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Nonequilibrium electron distribution in metals

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We present a theoretical microscopic model for the calculation of the nonequilibrium distribution function of electrons in a metal excited by ultrashort laser pulses of moderate intensity. This model is based on a kinetic differential equation of the nonequilibrium population of excited electrons. It includes the transport phenomena that may be important at initial stages of the excitation. Our theoretical results compare favorably with the experimental measurements of Fann *et al.* [Phys. Rev. B **46**, 13 592 (1992)] obtained for a gold film. [S0163-1829(97)06607-1]

I. INTRODUCTION

Impact of ultrafast lasers on metallic surfaces generates nonequilibrium conditions for excitation processes and relaxation phenomena. These processes are directly connected to the metallic continuum. After irradiation with a short laser pulse (10^9 W/cm^2 intensity) of a clean metallic surface having a temperature of 140 K, the temperature of the electrons can be as high as 4500 K,[1] whereas the substrate temperature (related to phonons) rises only slightly and slowly to about 610 K. The above temperatures only indicate the energy distribution of particles. In such nonequilibrium conditions one can hardly fit the measured distribution to a Fermi-Dirac statistics and obtain an unambiguous temperature. Time-resolved measurements of the change of the reflectivity in Au and Ag submitted to a laser pulse of 10^{12} W/cm^2 show also a nonthermal electron distribution.[2,3]

Nonequilibrium excitation by femtosecond lasers has also been shown to strongly affect the desorption kinetics of molecular adsorbates on metallic surfaces. For example, the desorption of CO from Cu surfaces was observed only with subpicosecond lasers (10^{10} W/cm^2 intensity).[9] Thermal desorption spectra of molecular oxygen absorbed on Pd(111) excited by nanosecond lasers[10] show strong similarities for all the laser wavelengths used in the experiment ($h\nu = 3.9$, 5.0, and 6.4 eV). However, the relative population of adsorbate states is strongly dependent on laser doses. This means that the excitation is weakly dependent on laser energy and relaxation generates the same states of the adsorbate. Therefore as for clean surfaces the excitation process of covered metallic surfaces involves the quasicontinuum of the electrons and is not directly related to the spacing between the energy levels of the adsorbate.

In experiments mentioned above the laser intensity was lower than the intensity required to generate a plasma in metals. Experiments made on gold[4] and other metals[5] evidenced a critical intensity greater than 4×10^{11} W/cm^2 for gold[4] and 10^{13} W/cm^2 for the other metals.[5] Consequently in the discussion below we neglect the possibility of plasma generation and the appearance of processes related to its formation, such as ionization by electron impact. Such processes have been fully analyzed in intense laser-induced damage in dielectrics[6] and semiconductors.[7] In the present work we will consider only the nonequilibrium distribution of an electron gas at lower laser intensity where it has neither the critical mass nor the critical temperature to become a plasma.[8]

Photoemission experiments made on gold[11,12] evidence the departure of the electron distribution from the Fermi-Dirac one. In Ref. 11 a polycrystalline gold film was irradiated by a 1.89-eV laser pulse of 400 fs duration. The electron energy distribution was measured with a probe laser of 5.52 eV of $\sim$ 700 fs duration using time-resolved photoemission spectroscopy. The measured distribution can be fitted by a Fermi-Dirac function at an elevated temperature except within $\sim$800 fs of the heating pulse, when a clear departure from this distribution is observed. In a second experiment[12] where a film of gold is used also the thermalization of electrons following 180 fs was measured. Depending on the excitation intensity, thermalization times as long as $\sim$1 ps were observed.

The standard model put forward by Anisimov, Kapeliovici, and Perel'man[13] describes the time evolution of the electron gas using two coupled subsystems of the metal—electrons and phonons. Each subsystem is in local equilibrium so the electrons can be characterized by a Fermi-Dirac distribution defined using a time-dependent temperature $T_e(t)$ while the phonon distribution is a Bose-Einstein one, characterized by the temperature $T_p(t)$. The local equilibrium is maintained by electron-electron (e-e) collisions and correspondingly by phonon-phonon collisions. The above assumptions are valid only if the electron-phonon (e-phonon) collision time is very different from the electron-electron one. In this case one can say that the electron thermal equilibrium is realized before the energy transfer to the phonons.

Theoretical estimation of the e-e collision time within the Fermi-liquid theory and recent measurements[14,2,3] of the e-e and e-phonon collision times put into question the validity of the standard model of coupled equations of Anisimov, Kapeliovici, and Perel'man[13] in the description of the short laser pulse excitation of metals.

