

Relaxation pathways in x-ray free-electron-laser heated iron

L. Ansia ^{*}

GoLP/Instituto de Plasmas e Fusão Nuclear, [Universidade de Lisboa](#), 1049-001 Lisboa, Portugal
Instituto de Fusión Nuclear, [Universidad Politécnica de Madrid](#), José Gutiérrez Abascal 2, 28006 Madrid, Spain

P. Velarde 

Instituto de Fusión Nuclear, [Universidad Politécnica de Madrid](#), José Gutiérrez Abascal 2, 28006 Madrid, Spain

M. Fajardo  and G. O. Williams 

GoLP/Instituto de Plasmas e Fusão Nuclear, [Universidade de Lisboa](#), 1049-001 Lisboa, Portugal



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Nonthermal photoionized plasmas are now established in the laboratory and require models that treat the atomic processes and electron distribution self-consistently. We investigate the effects of inelastic thermalization in iron under intense x-ray irradiation using the atomic model BigBarT, suited for the self-consistent evolution of the electron continuum, including degeneracy effects. Our study focuses particularly on collisional *M*-shell ionization, which we identify as the dominant relaxation process of the nonthermal electrons. We show that *M*-shell satellite intensities are sensitive to nonthermal ionization, providing a potential method to refine collisional cross sections that are otherwise difficult to compute due to their proximity to the continuum and the associated plasma screening effects.

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I. INTRODUCTION

Nonequilibrium dynamics are central to understanding complex many-body behaviours across various disciplines. In high-energy-density plasmas, this topic is increasingly important due to its relevance in inertial fusion, where hot electrons can be detrimental to achieving optimal compression and energy gain [1–3].

X-ray free-electron lasers (XFELs) create a highly nonequilibrium system among photons, electrons, and ions. The processes that generate these hot electron distributions are generally well understood, linear, and can be modeled with reasonable accuracy. However, the relaxation pathways depend on collisional cross sections, which are often approximated or derived from gas-phase experiments. This becomes increasingly challenging for higher quantum numbers, especially as they approach the continuum.

In the past two decades, XFELs have made significant advancements, achieving peak intensities in the XUV and x-ray regions, previously only possible in the optical and infrared ranges. They allow for the creation of samples with greater uniformity and well-defined properties such as temperature and density [4,5], while achieving peak intensities exceeding 10^{20} Wcm⁻². This technology has enabled unprecedented

characterization of plasmas, critical in astrophysics for studying conditions in planetary interiors [6,7].

Different approaches have been proposed in the literature to simulate x-ray-driven warm dense matter (WDM). Among the earliest studies, Hau-Riege *et al.* used molecular dynamics (MD) simulations to investigate the evolution of carbon plasmas at intensities comparable to those in this work [8]. Similarly, Medvedev and coworkers employed Monte Carlo methods to model the temporal evolution of XFEL-produced aluminum plasmas, achieving fluences up to 5 Jcm⁻² [9].

Collisional radiative models (CRM) are particularly useful simulations tools, as self-emission serve as the primary diagnostic for XFEL-driven plasma [10]. These models have been extensively employed to simulate XFEL experiments under various conditions [11,12]. They allow to recreate, based in the fluorescence spectra, the temporal evolution of the plasma, focusing on the atomic kinetics. Particularly important to this work are the results of Q. Y. van den Berg *et al.*, in which magnesium was resonantly pumped at the *1s-2p* transition to measure the collisional ionization cross section by comparison with several existing models [13].

Several efforts have been made to couple collisional-radiative models (CRM) with Nonequilibrium dynamics. One of the earliest applications of the Fokker-Planck approach for self-consistently evolving continuum electrons was introduced by J. Bretagne *et al.*, who studied electron-beam-generated argon plasmas [14]. This approach was later extended to x-ray-produced plasmas by J. Abdallah *et al.*, which coupled atomic rate equations with the self-consistent evolution of distributions [15,16]. These developments enabled early studies on XFEL-driven electron dynamics [17]. Building on this foundation, de la Varga and colleagues

^{*}Contact author: lucas.ansia.fernandez@tecnico.ulisboa.pt

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developed the BigBarT code and parallelly investigate the effects of non-Maxwellian plasmas in x-ray-pumped neon [18], later incorporating degeneracy to better model dense plasmas [19].

Recently, similar approaches have been applied to solid-density plasmas. For instance, CCFLY, an extension of the SCFLY code, has been used to study nonthermal emission signatures in aluminum and magnesium plasmas [20]. Additionally, it was also employed to propose a method for refining the Coulomb logarithm [21]. Cheng Gao and collaborators further examined the effects of nonthermal dynamics on XFEL transmission in solid aluminum [22].

Despite these advances, studies on higher- Z materials remain limited due to their computational complexity. B. Ziaja *et al.* developed a kinetic Boltzmann code designed for modeling x-ray-created WDM by reducing the number of atomic paths in the CRM system [23–25]. This approach has been recently used to characterize XFEL transmission in copper at intensities up to $10^{17} \text{ W cm}^{-2}$ [26]. Hai P. Le *et al.* looked at the interplay between atomic kinetics and nonthermal electrons, focusing on inverse bremsstrahlung heating and nonlocal transport effects, in materials up to molybdenum [27].

For this work, we adapted the BigBarT code to simulate arbitrary materials, with a particular focus on the first transition metals. It models the self-consistent evolution of the nonthermal part of the electronic continuum, coupling the collisional-radiative model with a kinetic description of free-electron dynamics. The code also accounts for degeneracy in both the electron distribution and rate calculations which has been shown to be important in solid density plasmas [28,29].

