

Nonequilibrium electron energy distribution in Au under subpicosecond laser irradiation: A kinetic study

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Abstract

We have performed a kinetic study of the electron dynamic relaxation inside a Au film subjected to a subpicosecond laser pulse. For this purpose, we have developed a time-dependent numerical solution of the Boltzmann equation for the electrons inside the film considering the collision integrals due to electron–electron and electron–phonon collisions and a perturbation term due to the laser pulse. Our results show that, after the pulse excitation, electron distributions are very far from equilibrium. Therefore it is not possible, especially in the first part of the temporal evolution, to describe the relaxation of the electron distribution through a two-temperature model.

Keywords: Boltzmann equation; Electron relaxation; Nonequilibrium electron energy distribution function; Subpicosecond laser irradiation; Two-temperature model

1. INTRODUCTION

The advance of femtosecond laser technology makes it possible to create and investigate transient nonequilibrium electron distribution functions in semiconductors and metals. These experimental investigations are based on thermomodulation techniques: Femtosecond optical pulses are used to excite the electron distribution out of equilibrium and subsequently femtosecond probe pulses monitor the transient changes of optical properties of the sample, such as reflectivity and transmissivity (Schoehlein *et al.*, 1987; Sun *et al.*, 1994; Del Fatti *et al.*, 1998). In the weak perturbation regime, the system response is linear and the measured changes in these optical properties can be related to the electron distribution function. Direct measurements of the transient electron distribution excited by a femtosecond laser pulse can also be performed using photoemission spectroscopy (Fann *et al.*, 1992). Such experimental investigations have shown that, after the femtosecond laser pulse excitation, the electron distribution is far from equilibrium.

In the theoretical study of the electron relaxation, however, an instantaneous electron thermalization is generally supposed and the relaxation of the electron distribution is described by a two temperature model (Anisimov *et al.*,

1974; Schoehlein *et al.*, 1987; Fann *et al.*, 1992; Sun *et al.*, 1994; Del Fatti *et al.*, 1998; Yilbas & Shuja, 1999). In this model, electron–electron collisions are assumed to be fast enough to thermalize the electron gas over a temporal scale shorter than the laser pulse duration. In this way, the metal can be described by two coupled subsystems, representative of the electrons and the phonons, each in local thermodynamic equilibrium at temperatures, respectively, T_e and T_L . The energy transfer between the two subsystems occurs via electron–phonon collisions and its rate is proportional to $T_e - T_L$ and to the electron–phonon coupling constant. The time evolution of the two temperatures is thus given by a system of two coupled nonlinear differential equations describing the electronic and lattice heat capacities, the heating due to the incident optical pulse, and the diffusion process along the energy axis. The nonlinearity of the equations is due to the dependence of the electron heat capacity on the electron temperature so that the effect of an increase of electronic temperature is reflected in an increase of the thermal-relaxation time.

Actually, in the case of noble metal systems, the screening of the Coulomb interactions and the Pauli exclusion principle effect reduce the electron–electron collisional rates with the consequence of a slower internal thermalization of the electron gas on a few hundred femtosecond time scale. Thus, for laser pulse duration of the order of femtosecond, the two-temperature model cannot be applied as, after the

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pulse, electron–electron collisions have not thermalize the electron distribution yet. The aim of this work is to study the temporal evolution of the electron distribution even before the thermalization. For this purpose, we have performed a kinetic study of the electron dynamic relaxation in a Au film subjected to a femtosecond laser pulse excitation through the numerical solution of the Boltzmann equation.

2. THEORETICAL MODEL

The Boltzmann equation for the electrons in the conduction band of the metal film can be written as

$$\frac{\partial f(k)}{\partial t} = \left(\frac{\partial f(k)}{\partial t} \right)_{e-e} + \left(\frac{\partial f(k)}{\partial t} \right)_{e-ph} + \Phi(k, t), \quad (1)$$