Let us critically comment on the validity of the standard model of Anisimov, Kapeliovici, and Perel'man[13] on the basis of a partly quantitative evaluation of the e-e and e-phonon collision time. A partly quantitative evaluation of the properties of electrons in metals, within several eV of excitation energy above the Fermi level, is given by the Fermi-liquid theory.[15] Under the random-phase approximation (RPA) the e-e collision time is

$$\tau_{e\text{-}e}=\tau_0\frac{E_F^2}{\delta E^2}, \tag{1}$$

where E_F is the Fermi energy, $\delta E=E-E_F$ is the electron excess energy above the E_F, and τ_0 is a proportionality constant that can be calculated using the Linhard dielectric function:

$$\tau_0=\frac{128}{\pi^2\sqrt{3}\omega_p}, \tag{2}$$

where ω_p is the plasma frequency. In the Fermi-liquid theory the excited electron and the distortion of surrounding particles brought by the adiabatic interaction among particles are treated as a quasiparticle. A critical parameter in this treatment is r_s, the radius of the sphere containing the effective volume of an electron. It determines the validity of different approximations in the theory and is defined by the relation:

$$r_s=\frac{r_0}{a_0}, \tag{3}$$

where r_0 is the spacing between particles and a_0 is the Bohr radius.

The e-e collision time expression (1) is deduced in the high-density limit ($r_s \ll 1$) and the corresponding RPA expression is valid in this case. As for the metals $1.8 \leqslant r_s \leqslant 5.5$, Eq. (1) cannot give an accurate account of the metallic electron gas.

Time-resolved two-photon photoemission from Cu(100) (Ref. 14) shows that the predicted lifetimes using Eq. (1) are reasonably close to the observations but the energy dependence shows a systematic deviation. This discrepancy was explained by the fact that the excited electron can move out of the region probed by the laser on a time scale faster than their relaxation time. Also it was mentioned that neglecting $3d^{10}$ electrons for Cu(100) may introduce some errors.

To evaluate the e-phonon collision time we use an approximate formula:[16]

$$\tau_{e\text{-phonon}}=\frac{\lambda_{\text{phonon}}}{v_f}, \tag{4}$$

where the mean-free path given by the e-phonon collision is

$$\lambda_{\text{phonon}}\simeq 50a\frac{T_m}{T_e}, \tag{5}$$

with a the lattice constant, T_m the melting temperature, and T_e the electronic temperature. This approximation is justified for T_e much higher than the Debye temperature (T_D).

If we take gold as an example, the above model gives $\tau_{e\text{-}e}$ varying from 4 to 400 fs when δE varies from 2 to 0.2 eV whereas $\tau_{e\text{-phonon}}$ is about 60 fs [for gold $T_e \gg 300$ K, $T_D=170$ K, so the above formula (5) can be applied]. Experimentally one finds a value of 700 fs for $\tau_{e\text{-phonon}}$.[2] We see that the e-e relaxation times strongly depend on energy: near the Fermi level the two times (e-e and e-phonon) are comparable. At higher energy they are very different.

Other estimations[12,3] result in different times but the general conclusion is that the electron gas has not reached a thermal distribution before the e-phonon energy relaxation process sets in. As a conclusion, we cannot use the model of Anisimov, Kapeliovici, and Perel'man[13] of two coupled systems of electrons and phonons to describe the time evolution of the distribution of the electron in the nonthermal regime because the lifetimes are too different near the Fermi level and at high energy.

Until now there have been only two attempts to our knowledge to construct a realistic distribution of the nonthermal electrons. First, Fann *et al.*[12] used an exponential decay to include the e-e collisions but they neglect the interband transitions that appear at the laser energies used in the experiments. Their distribution function does not fulfill the initial condition

$$f(E,t=0)=f_{\text{FD}}(E) \tag{6}$$

and is completely independent of the laser energy and fluence. Moreover the equation describing the energy transfer from the nonthermal distribution into the thermal one is not physically homogeneous. So it cannot be used, at least in its published form.