We investigate the impact of nonthermal electron distributions on the evolution of XFEL heated, solid-density iron. Additionally, we explore the effect of modifying outer collisional ionization cross sections. This is particularly interesting because precise description of near-continuum wave functions and many-body effects remains a significant challenge for determining cross-section values. Inelastic collisions, as the primary thermalization mechanism for high energy electrons, could leave observable signatures that help validate existing models. Iron was chosen for our simulations due to its astrophysical importance and the lack of studies addressing the impact of nonthermal electron distributions on its emitted spectra, thereby extending prior work on lower- Z materials [20].

The paper is organized as follows. In Sec. II, we describe BigBarT, both the computational framework and the simplifications made to make the problem tractable. In Sec. III, we devote a section to clarify the evolution of a plasma when subjected to x-ray radiation, emphasising on the effects of nonthermal distributions and Fermi-Dirac statistics. Lastly, in Sec. IV, nonequilibrium effects on the self-emission are discussed.

II. SIMULATION APPROACH

Simulations have been carried out using the CRM BigBarT [18]. It couples the atomic rate equations with a degenerate Fokker-Planck approach to self-consistently evolve the ion and electron distributions. In this fashion, nonthermodynamic equilibrium is assumed in both systems. Ionic populations are updated following the usual rate equation,

$$\frac{dn_i}{dt} = \sum_{j \neq i}^m n_j R_{ji} - n_i \sum_{j \neq i}^m R_{ij}, \quad (1)$$

where n_i is the population of each state, and R_{ij} and R_{ji} represent the total rates between complex i and j respectively.

The processes include photoionization (PI), collisional ionization (CI), Auger effect (AU), collisional excitation (CE), and spontaneous emission (SE), along with their inverse processes. The cross sections for PI, SE, and AU are obtained in relativistic detail using the configuration average mode (i.e., UTA) of the flexible atomic code [30]. CE is calculated using the plane-wave Born (PWB) approximation with the JJATOM model [31], which allows for efficient computation at the relativistic level and compares well with those obtained by FAC and HULLAC in the distorted wave approximation.

The CI differential cross section is obtained using the coulomb born exchange fitting from C. Fontes and colleagues [32,33]. Nonrelativistic cross sections for any type of ion can be obtained in significantly less time and can include IPD scaling convenient for dense scenarios. Moreover, this fitting has been successfully applied to WDM experiments before [13]. All inverse processes are obtained by means of the microscopic reversibility relations.

To reduce computational effort, the super-configuration approach has been adopted, where complex states are only distinguished by their principal quantum number. In this paper, we follow the usual *KLM* nomenclature, where each number represents the number of electrons in the K , L , or M shell, respectively (e.g., an arbitrary complex with the first two shells completely filled and an extra electron in the third level, will be formed by the relativistic configurations $3s_{1/2}$, $3p_{1/2}$, $3p_{3/2}$, $3d_{3/2}$ and $3d_{5/2}$, and referred to as K2L8M1). Transition rates are thus grouped, forming initial and final super configurations, taking into account the statistical weight of each relativistic level.

Rates are calculated as functions of the atomic cross section and the electron distribution function. To capture the effect of degeneracy, Pauli blocking is included. Due to its importance in this work we explicitly write here the used expression for CI and three body recombination (3B) process. Given an incident electron of energy ε_1 , ionization potential I and two outgoing electrons of energy $\varepsilon_{1'}$ and $\varepsilon_{2'}$ such that $\varepsilon_1 = \varepsilon_{1'} + \varepsilon_{2'} - I$,

$$R_{\text{CI}} = \iint_0^{\frac{\varepsilon_1 - I}{2}} \sqrt{\frac{2\varepsilon_1}{m_e}} g(\varepsilon_1) \tilde{f}(\varepsilon_1) \sigma_{ci}(\varepsilon_1, \varepsilon_{1'}) P(\varepsilon_{1'}) P(\varepsilon_1 - \varepsilon_{1'} - I) d\varepsilon_{1'} d\varepsilon_1 \quad (2)$$

$$R_{\text{3B}} = \frac{g_i}{g_j} \frac{h^3}{8\pi m_e^2} \int_I^\infty \varepsilon_1 P(\varepsilon_1) \left(\int_0^{\frac{\varepsilon_1 - I}{2}} \frac{g(\varepsilon_{1'}) \tilde{f}(\varepsilon_{1'}) g(\varepsilon_1 - \varepsilon_{1'} - I) \tilde{f}(\varepsilon_1 - \varepsilon_{1'} - I)}{\sqrt{\varepsilon_{1'}(\varepsilon_1 - \varepsilon_{1'} - I)}} \sigma_{ci}(\varepsilon_1, \varepsilon_{1'}) d\varepsilon_{1'} \right) d\varepsilon_1 \quad (3)$$

where g_i and g_j are the statistical levels of the ionizing and ionized levels, h is the planck constant and m_e is the electron mass. $g(\varepsilon) \propto \sqrt{\varepsilon}$ represents the density of states (DOS), which determines the number of available levels at a given energy. Here, we use the free-electron gas approximation, as a full treatment would require calculating the electronic structure and DOS for all ionization states, which is beyond the scope of this work. While a more realistic DOS would lead to slightly slower thermalization at lower temperatures [34,35], this does not significantly impact our results. As discussed in the next section, we identify collisional ionization as the main thermalization mechanism under the conditions studied here. The function $\tilde{f}(\varepsilon)$ is the occupation factor, which varies between 0 (no electrons occupying the state) and 1 (full occupation of the state). The total electron density is given by the integral $n_e = \int f(\varepsilon) d\varepsilon = \int g(\varepsilon) \tilde{f}(\varepsilon) d\varepsilon$. Finally, $P(E) = 1 - \tilde{f}(E)$ represents the Pauli blocking factor, which describes the probability that a state is unoccupied and thus available for transitions. The 3B rate employs the CI differential cross section since the Fowler relation have been inserted [36].