where $f(k)$ is the electron distribution function. In the approximation of a parabolic and isotropic conduction band, the Boltzmann equation can be written only in terms of electron energy: $f(k) = f(E)$. The first two terms on the right side are the collision integrals for electron–electron ($e-e$) and electron–phonon ($e-ph$) scattering processes, while the last term describes the perturbation due to the laser pulse (electron–photon interaction). The injected laser energy is collected by the free electron gas, and we assume a low perturbative regime to hold, in which the increase of the electron temperature is a few hundred degrees Kelvin. Due to the high heat capacity of the lattice, we can suppose that the lattice temperature remains more or less constant. Moreover, the changes in the phonon occupation numbers can be considered negligible during the relaxation so that we can describe the phonon gas by the equilibrium Bose–Einstein distribution at the initial temperature T_0 , during the whole time evolution. After the laser pulse excitation, energy is redistributed among the electrons through electron–electron collisions. Simultaneously, the electron gas loses energy towards the lattice thanks to electron–phonon collisions. The metal system studied is gold. This choice is due to the simple electronic structure of the metal: Since the d bands lie 2 eV below the Fermi energy E_F , gold may be considered as a free-electron metal for energy $E_F \pm 1.84$ eV, where 1.84 eV is the laser energy of the photons considered in the present study. For this photon energy, the initial nonequilibrium electron distribution is created due to an intraband absorption of the laser pulse without involving inner energy bands. The absorption of the injected laser energy can be described as an electron–photon interaction

$$e(E) + \gamma(h\nu) \rightarrow e(E + h\nu). \quad (2)$$

In this way, a non-Fermi distribution is created with energies up to the pump photon energy above the Fermi level. Supposing the density of states of gold almost constant in the vicinity of the Fermi level, the electron distribution change for instantaneous excitation and small perturbation can be written (Sun *et al.*, 1994)

$$\Delta f(E) = \Delta\rho^0 [f_0(E - h\nu)(1 - f_0(E)) - f_0(E)(1 - f_0(E + h\nu))], \quad (3)$$

where

$$\Delta\rho^0 \approx \frac{E_V}{h\nu} \frac{1}{h\nu} \frac{1}{D(E_F)} \quad (4)$$

is a constant which depends on the laser energy E_V absorbed per unit volume and on the state density $D(E_F)$ at the Fermi energy. If the photon absorption cannot be considered instantaneous and τ_L is the laser pulse length, the change in the distribution function is

$$\frac{\partial f(E, t)}{\partial t} \cong \frac{\Delta\rho^0}{\tau_L} (f(E - h\nu)(1 - f(E, t)) - f(E, t)(1 - f(E + h\nu, t))). \quad (5)$$

Concerning the electron–electron collision term, we must take into account any two-particle collision that occurs. Moreover, since the Coulomb potential has a long range, each binary interaction cannot be uncoupled from the interaction among the nearby ones. In the Thomas–Fermi theory of screening, such a problem has been solved considering each electron–electron interaction as a two-particle interaction with a screening Coulomb potential (Ziman, 1960; Ashcroft & Mermin, 1976; Snoke *et al.*, 1992)

$$H_{e-e}(\bar{r}_1, \bar{r}_2) = \frac{e^2}{\epsilon |\bar{r}_1 - \bar{r}_2|} \exp(-\bar{q}_0 |\bar{r}_1 - \bar{r}_2|), \quad (6)$$

where $1/\bar{q}_0$ represents the screening length. Its value ranges between the Pines expression (Ziman, 1960) $1/(0.353 r_s^{1/2} R_F)$ where R_F is the Fermi radius and $r_s = (3/4\pi n_e)^{1/3}$ (measured in Bohr units) and the inverse of the Debye length λ_D .

The change of the distribution function due to $e-e$ collision can be written

$$\begin{aligned} \left(\frac{df(\bar{k})}{dt} \right)_{e-e} &= \frac{3}{4} \frac{4\pi^2}{h} \frac{V^2}{(8\pi^3)^2} \int d\bar{k}_1 d\bar{k}_2 d\bar{k}_3 M^2(\bar{q}) \\ &\times f(\bar{k}_2) f(\bar{k}_3) [1 - f(\bar{k}_1)] [1 - f(\bar{k})] \\ &\times \delta(\bar{k}_2 + \bar{k}_3 - \bar{k}_1 - \bar{k}) \delta(E_2 + E_3 - E_1 - E) \\ &- \frac{3}{4} \frac{4\pi^2}{h} \frac{V^2}{(8\pi^3)^2} \int d\bar{k}_1 d\bar{k}_2 d\bar{k}_3 M^2(\bar{q}) \\ &\times f(\bar{k}) f(\bar{k}_1) [1 - f(\bar{k}_2)] [1 - f(\bar{k}_3)] \\ &\times \delta(\bar{k} + \bar{k}_1 - \bar{k}_2 - \bar{k}_3) \delta(E + E_1 - E_2 - E_3), \quad (7) \end{aligned}$$