A second nonequilibrium distribution function is proposed by Lugovskoy, Usmanov, and Zinoviev.[17] They describe the interaction of an electron with the electromagnetic field as a process of an inelastic photon-electron collision. To account for the energy transfer between the electron and the photon they introduce a phenomenological absorption rate. The time variation of the nonequilibrium distribution is given by a differential equation of first order in time that depends linearly on the absorbed laser irradiance. The solution fulfills the initial condition (6) and has a Gaussian time dependence (for a Gaussian temporal profile of the laser pulse). However, the maximum is reached at $t=0$, a result that is not physically correct because for that time the laser almost began to transfer energy. The resulting step structure of the electronic distribution function was not observed in the experiment[12] and step magnitude strongly depends on e-e collision time, which is not given by Lugovskoy, Usmanov, and Zinoviev.[17]

In the present paper we develop a microscopic model for the calculation of the nonequilibrium distribution of the electrons excited by short time laser pulses. We suppose that electron and phonon subsystems are weakly coupled. The results of this model are compared to the experiments of Fann *et al.*[12] Our model involves two steps: first we calculate the excitation neglecting the transport of the electrons; second, we introduce this transport of electrons by including the pump laser oscillating electric field but neglecting the spatial variation of the distribution function. In the Appendix we will briefly discuss the spatial distribution of hot electrons.

II. THE MODEL

Let a laser pulse be incident on a metal. The pulse duration is less than 300 fs and the quantum energy less than the work function of the metal. As a result a distribution of electrons with kinetic energy $E_F \leqslant E_{\mathrm{cin}} \leqslant E_F + h\nu$ is formed. The excited electrons can collide with other electrons of the metal and with phonons. To calculate time and energy variation of the nonequilibrium distribution of photoelectrons, we propose a simple model that describes the interaction with the electromagnetic radiation as a resonant dipole transition between two levels $E \rightarrow E + h\nu$. The energy loss of the excited electrons is described by an average relaxation time τ given by the Fermi-liquid theory (1). This approximation is valid for electrons in the sp band considered here. In this work we neglect completely the d bands, the surface states, and sp band structures. Also we do not take into consideration the Fermi-level smearing. At present the electron-phonon interaction is neglected. As mentioned above, we start by deriving a model discarding the transport phenomena then include them.

A. Excited electrons without transport

The kinetic equation for the distribution function $f(E,t)$ is

$$\frac{df}{dt} = P_{\mathrm{ex}} - P_{\mathrm{desex}} \tag{7}$$

where

$$P_{\mathrm{ex}} = p_0 t[1 - f(E,t)]. \tag{8}$$

Here P_{ex} is the probability of electron transition, in the time unit, from the energy $E_i = E - h\nu (\leqslant E_F)$ to $E(\geqslant E_F)$ and p_0 is the initial transition probability of the electron defined by the following equation:

$$p_0 = \frac{e^2 E_0^2}{8\pi^2 h^2} f_{\mathrm{FD}}(E_i) |M_{E,E_i}|^2, \tag{9}$$

where e is the charge of the electron, h is Planck's constant, E_0 is the modulus of the electric field intensity, $f_{\mathrm{FD}}(E_i)$ is the Fermi-Dirac distribution of the initial level having the energy $E_i(\leqslant E_F)$, $[1 - f(E,t)]$ is the probability that the energy level E where the electron is excited is unoccupied, and M_{E,E_i} is the transition probability. Equation (8) was deduced in the approximation of a dipolar electromagnetic transition between two resonant levels (see, for example, Refs. 18 and 16).

P_{desex} is the probability of electron energy loss in the time unit caused by e-e collisions. It is given by

$$P_{\mathrm{desex}} = \frac{f(E,t)}{\tau}, \tag{10}$$

where τ is the collision time given by Eq. (1). We are omitting the index e-e in Eq. (10) and in the following formulas.

Using Eqs. (8), (9), and (10), we can write the kinetic equation (7) explicitly in terms of $f(E,t)$:

$$\frac{df}{dt} = p_0 t - \left(p_0 t + \frac{1}{\tau}\right) f(E,t). \tag{11}$$

This differential equation has the following analytical integral solution:

$$f(E,t) = 1 - \exp\left[-\left(\frac{p_0 t^2}{2} + \frac{t}{\tau}\right)\right] \times \left[1 - f_{\mathrm{FD}}(E)\frac{1}{\tau}\int_0^t dt_1 \exp\left(\frac{p_0 t_1^2}{2} + \frac{t_1}{\tau}\right)\right], \tag{12}$$