The electron distribution evolves according to the Fokker-Planck equation [37–39],

$$\frac{1}{\Gamma} \frac{\partial f(\mathbf{v}, t)}{\partial t} = -\nabla_{\mathbf{v}} \cdot [\mathbb{H}(\mathbf{v}, t) f(\mathbf{v})] + \frac{1}{2} \nabla_{\mathbf{v}} \nabla_{\mathbf{v}} : [\mathbb{G}(\mathbf{v}, t) f(\mathbf{v})] + \left(\frac{\partial f(\mathbf{v})}{\partial t} \right)_I + S(t), \quad (4)$$

which is coupled to the atomic system via source terms, S , that include photo-ionization and Auger effects, as well as inelastic terms $(\frac{\partial f(\mathbf{v})}{\partial t})_I$, which account for collisional ionization and collisional excitation, along with their inverse processes.

Γ is defined as

$$\Gamma = \frac{n_0 e^4 \ln \Lambda}{4\pi \epsilon_0^2 m_e^2}, \quad (5)$$

where n_0 is the electron density, e is the electron charge, m_e is the electron mass, and $\ln \Lambda$ is the Coulomb logarithm. $\mathbb{H}(\mathbf{v}, t)$ and $\mathbb{G}(\mathbf{v}, t)$ are the Rosseblunt potentials [39] associated with friction and diffusion, defined as:

$$\mathbb{H}(\mathbf{v}, t) = 2 \cdot \nabla_{\mathbf{v}} \int d\mathbf{v}' \frac{f(\mathbf{v}', t)}{|\mathbf{v} - \mathbf{v}'|}, \quad (6)$$

$$\mathbb{G}(\mathbf{v}, t) = \nabla_{\mathbf{v}} \nabla_{\mathbf{v}} \int d\mathbf{v}' |\mathbf{v} - \mathbf{v}'| f(\mathbf{v}', t), \quad (7)$$

here $\nabla_{\mathbf{v}} \nabla_{\mathbf{v}}$ and $\nabla_{\mathbf{v}} \nabla_{\mathbf{v}} :$ are the tensor generalization of the gradient and divergence, respectively [37].

The numerical solution is carried out using the scheme presented by Bobylev *et al.* [40], which was later applied by Tzoufras and colleagues to study high-energy-density physics [41]. Spatial dimensions are not considered, and thus only the isotropic component is solved. This scheme has been modified to account for Fermi-Dirac statistics [19,42] and ensures particle and energy conservation. Both systems are evolved at each time step as an initial value problem using the CVODE solver from the SUNDIALS package [43,44].

Ionization potential depression (IPD) is calculated using the Ecker-Kröll (EK) model [45] based on the initial conditions and is held constant throughout the simulation. This

simplification is adopted as the correct way to treat the self-consistent evolution of the continuum with a dynamically varying IPD is still an open question.

The Coulomb logarithm, a crucial factor for accurate electron-electron collision simulations, faces similar challenges. Various models have been proposed, many of which exhibit divergent behavior at lower temperatures. We adopt the formulation by Shaffer and Starrett, which substantially improves the low-temperature behavior [46]. In the low-temperature limit, it follows the functional form:

$$\ln \Lambda_{ee} = \frac{5}{4} \operatorname{erf} \left[\left(\frac{2T}{3T_F} \right)^3 \right], \quad (8)$$

where T and T_F are the electron and Fermi temperatures, respectively. Here, we define temperature as that of a thermal system with the same density, n , and total energy, E , as the nonthermal one. The temperature and chemical potential are determined by solving the following system of equations:

$$\begin{aligned} n &= \frac{(2m_e)^{3/2} T^{3/2}}{2\pi^2 \hbar^3} F_{1/2}(\eta), \\ E &= \frac{(2m_e)^{3/2} T^{5/2}}{2\pi^2 \hbar^3} F_{3/2}(\eta), \end{aligned} \quad (9)$$

where $\eta = \mu/T$ is the reduced chemical potential, and the Fermi integral is defined as

$$F_j(\eta) = \int_0^\infty \frac{x^j}{e^{x-\eta} + 1} dx. \quad (10)$$

The emission spectra are computed following the procedure detailed in [19]. The bound-bound and bound-free contributions are obtained using atomic cross sections from the Flexible Atomic Code (FAC), which are the same as those used in the collisional-radiative model. The free-free contribution is calculated using Kramers' semiclassical formula. Broadening effects, including Stark, Doppler, and natural broadening, are applied to bound transitions. The spectrum is then convolved with a Gaussian function to simulate detector response.

All the simulations presented here are for iron. The initial conditions are determined by solving the degenerate Saha equation, which yields an initial configuration of K2L8M8, with the 3p electrons being the last bound levels. We do not consider the magnetic properties of the material as magnetic ordering is assumed to be lost at above ~ 2000 K (above the Curie temperature of all common ferromagnetic materials).

III. NONTHERMAL EVOLUTION

The interaction between x-rays and solid matter primarily involves photo-ionization, which generate a stream of non-thermal electrons while creating inner shell holes. These holes filled either by spontaneous emission or through the Auger effect, the latter acting as an additional source. Once generated, electrons thermalize through two main mechanisms: elastic collisions between themselves and inelastic collisions with ions. Among them, CI is the most significant mechanism affecting the overall electron distribution.