which includes the squared magnitude of the matrix element M for $e-e$ interaction, which depends only on the momen-

tum exchange $\bar{q} = \bar{k} - \bar{k}_2 = \bar{k}_1 - \bar{k}_3$ and which can be written, in the first order perturbation theory, as

$$M(\bar{q})^2 = |\langle \bar{k}, \bar{k}_1 | H_{e-e} | \bar{k}_2, \bar{k}_3 \rangle|^2 = \left| \frac{4\pi e^2}{\epsilon V} \frac{\delta(\bar{k} + \bar{k}_1 - \bar{k}_2 - \bar{k}_3)}{\bar{q}^2 + \bar{q}_0^2} \right|^2. \quad (8)$$

The factor 3/4 in Eq. (7) takes account of the fact that if electrons have the same spin, then the scattering processes which are identical except for an exchange of the particles in the final states will contribute only once. For a given set \bar{k} , \bar{k}_1 , \bar{k}_2 , and \bar{k}_3 , only three out of the four possible collisions events are distinguishable. Equation (7) involves an integral over 12 momentum dimensions. In the energy space, supposing a parabolic and isotropic conduction band, this integral can be reduced to two over three energies and the change of the energy distribution function $f(E)$ can be written (Snook *et al.*, 1992)

$$\left(\frac{\partial f(E)}{\partial t} \right)_{e-e} = \frac{3(2m)^{5/2} \pi^3 V^3}{h^6} \frac{1}{\sqrt{E}} [\Gamma_I(E) - \Gamma_O(E)], \quad (9)$$

where $\Gamma_I(E)$ and $\Gamma_O(E)$ are the rate of scattering in and scattering out of electrons in the energy state E . In equilibrium conditions $\Gamma_I(E) = \Gamma_O(E)$.

The explicit expressions of $\Gamma_I(E)$ and $\Gamma_O(E)$ are

$$\Gamma_O(E) = \int_0^\infty \int_0^\infty dE_1 dE_2 \left[\int_{k_{low}}^{k_{up}} d\bar{q} M^2(\bar{q}) \right] \times f(E) f(E_1) (1 - f(E_2)) (1 - f(E_3)) \quad (10)$$

$$\Gamma_I(E) = \int_0^\infty \int_0^\infty dE_1 dE_2 \left[\int_{k_{low}}^{k_{up}} d\bar{q} M^2(\bar{q}) \right] \times f(E_2) f(E_3) (1 - f(E)) (1 - f(E_1)) \quad (11)$$

with

$$\begin{cases} k_{up} = \min(\bar{k} + \bar{k}_2, \bar{k}_1 + \bar{k}_3) \\ k_{low} = \max(|\bar{k} - \bar{k}_2|, |\bar{k}_1 - \bar{k}_3|), \\ E_3 = E + E_1 - E_2 \end{cases} \quad (12)$$

and the explicit expression of the square root of the scattering amplitude is (Snook *et al.*, 1992)

$$\int_{k_{low}}^{k_{up}} M^2(\bar{q}) d\bar{q} = \frac{(4\pi)^2 e^4}{\epsilon^2 V^2} \times \left[\frac{q}{2q_0^2(q^2 + q_0^2)} + \frac{1}{2q_0^3} \arctan\left(\frac{q}{q_0}\right) \right] \Big|_{k_{low}}^{k_{up}}. \quad (13)$$

Considering a small amount of laser energy absorbed in such a way to consider small lattice temperature changes and due to the fast decay of high-energy electrons by electron–electron collisions, the electron–phonon collision rate can be introduced in the relaxation time approximation (Sun *et al.*, 1994)

$$\left(\frac{df_k}{dt} \right)_{e-ph} = \frac{f_{0,k} - f_k}{\tau_p}, \quad (14)$$

where $f_{0,k}$ is the equilibrium electron distribution after the pulse, which, due to the hypothesis of the small change between the initial and final lattice temperature, can be put equal to the initial electron distribution. τ_p is the characteristic time of electron–phonon collisions and it can be calculated from the two-temperature model obtaining

$$\tau_p = \frac{C_e}{G}, \quad (15)$$

where C_e and G represent, respectively, the electron thermal capacity and the electron–phonon coupling constant (Sun *et al.*, 1993). In the weak perturbation regime, we can use $\tau_p = 1$ ps (Sun *et al.*, 1993).