which verify the following initial conditions: (i) For $t=0$,

$$f(E,t=0) = f_{\mathrm{FD}}(E); \tag{13}$$

(ii) if the laser is not operating then E_0 and p_0 are zero, and

$$f(E,t) \simeq f_{\mathrm{FD}}(E) \exp\left(-\frac{t}{\tau}\right), \tag{14}$$

which for $E = E_F$ gives

$$f(E_F, t) = f_{\mathrm{FD}}(E_F). \tag{15}$$

The dependence in the laser intensity is contained in p_0. For times short enough, $p_0 t^2$ and t/τ are much smaller than 1 and the development of the exponential in power series gives

$$f(E,t) \sim p_0^2 \sim I^2 \tag{16}$$

but this quadratic dependence is not valid for long times. We see that the electronic distribution is strongly influenced by the adsorbed power. This dependence may explain why, in the subpicosecond experiments, the relaxation probability and the desorption yield depend nonlinearly on the laser intensity.[9,10,19,20] Equations (7) or (11) and (12) are effective only during the laser action. After laser extinction at time t_f, Eq. (11) simplifies to

$$\frac{df(E,t)}{dt} = -\frac{f(E,t)}{\tau}, \tag{17}$$

which can be integrated to give the equivalent of Eq. (12):

$$f(E,t) = \exp\left(-\frac{(t - t_f)}{\tau}\right) f(E,t_f). \tag{18}$$

The electronic distribution goes exponentially to the equilibrium distribution $f_{\mathrm{FD}}(E)$ corresponding to an electronic temperature greater than the initial one and characterizing the mean energy of the electronic population excited above E_F. The first step of thermalization occurs very rapidly but slows down as more energy has been shared and the average electron energy gets closer to the Fermi level. Also, the e-phonon energy relaxation process sets in and accelerates the dissipation of energy.

B. Excited electrons including electric field transport

The electromagnetic field excites electrons but can also produce their transport in the band of the metal. To introduce the transport we use the classical Boltzmann equation[21]

$$\left(\frac{\partial f}{\partial t}\right)_{\mathrm{transp}} = \frac{\partial f}{\partial t} + \vec{v}\frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{\hbar}\frac{\partial f}{\partial \vec{k}}, \tag{19}$$

where f is the distribution function obtained either without transport (right-hand side of the equation) or including it