Various snapshots of the electron distribution at peak pulse for different values of the M -shell CI cross sections, σ_{CI-M} ,

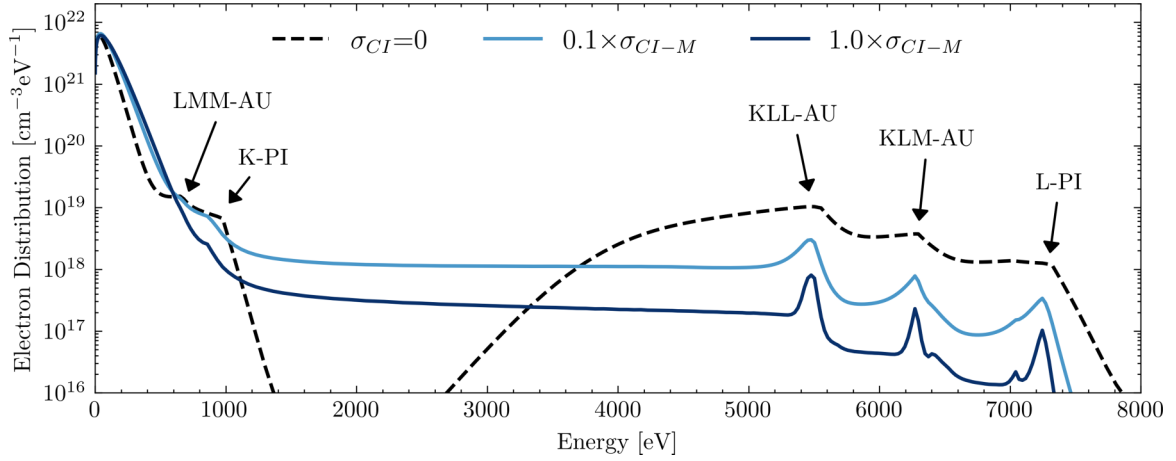


FIG. 1. Electron distributions at the pulse peak (60 fs) for varying collisional ionization cross sections of the M-shell. The dotted line represents the scenario without collisional ionization under the same conditions. Key features of photoionization (PI) and Auger (AU) processes are highlighted. For PI, the labels indicate the photoionized shell, while for AU, the first two labels correspond to bound-bound transitions, and the last one designates the ionized level. Conditions for all simulations are 30 fs FWHM pulse at $1 \times 10^{18} \text{ Wcm}^{-2}$, and an incoming photon energy of 8100 eV.

including one with suppressed CI, are shown in Fig. 1 for a 30 fs FWHM pulse at $1 \times 10^{18} \text{ Wcm}^{-2}$, and an incoming photon energy of 8100 eV. Despite differences in the overall shape, the main features are consistent across all simulations. Since the *K*-edge of Fe sits around 7.1 keV, the *K*-shell photoionization peak will be at 1000 eV. Peaks around 800 eV correspond to the Auger-LMM peak. Higher energy features correspond to *L* and *M* photo-peaks and other combination of Auger corresponding to *L* → *K* shells decay. Smaller signatures arise from collisional excitation/de-excitation of main features.

The importance of inelastic collisions is clearly illustrated by the effect of their absence (black dotted line in Fig. 1). As noted in other works [21], elastic electron-electron collisions primarily act to diffuse features in the electron spectrum. This process also plays a key role in shaping the thermal part of the distribution by redistributing energy among low-energy electrons. However, for electrons with energies above the ionisation thresholds of the plasma, inelastic collisions dominate and elastic electron-electron collisions are far less effective. CI is the mechanism that transports electrons from the high-energy tail. It creates large plateaus between peaks as a result of many small energy collisions. This occurs because almost any hot electron has enough energy to ionize outer shells, and this energy is much smaller than the electron's total energy.

While modifying σ_{CI-M} does not affect photo and auger peaks, it has an important effect on the thermalization. Figure 1 shows how lower σ_{CI-M} , leads to bigger deviations from equilibrium, stacking more electrons at high energies. This effect is important since it delays the heating of the thermal portion of the distribution, which will affect the plasma population in time, especially for the M-satellites.

To quantify deviations from equilibrium, we calculate the system entropy:

$$S = - \int g(E) \tilde{f}(E) \ln \tilde{f}(E) dE \quad (11)$$

The deviation from equilibrium is then defined as

$$\Delta S = S_{\text{eq}} - S_{\text{neq}}, \quad (12)$$

where S_{neq} is the entropy of the electron distribution, and S_{eq} is the entropy of the corresponding equilibrium distribution with the same total energy and electron density. This provides a direct way to quantify how far the system is from thermal equilibrium.

Figure 2 illustrates the evolution of the ΔS parameter for simulations with both regular and suppressed CI cross sections. It reveals two distinct regimes. The second one corresponds to overall thermalization, reaching its maximum around the peak of the pulse. In contrast, the first peak arises from nonthermal contributions in the low-energy region, driven by M-shell 3B processes in the full simulation,

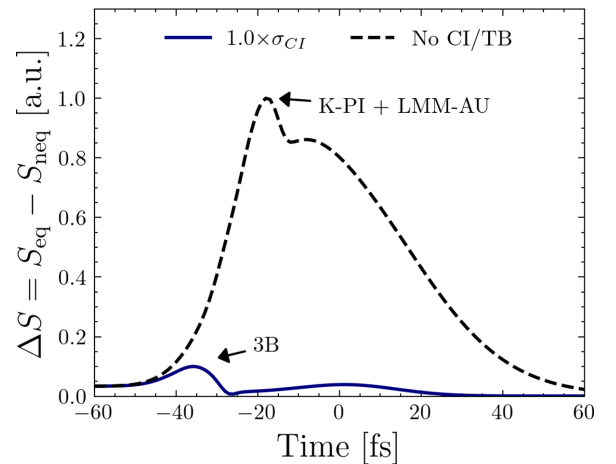


FIG. 2. Deviation from equilibrium entropy (ΔS) as a function of time for a fully inelastic simulation compared to one without collisional ionization and three-body recombination. Conditions for both simulations are a 30 fs FWHM pulse at $1 \times 10^{18} \text{ Wcm}^{-2}$ with an incoming photon energy of 8100 eV.

