq. (5). This potential accounts for changes close to the nucleus, which are taken into account with a parametrized (Santra & Greene 2003) or a modified Herrman-Skillman pseudo-potential (Walters et al. 2006). These potentials coincide for large  $r$  with a Debye-screened Coulomb potential of a  $q$ -fold charged ion  $V(r \rightarrow \infty) = -q \exp(-r/\lambda_D)/r$  with the Debye screening length  $\lambda_D$ . But they are much deeper at the nucleus  $V(r \rightarrow 0) = -Z/r$  with the nuclear charge  $Z \gg q$ . Although the potentials are modified for small values  $r \lesssim 1 \text{ \AA}$  only, the IBS rates are sometimes increased by orders of magnitude (Santra & Greene 2003, Walters et al. 2006). Calculations were done for free atoms without any (charged) environment. IBS heats the nanoplasma up to temperatures where due to electron-impact ionization high charge states are produced. Interestingly, the required temperatures are considerably higher than those measured by photo-electron spectroscopy (Laarmann et al. 2005).

Calculated ion charge distributions of both approaches have shown good agreement with experimental data (Siedschlag & Rost 2004, Ziaja et al. 2009b). Thus, more refined experiments, e. g. time-resolved measurement of transient ion charge states as discussed in the outlook, are necessary.

### *Relaxation and cluster explosion*

Due to the multiple charging of the clusters they will undergo fragmentation. The expansion typically becomes relevant at a few tens of femtoseconds, cf. Fig. 3d, depending on charge states and mass of the atomic species. Thus the heated plasma may cool down due to expansion during the laser pulses as can be seen in Fig. 3c. In contrast to NIR pulses, where the laser drives the plasma through the whole cluster and diminishes charge imbalances, here the electron plasma is “confined” to the center of the cluster. Thus the central part is screened and the charge accumulates at the surface (Siedschlag & Rost 2004, Ziaja et al. 2008). Therefore outer ionic shells are the first to expand, whereby the neutralized inner part survives much longer. During the expansion electron-ion recombination will lower ionic charge states, which is relevant for

quantitative comparisons with measured ion spectra.

Unfortunately, a theoretical description of this situation is difficult since very different time and length scales are involved. E.g., propagation methods are not able to track the dynamics on picosecond or even nanosecond time scale. Therefore recombination during the cluster explosion is a hardly investigated. An alternative to study the relaxation dynamics are pump-probe measurements (cf. also Sect. 5) which will become available in future beam times at FLASH.

### *Strong XUV laser pulses*

The lasing mechanism of FEL machines allows to change the frequency easily. Over the last years the available frequency at FLASH has steadily increased (Ackermann et al. 2007), starting from about  $\hbar\omega=12$  eV to about  $\hbar\omega=90$  eV. For experiments with clusters this has dramatic consequences. Firstly, new channels become accessible, e. g., when the photon frequency exceeds an ionization potential. Secondly, photo-absorption cross sections (for PI and IBS) depend critically on the wavelength. For example, the PI cross section scales asymptotically with  $\omega^{-7/2}$  (Bransden & Joachain 2003). Similarly, IBS cross sections decrease for larger frequencies and scales as  $\omega^{-11/3}$  and  $\omega^{-3}$  (Krainov 2000) for slow and fast electrons, respectively. Altogether, clusters will become much less reactive for larger photon energies, i. e., nanoplasma formation will be suppressed. Indeed, experiments measuring electron spectra from argon clusters at  $\hbar\omega=40$  eV (Bostedt et al. 2008) have shown that a nanoplasma is formed only for the highest intensity. That there is no nanoplasma for all other intensities was deduced from the fact the electron spectra could be fully explained with an independent-electron model (Bostedt et al. 2008). This model takes into account the gradual or multi-step charging of the cluster resulting in a flat electron spectrum.

Very recent FLASH experiments with xenon clusters at  $\hbar\omega=90$  eV (Bostedt et al. 2010) have shown that this trend can be reversed. Due to the giant resonance of the 4d shell in xenon around 90 eV, which is connected with a large cross section (Haensel et al. 1969), PI becomes by far the dominating process of photon absorption. The formed dense nanoplasma becomes “visible” through the emission of fast electrons in a process termed collisional auto-ionization (Bostedt et al. 2010).