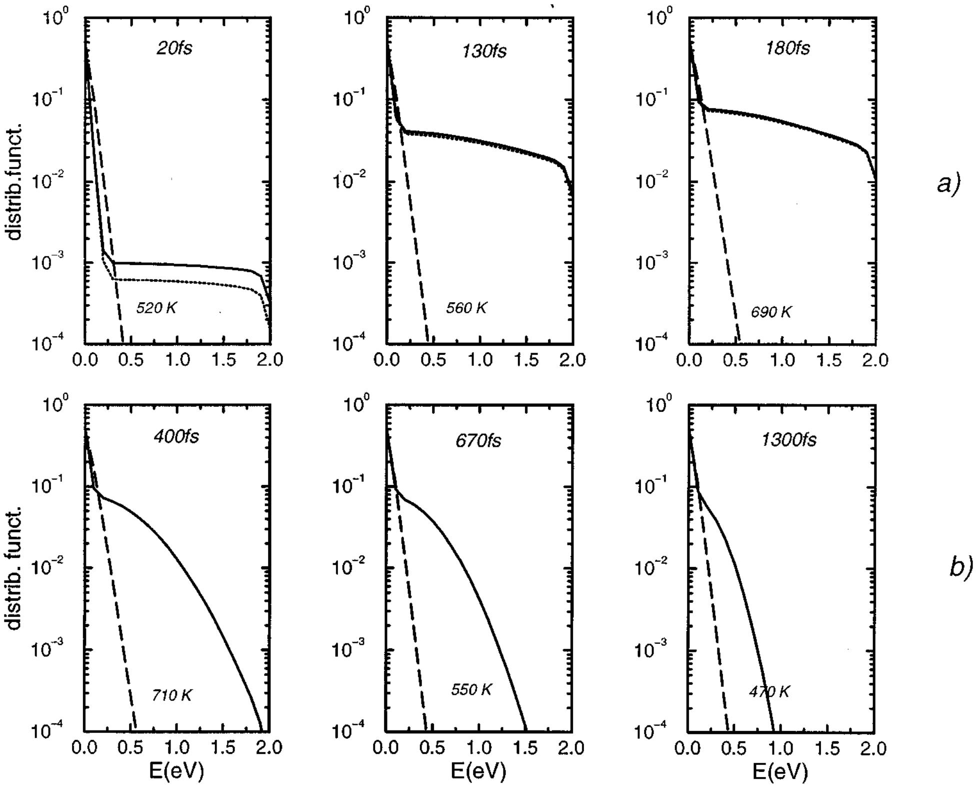

FIG. 1. Energy dependence of the electron distribution function for a laser adsorbed intensity of 0.6×10^{9} W/cm^{2} at six instants. For the first line (a) the laser is on whereas for the second line (b) the laser is off. The full line corresponds to electronic distribution f given by Eq. (12), the dotted line corresponds to the distribution f_{transp} given by Eq. (24) including the transport by the field, and the dashed line is the Fermi-Dirac fit established by Fann *et al.*,[12] Fig. 1, corresponding to the displayed temperatures.

(left-hand side of the equation; subscript transp), $\vec{v}$ is the electron speed in the band, and $\vec{F}$ is the driving force. Now this equation takes into account the intraband collisions during the transport. The laser electric field is oscillating and can be written as $\vec{E}(\vec{r},t)=\vec{E}_0\cos(kr-\omega t)$. It induces a variation in space and time of the local population of electrons:

$$\delta n(\vec{r},t)=\delta n_0\cos(kr-\omega t). \tag{20}$$

This variation gives rise to a change $\delta\mu$ of the chemical potential:

$$\mu(\vec{r},t)=\mu_0+\delta\mu\cos(kr-\omega t). \tag{21}$$

It was demonstrated in Ref. 21 that, for the electrons of the valence band not having interband transitions, the maximal spatial variation induced in the distribution function by a variation of the local population of electrons of $\Delta n=1$ is

$$\Delta f=\frac{E_F}{6k_BTn}, \tag{22}$$

where k_B is the Boltzmann constant. For gold Eq. (22) gives $\Delta f_{\text{FD}}=[1.7910^{-19}]/T$, which is very small compared with the value of our distribution function having a typical value of 10^{-3}. So one can neglect the induced space variation of the electron distribution function (see the Appendix for a more careful consideration of this approximation) and calculate, as we did in the present work, only the temporal one. So, we neglect below $\partial f/\partial\vec{r}$ and simplify Eq. (19) as follows:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{transp}}=\frac{\partial f}{\partial t}-e\vec{v}\vec{E}(t)\frac{\partial f}{\partial E}. \tag{23}$$

In the relaxation time approximation,[21] one integrates Eq. (23) to obtain

$$f_{\text{transp}}(E,t)=f(E,t)-\exp\left(-\frac{t}{\tau_1}\right)\times\int_0^t\left(\frac{\partial f}{\partial t_1}-e\vec{v}\vec{E}_0\sin\omega t_1\frac{\partial f}{\partial E}\right)\exp\left(\frac{t_1}{\tau_1}\right)dt_1, \tag{24}$$

where τ_1 is the intraband collision time. Making the approximation that $\tau_1\simeq\tau$ [where τ is given by Eq. (1)], the expression (24) demonstrates that $f_{\text{transp}}(E,t)$, the distribution including transport, is smaller than or equal to $f(E,t)$, the distribution discarding transport. The difference between the two distributions is rather small. We will see that only for very short times after the beginning of the excitation is this difference significant because exponential multiplying of the integral in Eq. (24) decays rapidly in time.

III. RESULTS

In the experiment of Fann *et al.*[12] a gold film of 300 Å was excited with a laser having an energy of 1.89 eV and a duration of 180 fs. The nonequilibrium electron distribution was probed with a laser of 5.52 eV and a 270-fs duration time, using delayed time-resolved photoemission spectroscopy. In the model presented above, we neglect the spatial variation of the electron distribution function. Does the thin film of gold of 300-Å depth behave like a metallic bulk in the present experimental conditions? In the Appendix we show that under the present experimental conditions the spatial transport phenomena can be neglected and therefore the 300-Å film behaves like a metallic solid. Another phenom-