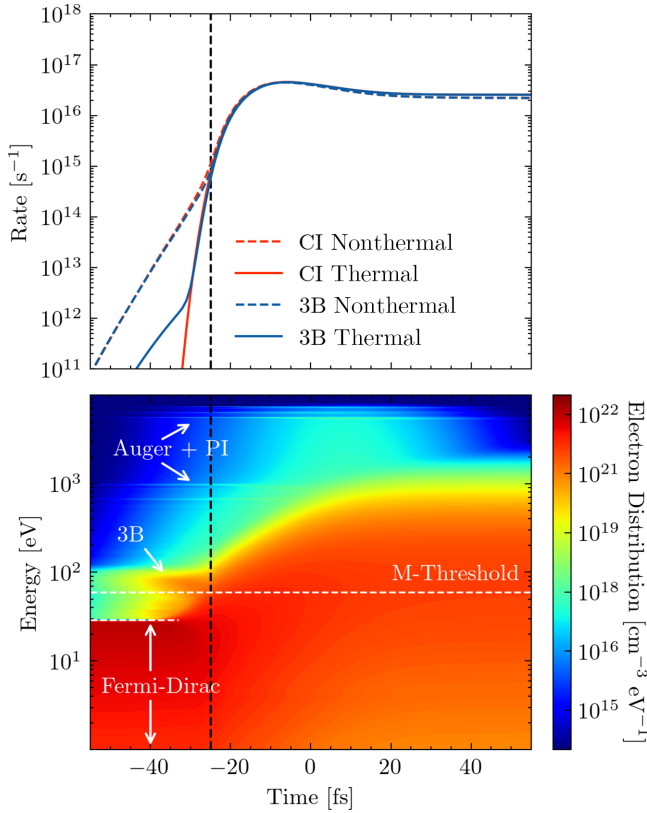


FIG. 3. Temporal evolution of the total collisional ionization (CI) and three-body recombination (3B) rates for both thermal and nonthermal simulations (top), along with the electron distribution for the nonthermal case (bottom), both plotted as functions of time. The M-threshold represents the minimum energy required to ionize the outermost electrons. The black dotted line indicates the point where the thermal (TH) and nonthermal (NT) rates converge and their intersection with the M-threshold. Conditions for both simulations are 30 fs FWHM pulse at $1 \times 10^{18} \text{ W cm}^{-2}$, and an incoming photon energy of 8100 eV. In the time axis, 0 correspond to the peak of the pulse.

and by *LMM*-AU and *K*-shell photoionization in the elastic case. As the distribution heats up, elastic processes diffuse these low-energy contributions, resulting in the two observed behaviours. The findings clearly demonstrate that in the absence of CI, the system exhibits significantly larger deviations from equilibrium.

Another feature, mainly important at low temperatures, is the collisional ionization paths only available for the high-energy Nonequilibrium electrons. This is better represented in Figure 3, where the comparison of CI and 3B rates for instant thermalized and nonthermal simulations, together with the temporal evolution of the distribution function, is shown. At the beginning of the XFEL pulse, only hot electrons can produce CI because the thermal distribution is confined within the Fermi energy, which is typically lower than the threshold required to ionize even the outermost shell. It can be seen that only nonthermal features are above the M threshold in the first 30 fs, where *K*-shell PI and 3B are the most important sources. This is reflected in the rates, where the Nonequilibrium simulation shows orders of magnitude higher CI. As the

distribution heats up, rates converge from both simulations. This is a consequence of the thermalized distribution being able to ionize outer shell, which as have been already identified, is the main mechanism for the plasma evolution. As a consequence, both simulations will present relatively similar trends in overall ionization and complex evolution.

The case of 3B is slightly different. Because this process is the main electron capture mechanism, it tends to balance any source of electrons. For the thermal simulation, in the beginning, it just tends to compensate for PI and AU effects, while in the other case it closely follows CI, as it is already the most efficient ionization source.

IV. SPECTRAL SIGNATURES

High-energy-density plasma experiments rely heavily on spectral analysis as the primary diagnostic tool, especially since extremely short timescales, often on the order of femtoseconds, make other methods challenging to implement.

For iron and other 3d transition metals, *K*-shell spectra are divided into *K_α* and *K_β* regions. The *K_α* region includes all possible transitions from the *L*-shell to the *K*-shell, while the *K_β* region corresponds to transitions from the *M*-shell to the *K*-shell. Both regions exhibit a complex structure of satellite lines that arise due to the number of spectator electrons in the *L* and *M* shells. The exact energy of each transition depends on the specific electron configuration at the time of emission, leading to a distribution of spectral lines rather than a single discrete feature. The *K_β* region is particularly useful for plasma diagnostics because its satellites are more widely spaced, making it easier to track plasma evolution through line shifts and broadening under varying conditions.

These satellites can be categorized into two types: *L*-satellites and *M*-satellites. The *L*-satellites are determined by the number of electrons remaining in the *L*-shell. For example, the primary *K_β* transition occurs when all eight *L*-shell electrons are present, while the first satellite appears when there are only seven. Similarly, *M*-satellites arise from the number of electrons in the *M*-shell, leading to further splitting of the *L*-satellite structure. Because of this interplay, each individual *L*-satellite can exhibit an emission spread of approximately 100 eV, depending on the number of *M*-shell electrons involved in the transition.