After making explicit the collisional integrals in Eq. (1), the next step is to numerically solve the Boltzmann equation. We have discretized the conduction band energy into constant steps. The electron distribution time evolution is calculated for each time step dt from Eqs. (3), (5), (9), (14), and

$$f(E, t + dt) = f(E, t) + dt \left[\frac{df(E)}{dt} \Big|_{e-e} + \frac{df(E)}{dt} \Big|_{e-ph} + \Phi(E, t) \right]. \quad (16)$$

3. RESULTS

In the following test case calculations, we have used the values reported in Table 1 for the different quantities that enter in the Boltzmann equation. Before the laser perturbation, the sample is considered in equilibrium condition at $T = 300$ K, so that the initial electron distribution is a Fermi–Dirac one. The value of the screening length chosen is 2×10^8 cm⁻¹, between the value predicted by the Pines expression (Ziman, 1960) (1.58×10^8 cm⁻¹) and the inverse of the Debye length at $T = 300$ K (2.03×10^9 cm⁻¹). First of all,

Table 1. Values used in test case calculations.

n_e	electron density	5.9×10^{22} cm ⁻³
$h\nu$	photon energy	1.84 eV
T_0	initial temperature	300 K
f_0	initial distribution	Fermi–Dirac
$1/q_0$	screening length	2×10^8 cm ⁻¹
τ_p	e - ph characteristic time	1 ps

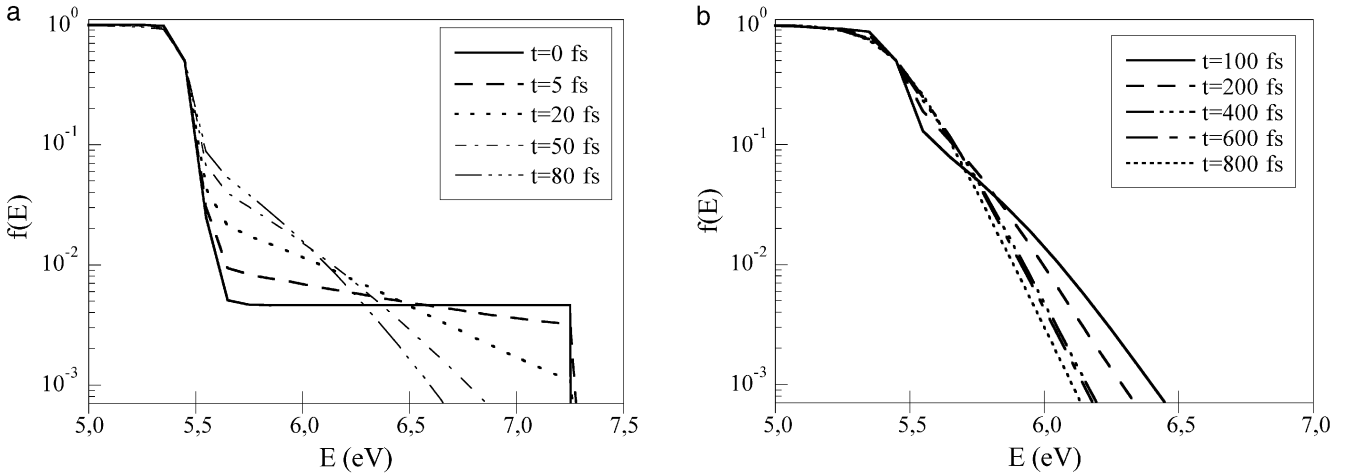


Fig. 1. Temporal evolution of the electron energy distribution function considering only electron–electron collisions and an instantaneous photonic absorption. The initial electron distribution is a Fermi–Dirac at $T_e = 300$ K and the laser energy absorbed per unit volume E_V is 40 J/cm^3 .

we have performed our calculations considering an instantaneous photonic absorption and neglecting electron–phonon interactions in order to analyze only the effect of electron–electron collisions over the distribution.