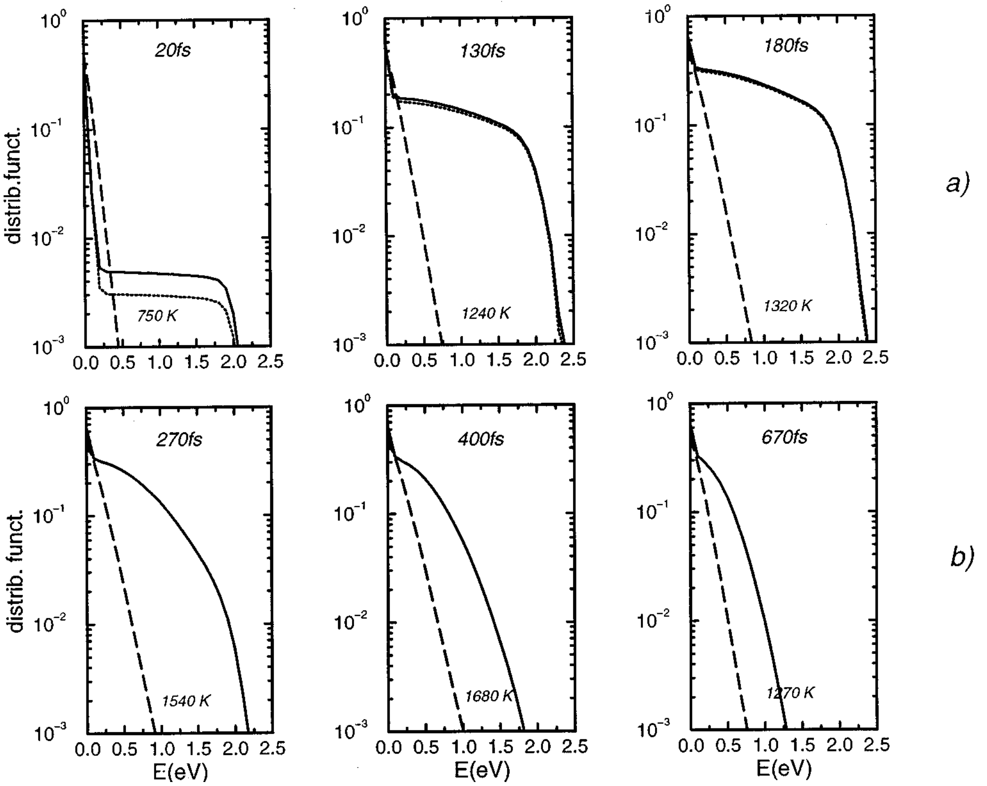

FIG. 2. Energy dependence of the electron distribution function for a laser adsorbed intensity of 1.6×10^{9} W/cm^2 at six instants. For the first line (a) the laser is on whereas for the second line (b) the laser is off. Same caption as Fig. 1 except that the figures should be compared with Fig. 2 of Fann *et al.*[12]

enon that is neglected here is the electron thermal diffusion that can be inhomogeneous in thin films. Under the present experimental conditions the thermal diffusion length can be estimated to be of the order of 2 nm. Therefore the thin film behaves again like a solid. Also the time scales considered in the model are short compared to the thermal diffusion times.

We have calculated the nonequilibrium distribution function using the expressions (12) discarding transport phenomena and (24) including it. In our calculations we have used the following constants (close to the one used by Fann *et al.*[12]): $E_0=6.7\times10^7$ V/m (for Fig. 1) and $E_0=3.3\times10^8$ V/m (for Fig. 2), $E_F=5.53$ eV, $t_f=180$ fs, $\tau_0=5$ fs. For $|M_{E,E_i}|^2$ we used a value $\leqslant 10^{-19}$ m^2. This value is justified by the fact that in atomic gold $|M_{E,E_i}|^2$ is about 10^{-21} m^2 for the $6s$-$6p$ transition.[22] The electronic configuration for gold is $[\mathrm{Xe}]4f^{14}5d^{10}6s^1$. So we suppose that the electronic transition from a level close to E_F to another above E_F at almost 1.84 eV can be approximated by a $6s$-$6p$ transition. In a metal the levels are completely displaced and form a continuum. The electron moves freely and consequently we expect a transition moment in the metal to be greater than the one in the single atom.

The electronic distribution functions displayed in Fig. 1 are obtained using the expressions (12) or (24) where we used a rectangular form of the laser pulse and an initial probability of $p_0=5\times10^{24}$ s^{-2} independent of time. In this figure the full curve represents the distribution function calculated without transport using Eq. (12). One can see that the electronic population excited above the Fermi level first grows in time until the laser extinction then diminishes exponentially. The full thermalization is not established until $\sim$1.3 ps. The energy dependence shows that the excited electrons are concentrated at low energy. The departure from the Fermi-Dirac distribution (long-dashed curve) calculated for the temperatures indicated in the figures of Fann *et al.*[12] appears very clearly because one cannot find a temperature fitting the shape of the nonequilibrium electron distribution function. Consequently in the present case the temperature displayed on the figures is not reliable.