The *L*-satellites in the *K_β* region exhibit significant overlap at their boundaries, meaning that the emission from one satellite often extends into the others. For example, the transitions $\text{K1L8M2} \rightarrow \text{K2L8M1}$ and $\text{K1L7M7} \rightarrow \text{K2L7M6}$ have center of energies of 7160.9 eV and 7161.9 eV, respectively, leading to closely spaced spectral features. As a result, resonant pumping can selectively enhance different transitions depending on the plasma state. In order to better understand the overall effect of nonthermal distributions, three different pump photon energies will be explored. In each setup, we scan a range of intensities and pulse durations. The first scenario uses a pump energy of 7.2 keV, positioned near the *K*-edge absorption, still allowing to ionize all *M* electrons in the first *L* satellite. The second uses a pump energy of 7.31 keV, aligning with the overlap between the second and third *L*-satellites. Finally, the third scenario involves a pump energy far from the initial

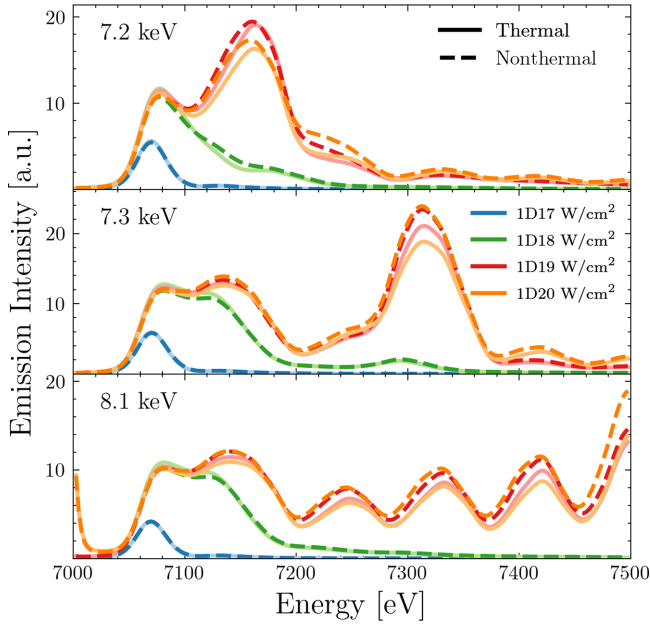


FIG. 4. Comparison of thermal and nonthermal spectra at varying intensities for the three pump energies analysed in this study. Results are shown for a 30 fs FWHM pulse. Spectra is focused in the first 4 K_β L -satellites. The top plot shows the main K_β transition at 7080 eV, where all L and M electrons are present ($K1L8M8 \rightarrow K2L8M7$), along with its last three M -satellites. These M -satellites appear from 7120 eV ($M3$) to 7180 eV ($M1$), corresponding to the resonant lines. The middle plot presents the main K_β transition at 7080 eV, now accompanied by a more complete set of its M -satellites. The strong spectral overlap between these satellites results in an emission that appears nearly continuous from 7080 eV to 7180 eV. Additionally, the most prominent emission features correspond to the resonantly pumped M -satellites at 7303 eV ($M3$) and 7322 eV ($M2$) of the $L6$ -satellite. The bottom plot highlights the main K_β transition at 7080 eV along with its M -satellites, as well as several distinct L -satellites: $L7 \sim 7240$ eV, $L6 \sim 7330$ eV, and $L5 \sim 7420$ eV. Each of these L -satellites is mainly formed by its last three M -satellites.

L -satellites, allowing to investigate the effects of off-resonant pumping on satellite features.

In our analysis, we examine both nonthermal effects and the sensitivity to collisional ionization for the different XFEL photon energies. The XFEL parameters chosen are readily available at current facilities, providing a realistic basis for comparison [47,48].

A. Spectrum under nonthermal conditions

The primary objective of this work is to determine whether nonthermal effects play a significant role and, if so, under which specific conditions they become prominent. In Fig. 4, we compare spectra across intensities ranging from 1×10^{17} to 1×10^{20} Wcm^{-2} for a pulse duration of 30 fs, that will corresponds to final thermalized temperatures ranging from 30 to 750 eV. Our results show trends similar to those observed in previous studies on lower- Z materials [20], where higher intensities enhance satellite line intensities under nonthermal electron conditions. At lower intensities, satellites are very

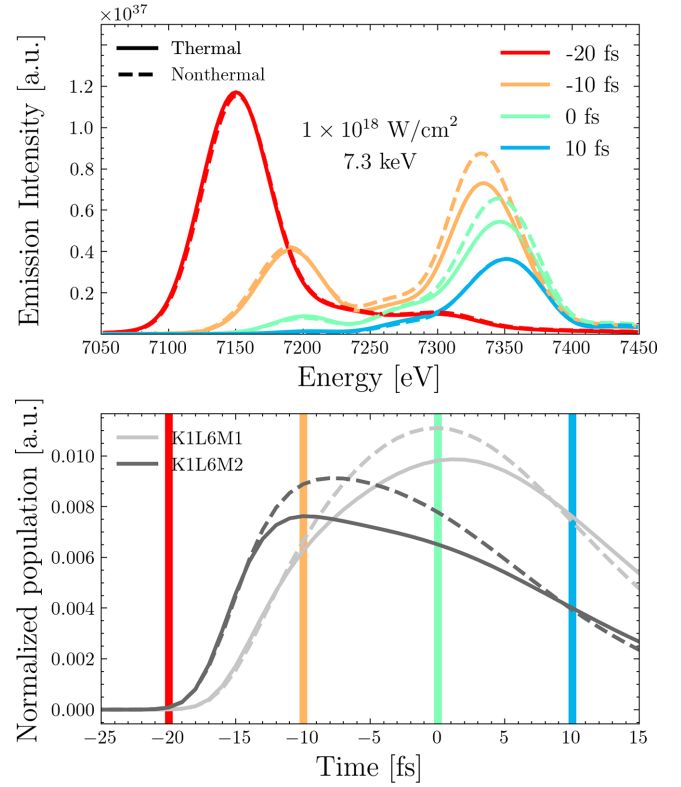


FIG. 5. Comparison of thermal and nonthermal self-emission as a function of time (top) and the evolution of the most significant contributing configurations (bottom) for an intensity of 1×10^{18} Wcm^{-2} , a 30 fs pulse duration, and a pump energy of 7.3 keV. Vertical color-coded lines in the bottom plot mark specific timestamps shown in the top plot. In the time axis, 0 corresponds to the peak of the pulse.

weak, and the differences are minimal. There are no appreciable line shifts or new lines present in the Nonequilibrium simulations.