Figure 1a and b show the electron distribution as a function of the electron energy during the temporal evolution in such conditions. In this case, the laser energy absorbed per unit volume (E_V) has been fixed to 40 J/cm^3 ($2.5 \times 10^{20} \text{ eV/cm}^3$). As we can see, the electron distribution is strongly nonthermal in the first part of the evolution. Moreover, energy losses due to the electron–electron collisions are faster for electrons with higher energy, and after about some tens of femtoseconds, the high energy tail of the distribution is reduced and the distribution tends to concentrate close to the Fermi level. This is in line with the expression of the relaxation time due to electron–electron collisions obtained from the theory of Fermi liquid (Ashcroft & Mermin, 1976; Pines & Nozieres, 1996),

$$\tau_{e-e} = \frac{1}{K(E - E_F)^2}, \quad (17)$$

where K is a constant depending on the particular metal. As you can see, the higher the electron energy, the shorter the relaxation time.

In Figure 1b, it is shown that the relaxation of the electrons near the Fermi level is much slower. This is essentially due to the screening of the Coulomb potential and to the Pauli principle effect, which strongly reduce the relaxation probability near the Fermi level.

The electron distribution can be considered in equilibrium at about 800 fs. This numerical result agrees with the theoretical value of the electron–electron thermalization time obtained by Fermi-liquid theory under the random-phase approximation, characterized by the following expression (Tas & Maris, 1994):

$$\tau_T \approx n_e \tau_0 \frac{E_F}{E_V}, \quad (18)$$

where

$$\tau_0 = \frac{128}{\pi^2 \sqrt{3} \omega_p} \quad (19)$$

and ω_p is the plasma frequency, E_V the laser energy absorbed per unit volume, and E_F the Fermi energy (5.53 eV for Au). The value predicted by Eq. (18) in our condition is 720 fs, which is very near to the value of the thermalization time obtained from Fig. 1b. The expression of Eq. (18) is correct if the density of the electron excitation is very low with respect to the electron density. This is a good approximation in our calculation as $E_V = 2.5 \times 10^{20} \text{ eV/cm}^3$, $h\nu = 1.83 \text{ eV}$, and assuming that each photon is instantaneously absorbed by electrons, the number of initial excited electrons is $1.36 \times 10^{20} \text{ cm}^{-3}$ which is two orders of magnitude lower than the electron density in the conduction band ($5.9 \times 10^{22} \text{ cm}^{-3}$).

Figures 2a and b are for the same condition of Figure 1, but with an increased E_V , that is 56 J/cm^3 ($3.5 \times 10^{20} \text{ eV/cm}^3$). As we can see, the relaxation is faster than the previous case. Here, the distribution can be considered in equilibrium already at $t = 600$ fs. This result is confirmed by expression (18), which shows an inverse proportionality between τ_T and E_V .

In the last calculation, we consider both electron–electron and electron–phonon collisions and impose photonic absorption lasting 180 fs, $E_V = 40 \text{ J/cm}^3$ and an initial Fermi–Dirac distribution at $T_e = 300$ K (Fig. 3). As we can see from Fig. 3a, the distribution rises until the energy pumping is active (in the graph, until $t = 0$ fs). In Fig. 3b, it can be noted that only for $t = 1700$ fs does the distribution reach the equilibrium condition at a temperature $T_e = 630$ K, which is lower than the final temperature in Fig. 1b, obtained without