## **5. Outlook**

The interest in experiments with clusters in short-wavelength intense FEL pulses will certainly continue. At the moment several proposals for measurements at FLASH or LCLS are submitted or planned. On one hand, new and more detailed experimental data, e. g. by using so far inaccessible frequencies, performing pump-probe measurements or studying composite clusters, will be in need of theoretical support. On the other hand, more differential measurement will stimulate more refined theoretical descriptions.

We will conclude with mentioning most interesting measurements to be performed

in future FEL experiments. These are theoretical proposals for experiments as well as first experimental realizations to be continued in forthcoming beam times.

#### *Clusters irradiated with X-ray pulses*

As discussed above, IBS becomes inefficient at higher frequencies. However, new channels are opened for PI. Additionally, due to the fast charging of the cluster “field ionization” from the cluster surface becomes important, cf. sect. 2. Nanoplasma formation occurs by trapping as shown in Fig. 2. It is therefore of particular interest to understand the time scale of this formation since efforts towards coherent diffractive single-molecule imaging (Gaffney & Chapman 2007) may be rendered impossible through an ultra-fast explosion of the sample, which could be slowed down by the formed plasma. Since the plasma “settles” at the sample’s center one could think of using a sacrificial layer which itself explodes but delivers electrons such that the sample of interest keeps its initial shape. Such a layer, also called tamper, was proposed recently for bio-molecules embedded in water (Hau-Riege et al. 2007). Taking the “field ionization” effect into account, the same result can be achieved also for clusters embedded in helium droplets despite the fact that helium is almost transparent for X-ray radiation and can only be ionized by the embedded core (Gnodtke et al. 2009).

#### *Pump-probe investigations*

As discussed in Sect. 4 the interpretation of the experimental results is still somewhat controversial. Pump-probe measurements are one way to discriminate between the different theoretical scenarios. Such experiments are already possible and are steadily improved at FLASH (Azima et al. 2009). With respect to the nanoplasma dynamics it would be interesting to trace the ionization stage of the cluster ions. This could be done through measuring kinetic energy spectra of the photo electrons from time-delayed pulses either from an attosecond HHG or a (shorter-wavelength) FEL source. The technical realization of such a scheme is challenging. However, it would provide time-resolved information of a multi-electron process which cannot be retrieved from energy-resolved observables. Calculations based on a molecular dynamics approach (Georgescu et al. 2007a) have shown the feasibility of such an approach, provided the interaction of the probe pulse is weak and, therefore, acts as a small perturbation. Furthermore, the “probe electron” should not undergo inelastic collisions and should be fast enough to be distinguished from the other electrons emitted. This requires higher photon frequencies for the probe pulses compared to the pump pulse and can only be applied to small clusters.

Another tool of probing the transient plasma state (Siedschlag & Rost 2005) is a short NIR pulse which drives collective ionization (Saalman & Rost 2003). Thereby the average ion charge in the cluster can be traced.

### Composite clusters

Composite clusters, i. e., clusters formed by at least two types of atoms, introduce a new degree of freedom which on the one hand may enrich the dynamics, as for NIR frequencies (Mikaberidze et al. 2009), but on the other hand allows for obtaining information which can be helpful in understanding the reaction of homo-nuclear clusters. First FEL experiments with core-shell systems made it possible to study the charge transfer dynamics inside clusters (Hoener et al. 2008, Ueda 2010).