To further investigate the underlying mechanisms, we analyze the evolution of the radiation emission. In particular, red focusing on the case where the solid is pumped at 7.3 keV, we track the super configurations $K1L6M2$ and $K1L6M1$, which are among the strongest contributors to the resonant line. In this case, M -satellites are mainly generated either through resonant pumping or by imbalances between CI and 3B processes, as the plasma approaches non-local thermodynamic equilibrium (NLTE).

In Fig. 5 (top) is represented the emitted spectrum at different simulation times, while the bottom plot shows the evolution of the specified super configurations within the $L6$ satellite. Not appreciable delay is found in the complex creation, but the nonthermal simulation shows a faster growth rate. This occurs because, with a nonthermal distribution, more electrons reside above the ionization threshold, leading to a greater CI. Although there are apparent differences in ionization rates between thermal and nonthermal conditions (reflected in the time-resolved emission and ionization rates shown in Fig. 4), these variations result in only minor differences in the time-averaged spectra, as depicted in Fig. 5.

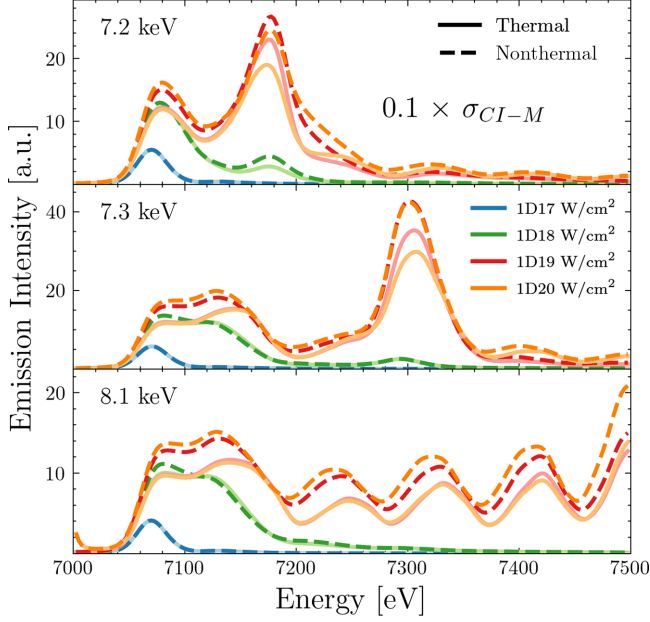


FIG. 6. Comparison of thermal and nonthermal spectra at varying intensities for the three pump energies analysed, with the M -shell collisional ionization cross section reduced by a factor of 10. Results are shown for a 30 fs FWHM pulse.

B. Cross-section influence

Reducing collisional ionization cross sections can enhance nonthermal effects because thermalization times are influenced by inelastic collisions. To see how this affects self-emission, we revisited the earlier cases with simulations where the σ_{CI-M} values were reduced by a factor of 10 (Fig. 6).

The emission spectra with a reduced M -shell cross section in Fig. 6 show a larger difference between thermal and nonthermal cases at high intensities (1×10^{19} , 1×10^{20} Wcm $^{-2}$) than the standard M -shell cross sections in Fig. 4. In addition to the previously observed L -satellites enhancements, the main K_β line also shows increased intensity. Additionally, satellite shifts become noticeable at higher intensities, especially in the off-resonance (8.1 keV pump) spectra, where a general blue shift of 6–7 eV is observed. These shifts arise from differences in the relative M -satellite populations during emission.

This effect becomes more evident when comparing the emission from two nonthermal simulations: one with regular cross sections and the other with reduced cross sections. The results are shown in Fig. 7. Shifts are now observed for all pumping energies. To further understand the origin of this signature, we track the emission and evolution of the K1L8M1 and K1L8M3 configurations, as they are the most significant contributors to the K_β M -satellites emission line at 7.2 keV.

Figure 8 shows the complex emission comparison for the 7.2 keV pumping case. The differences in this case arise not only from the reduced cross section allowing a build-up of more nonthermal electrons but also from the altered timescales in the overall plasma evolution. In the regular simulation, the intensity of the M1 satellite is approximately twice that of M3 at the peak. However, in the reduced

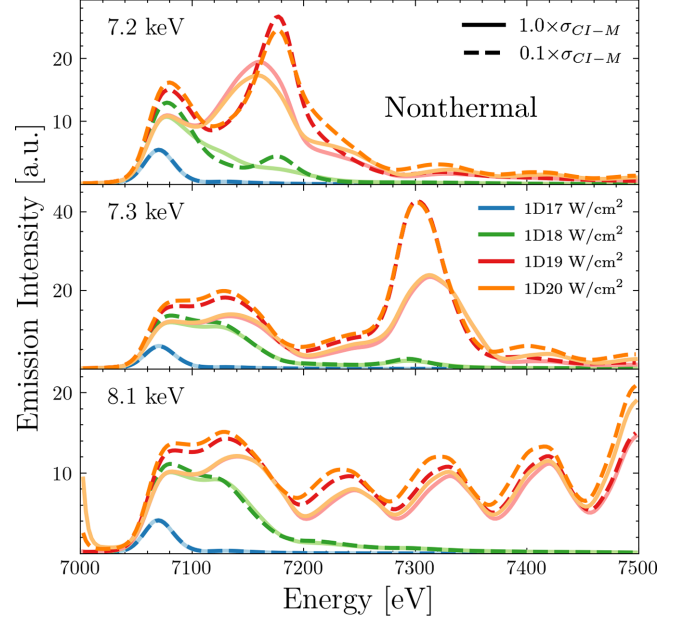


FIG. 7. Comparison of nonthermal simulation spectra with regular and reduced cross sections, plotted as a function of intensity for the three pump energies discussed. Results are shown for a 30 fs FWHM pulse.