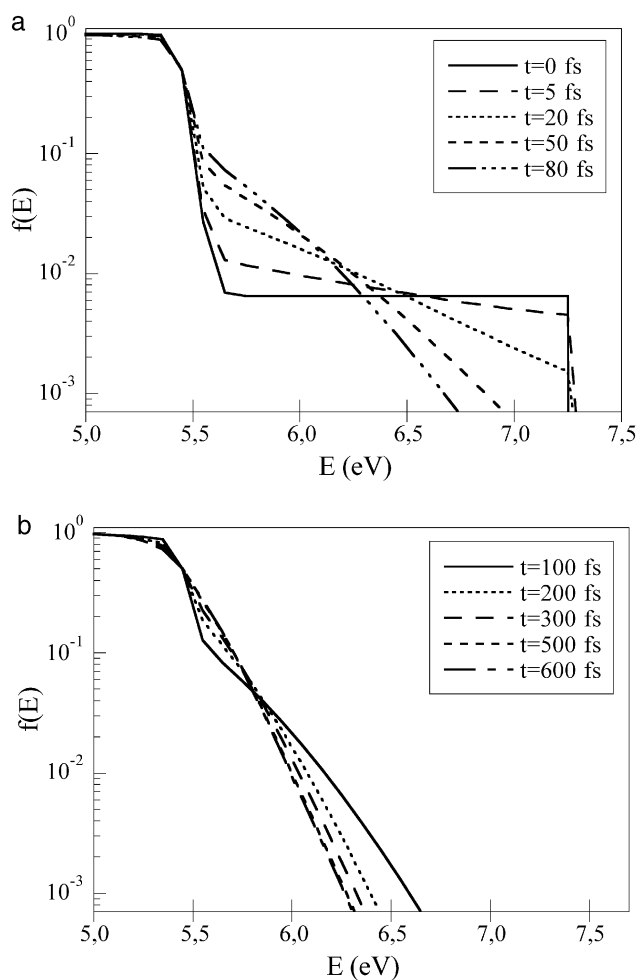


Fig. 2. Temporal evolution of the electron energy distribution function considering only electron–electron collisions and an instantaneous photonic absorption. The initial electron distribution is a Fermi–Dirac at $T_e = 300$ K and the laser energy absorbed per unit volume E_V is 56 J/cm^3 .

considering the thermal relaxation between electrons and lattice (adiabatic condition). The effect of the e – ph processes is to reduce the kinetic energy of the electrons and to restore the local equilibrium condition between electrons and lattice.

4. CONCLUSIONS

The solution of the Boltzmann equation has pointed out some important characteristics of the electron relaxation dynamic in a Au target under a subpicosecond laser pulse. The short laser pulse creates nonthermal initial electron distributions and through the numerical solution of the Boltzmann equation, one can follow their temporal relaxation. Considering only e – e collisions, relaxation times are of the order of some hundreds of femtoseconds due to the Pauli principle effect and to the screening Coulomb potential which reduce the probability of e – e collisions. This result shows

that e – e collisions thermalize the electron gas over a temporal scale greater than the femtosecond laser pulse. Therefore, for such short laser pulse, the two-temperature model is inadequate to describe the relaxation of the electron distribution and the heat transfer between electrons and phonons. Considering also the electron–phonon collisions, relaxation times increase to the order of picoseconds as electrons need more time to reach the local equilibrium condition with the lattice.

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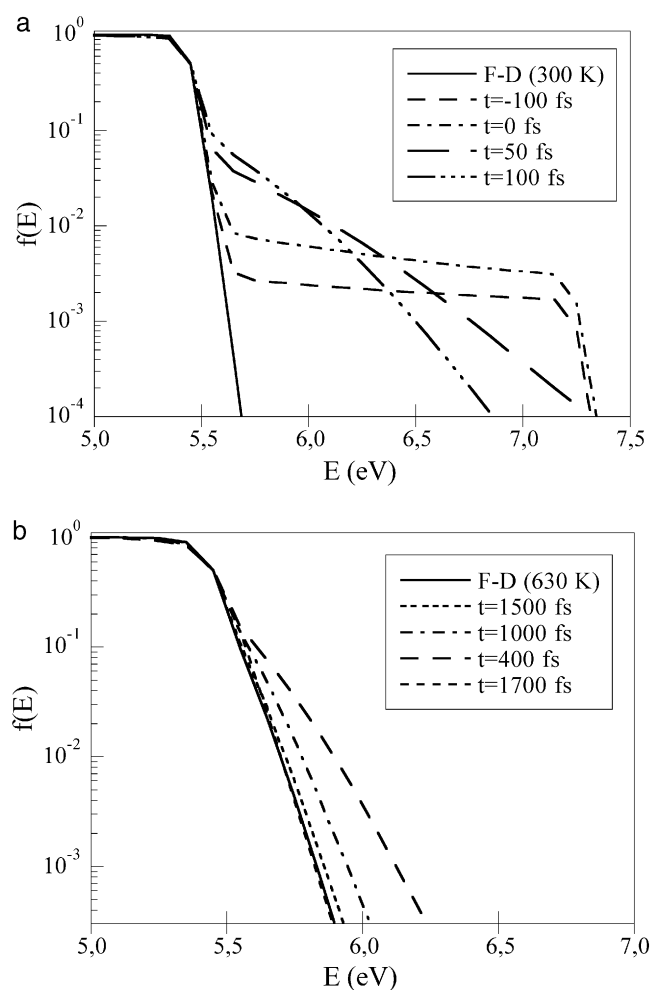


Fig. 3. Temporal evolution of the electron energy distribution function considering both electron–electron and electron–phonon collisions and a photonic absorption lasting 180 fs. The initial electron distribution is a Fermi–Dirac at $T_e = 300$ K and the laser energy absorbed per unit volume E_V is 40 J/cm^3 .

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