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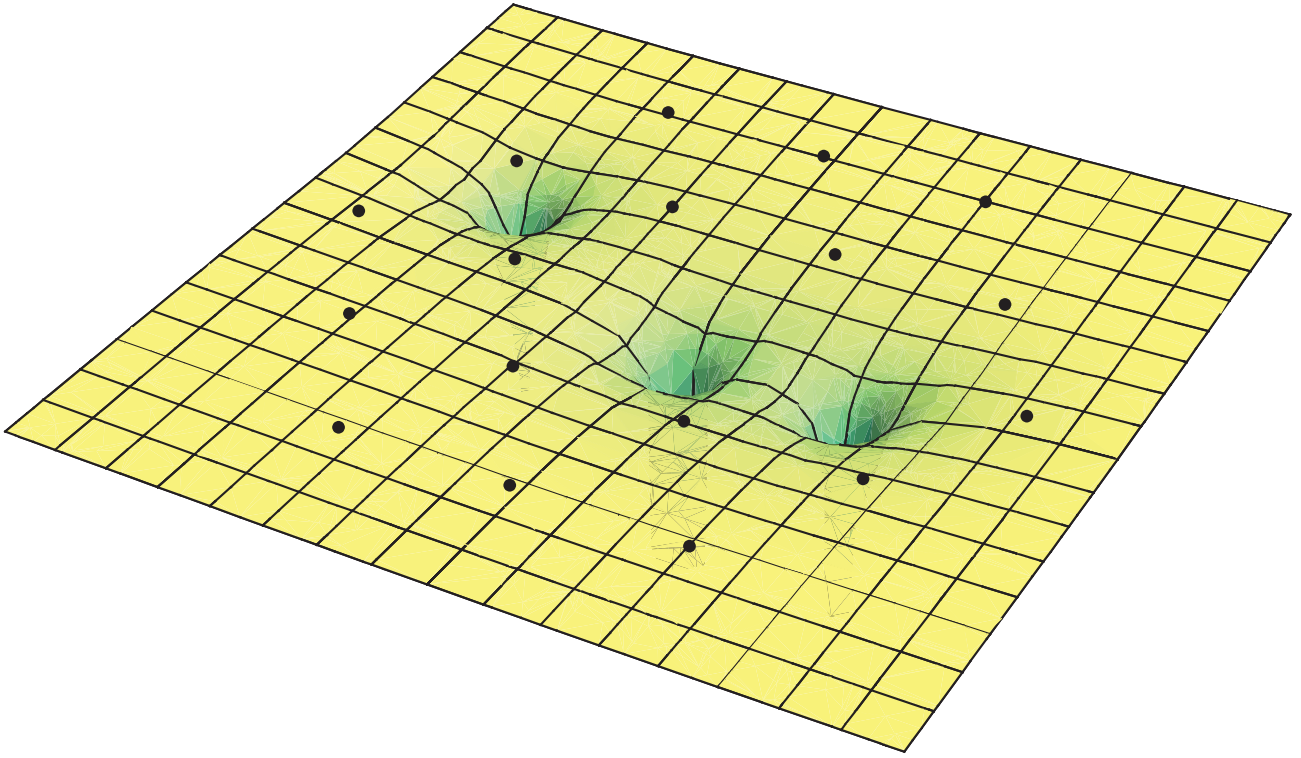
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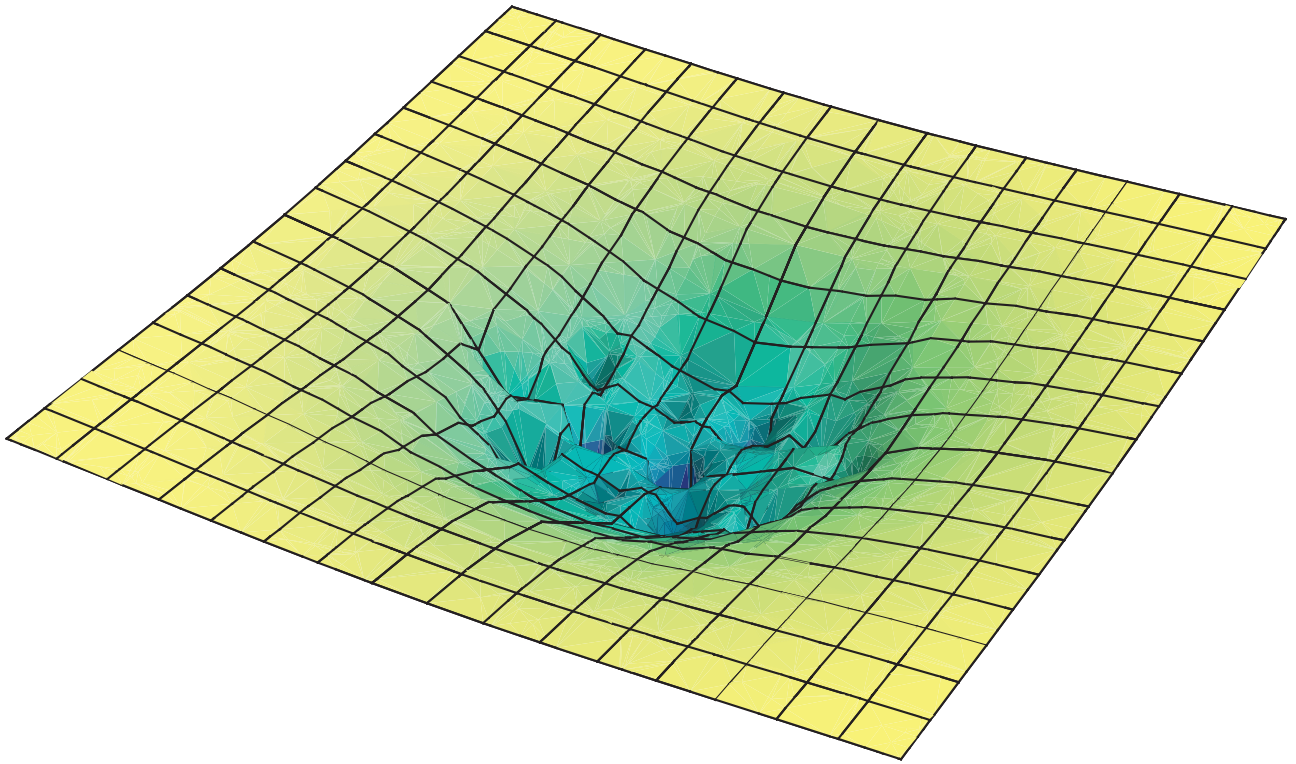