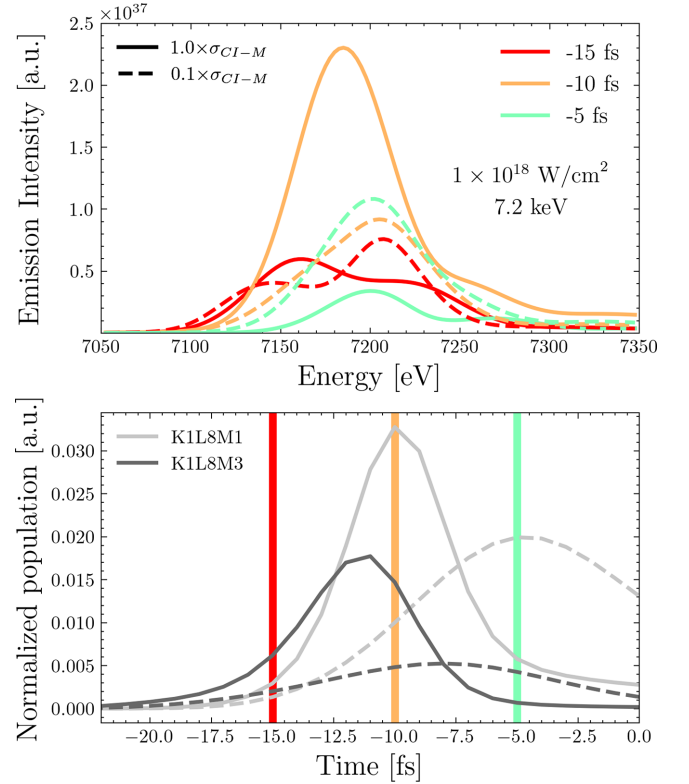


FIG. 8. Comparison of time-dependent emission for reduced and regular cross sections as a function of time (top) and the evolution of the most significant contributing configurations (bottom) for an intensity of 1×10^{18} Wcm $^{-2}$, a 30 fs pulse duration, and a pump energy of 7.2 keV. Vertical color-coded lines in the bottom plot denote specific timestamps shown in the top plot. In the time axis, 0 corresponds to the peak of the pulse.

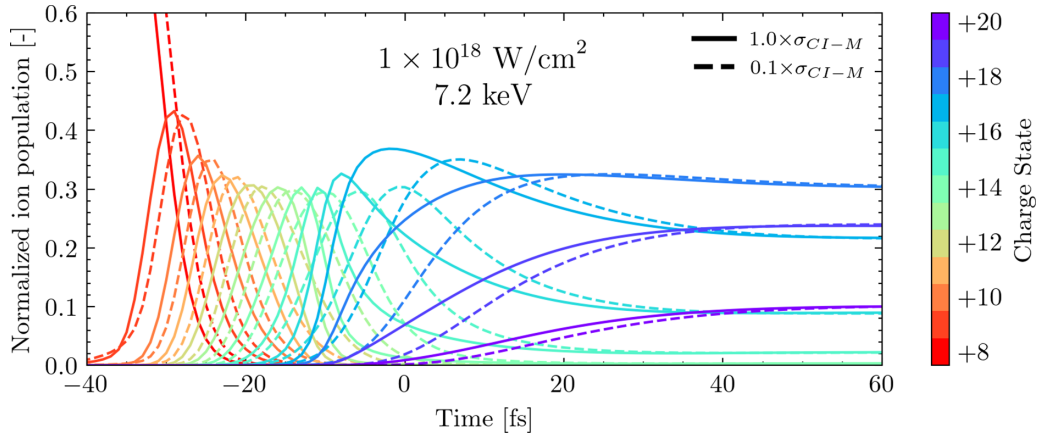


FIG. 9. Comparison of the evolution of ionic states as a function of time for reduced and regular cross sections, with an intensity of $1 \times 10^{18} \text{ W cm}^{-2}$, a 30 fs pulse duration, and a pump energy of 7.2 keV. In the time axis, 0 corresponds to the peak of the pulse.

cross-section case, M1 becomes nearly four times stronger than M3. This disparity ultimately leads to the observed blue shift in the emission spectrum. Resonant lines also become significantly more pronounced due to two main factors. First, the satellites have a longer lifetime because of the overall delay. Second, they appear closer to the pulse peak, leading to more efficient resonant pumping.

Although these simulations show significant differences during their evolution, it is important to note that the cross sections were modified according to Fowler's relation. As a result, the final equilibrium conditions are the same for both cases (Fig. 9). In other words, the energy deposition remains consistent, leading to identical final states despite the distinct temporal behaviours observed.

V. CONCLUSIONS

In this study, we investigated the impact of nonequilibrium electron distributions on the evolution and spectral signatures of isochorically heated solid-density iron. We identified collisional ionization of outer *M*-shell electrons as the primary thermalization mechanism, leading to the formation of nonequilibrium plateaus between resonant peaks in the electron distribution.

Nonthermal electrons influence the plasma evolution, particularly during the initial femtoseconds, where enhanced collisional ionization rates from high-energy electrons serve as the dominant collisional pathway. As the plasma evolves, these rates gradually converge with those of the thermalized distribution. Additionally, the formation of the thermalized electrons can be delayed under nonequilibrium conditions, slowing overall plasma relaxation.

These changes in the plasma's temporal evolution are directly reflected in the emitted spectra. Distinct signatures in the K_β spectra were observed at higher intensities that resulted in stronger satellite lines. These effects were further enhanced when collisional cross sections were reduced, as expected due

to slower thermalization and an increased number of electrons driving L-shell CI processes, resulting in even more prominent satellites.

Additionally, the K_β spectra were found to be sensitive to variations in σ_{CI-M} , with 5–7 eV line shifts occurring under different cross-section assumptions, that would be experimentally observable. This sensitivity provides a potential avenue for refining collisional cross-section models using either existing experimental data or new campaigns at XFEL facilities, where the simulated conditions are already achievable.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [50].

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