The dotted curve represents the distribution function including the transport by the oscillating electric field of the photon. The difference between the two curves (without and with transport) is significant only at short probe times (20 fs) and it is strongly attenuated for larger ones. This behavior can easily be inferred from Eq. (24) because the coefficient multiplying the integral is exponentially decaying in time.

Comparing Fig. 1 with the experimental curves of Fann *et al.*[12] displayed in their Fig. 1 one observes the strong similarities between the two figures. Discarding the small oscillations (they could be artifacts), the time evolution and energy dependence are nearly the same. As mentioned above the comparison with the Fermi-Dirac distribution can be used only as a rough indication of the temperature of the electrons.

In Fig. 2 we represented the results corresponding to the second laser fluence used in the experiment of Fann *et al.*[12] One can see that now the distribution function reaches values greater than above during laser action and the decay to the equilibrium Fermi-Dirac function, calculated by Fann *et al.*[12] is faster. The comparison with the experimental values (see Fann *et al.*,[12] Fig. 2) shows again a good coincidence in the time and energy evolution of the distribution function. We see also that the plateau from 0.25 to 2 eV has the same shape for the two fluences as can be seen in the experimental graphics. In the two figures we observe that the levels situated at an energy above 1.84 eV have a significant population. This can be explained by the excitation of few populated levels above the Fermi energy.

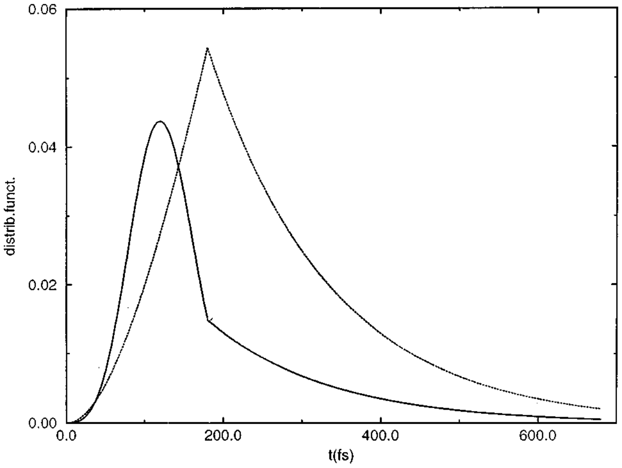

FIG. 3. Time dependence of the electron distribution function f (without transport) calculated for $E-E_F=1.0$ eV. The full curve corresponds to a Gaussian laser pulse with FWHM of 105.96 fs and the dotted curve to a rectangular one.

The above calculations were performed using a rectangular laser pulse because our tests demonstrated that the energy dependence is not significantly influenced by the form of the laser pulse. However, time dependence is strongly modified by the form of this pulse. This time variation for $\delta E=1.0$ eV is illustrated in Fig. 3 for Gaussian and rectangular laser pulses. The distribution function has a Gaussian form during laser action for the first and a rising exponential form for the latter. After 180 fs the laser is switched off and the decay is always exponential.

Above, we have presented the results for two laser pulses. In Fig. 4 we display the behavior of the distribution function for a rectangular laser pulse as a function of time and laser intensity. One sees that the dependence of the distribution function of the electrons on the laser intensity changes from a quadratic to a clearly exponential form. For larger intensities of the laser pulse (about 10^{11} W/cm^2) the distribution function reaches a saturation plateau above which the electron plasma can be generated.[4–7]

IV. CONCLUSION

In summary, we have proposed a microscopic model for the nonequilibrium or ''hot'' electron distribution that accounts for the processes taking place in a metal submitted to a laser pulse of moderate intensity. This model does not apply to interaction of lasers with intense lasers pulses (intensity greater than 10^{13} W/cm^2) where plasma is created and other microscopical processes take place. The model is physically coherent and gives microscopic insight concerning the excitation and relaxation of these hot electrons. The obtained results are in good agreement with the experimental data for a film of gold of 300-Å depth and show nonlinear behavior of this population with the laser intensity. The model can be used to describe the behavior of the electrons in a desorption mechanism in the femtosecond regime where the same nonlinear dependence was observed. In the Appendix, we show that the spatial transport phenomena can be neglected for a studied case of a thin film of 300-Å depth. Also the electron thermal diffusion length is short compared to the film thickness. Other effects, such as the influence of the band structure, the laser light polarization on the spatial distribution, and full three-dimensional distribution of electrons, are now studied and will be presented in a future paper. The model can be successfully applied to other metals (Cu, Pt, etc.).