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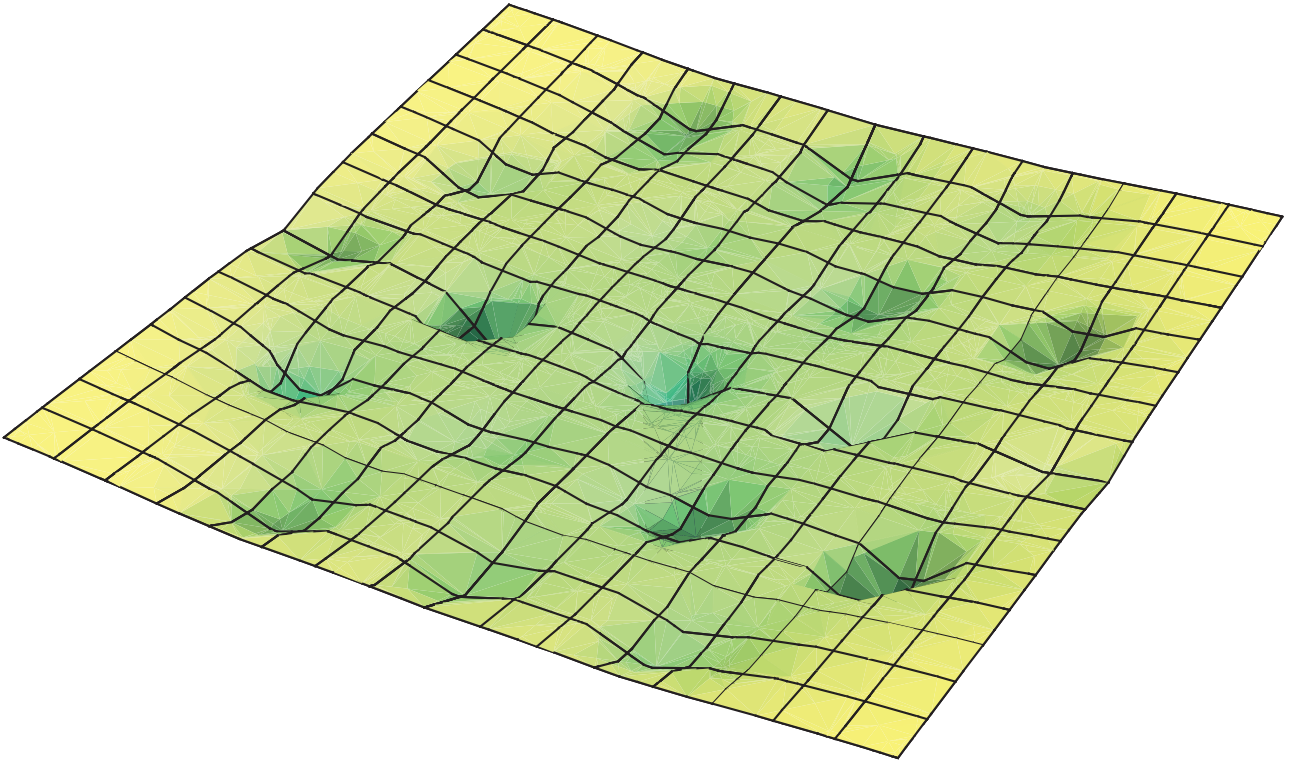




**Figure 1a (fig1a-potential.eps)**



**Figure 1b (fig1b-potential.eps)**



**Figure 1c (fig1c-potential.eps)**