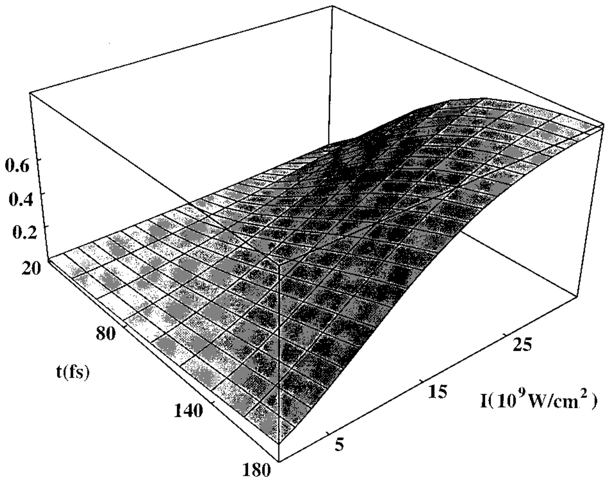

FIG. 4. Time and laser intensity dependence of the electron distribution function f (without transport) calculated for $E-E_F=1.0$ eV.

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APPENDIX: INCLUDING THE SPATIAL DISTRIBUTION

In this appendix we briefly discuss the spatial distribution of electrons neglected in the main body of the paper. Light absorption determines a finite photon path and e-e collisions determine an electron mean-free path dependent on its energy. The laser field produces also an electron drift parallel or perpendicular on the surface according to light polarization. These facts contribute to an anisotropic spatial distribution of the electrons.

In a first approximation, we consider only the variation of the distribution function with a z coordinate (perpendicular on the surface) and neglect the other coordinates. Extinction of the photon when it penetrates the metal introduces a spatial factor dependent on its mean-free path λ_{photon}.[10] The probability of finding a photon at depth z is given by $f_{\text{photon}}(z)=(1/\lambda_{\text{photon}})\exp(-z/\lambda_{\text{photon}})$. Another spatial factor arises from electron scattering: the electrons created at z' can arrive at point z after a scattering at point z' according to the integral

$$f_e(z)=\int_0^\infty dz'\,\frac{1}{\lambda_e}\exp\left(-\frac{|z-z'|}{\lambda_e}\right)\frac{1}{\lambda_{\text{photon}}}\exp\left(-\frac{z}{\lambda_{\text{photon}}}\right).$$

Here λ_e is the electron mean-free path. The total spatial factor reads

$$\begin{aligned}f(z)&=f_{\text{photon}}(z)+f_e(z)\\&=\frac{1}{\lambda_{\text{photon}}}\exp\left(-\frac{z}{\lambda_{\text{photon}}}\right)+\int_0^\infty dz'\,\frac{1}{\lambda_e}\\&\quad\times\exp\left(-\frac{|z-z'|}{\lambda_e}\right)\frac{1}{\lambda_{\text{photon}}}\exp\left(-\frac{z}{\lambda_{\text{photon}}}\right).\end{aligned}\quad\text{(A1)}$$

The complete distribution function now reads $f(E,t,z)=f(E,t)f(z)$. Our calculus is simpler than the one done by Weik, de Meijere, and Haselbrink[10] because here we are interested mainly in obtaining the electron distribution function at each point in the solid, not in calculating the number of surface electrons.

Strictly speaking the present distribution function cannot be compared with Fann's experimental curves because there the pump laser of 2 eV excites electrons that are later extracted by the probe laser of 5.52 eV. The extraction is more efficient closer to the surface. Our model include only the effect of the pump laser.

We calculated the modification of the distribution function by introducing the spatial factor described above. For the pump laser wavelength used in Refs. 11 and 12, the photon mean-free path $f_{\mathrm{photon}}(z)$ (Ref. 23) is about 150 Å and the variation of the spatial factor $f(z)$ is rather small within the 300-Å gold film thickness. One should also introduce the electron thermal diffusion mean-free path but it was estimated to be small (about 20 Å) and should contribute for much longer times. Moreover, introducing the spatial factor in the Boltzmann transport equation for the experiment of Fann *et al.*[12] does not result in a significant change of the electron distribution in the metal.

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