BALLISTIC ELECTRON DISTRIBUTION
FOR HOT ELECTRON IN METALS

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Abstract. In many modern fields like fs-chemistry and electronics an understanding of the rate limiting process can be elucidated by studies of photoexcited electrons. For thin films and short times, the ballistic transport may strongly influence the excited electron distribution. We present here a simple model for the hot electron ballistic distribution that neglect the band structure effect.

Key words: thin films, femtoseconds, hot electrons, ballistic transport.

1. INTRODUCTION

The immense progress in the field of ultrashort pulsed lasers made it possible to study ultrafast dynamics of photoexcited hot electrons in metals by means of a variety of pump-probe techniques. The most important ones are femtosecond thermomodulation spectroscopy (FTS) [1–9], surface-plasmon-polariton resonance (SPPR) [10–12] and time-resolved two-photon photoemission spectroscopy (TR-2PPE) [13–23]. The recent extension of TR-2PPE to higher energies (ultraviolet photoemission spectroscopy-UPS mode) and high lateral resolution (photoemission electron emission spectroscopy-PEEM mode) [23] allow to monitor the chemical reaction on the time scale of the nuclear motion and to visualize lateral variations in hot electron dynamics on heterogeneous surfaces.

In FTS an ultrashort "pump" laser heats up the sample. A second "probe" pulse is time delayed with respect to the pump pulse. Measuring the change of the probe reflectivity/transmissivity as a function of the time delay between pump and probe pulse maps out the cooling dynamics of electrons in the femtosecond time scale. A variety of effects may contribute to the reflectivity/transmissivity signal, including smearing of the electronic occupancy near the Fermi level, Fermi level shifting, lattice expansion, ballistic transport, diffusive transport, electron-phonon collision and collision of the electron to the grain boundaries for polycrystalline samples. Ballistic transport designates the free motion of the electrons, without any

collision, that transports them away from the surface region. Diffusive transport means transport of electrons away from the surface due to the existence of a temperature gradient at the surface. In noble metals, differential reflectivity/transmissivity measurements can be used to monitor interband electronic transitions – from the d bands to conduction band energies near the Fermi level. For photon energies near this interband transition, the dominant contribution to the signal is Fermi smearing resulting from electron heating. This smearing is characterized by increasing electron occupancy above the Fermi energy and decreased occupancy below the Fermi energy.

Changes in electron occupancy produce changes in the interband absorption which are directly proportional to the change in the imaginary component $\delta\varepsilon_2$ of the dielectric constant ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) [1, 6]. The corresponding change in $\delta\varepsilon_1$ can be determined by Kramers-Kronig analysis [1]. The reflectivity (R) and the transmissivity (T) are related to the real and the imaginary part of the dielectric constant through the Fresnel formula [24] resulting in $\delta R/R$ and $\delta T/T$ that are proportional to variations in $\delta\varepsilon_1$, $\delta\varepsilon_2$ [1].

Transient reflection and transmission experiments have been performed on Au, Cu, Ag and various superconductors. These experiments put into evidence the generation of nonequilibrium (hot) electrons which 'cool' down to a new equilibrium distribution on a 2–3 ps time scale [1, 5, 6].

Experiments performed on polycrystalline and single crystalline Au films [5] showed that the time for the first wave of electrons to traverse the films is linear with the sample thickness if this one is less than or equal to 300 nm. This linear dependence is characteristic of the ballistic transport, when the motion of the excited electrons occurs without any interactions among the electrons or between the electrons and the lattice. For thicker films deviations from the linear dependence are observed [2, 5]. In these cases the fraction of the ballistic component decreases and the excess energy is carried by electrons interacting with other electrons or/and the lattice undergoing one or more scattering events. The pure diffusion is also included. This effect appears to be stronger in polycrystalline Au samples [6], indicating that the grain boundaries cause a slowing of the transport of the excited electrons. Experiments performed on gold films have shown also that the heat transport occurs at the Fermi velocity [2] and therefore is due to electrons.

Another important technique is SPPR, a powerful method of enhancing the electromagnetic field at surfaces. A SPP is a coupled surface mode of the electron gas and the electromagnetic field and may be regarded as a photon travelling along the metal-vacuum interface. Combining the SPP with the femtosecond pump-probe technique, it was proved [10–11], for Au and Ag thin films, that the excited electrons do not reach a thermal distribution on the time scale of the electron-

phonon (e-ph) energy relaxation. The measured change of the reflectivity shows a nonlinearity that is much smaller than the nonlinearity predicted by the classical two-temperatures model (TTM) [25]. Also the independence on laser fluence is in striking contradiction with the TTM. This model considers the metal composed of two subsystems, electrons and phonons. Each subsystem is supposed to be in a local equilibrium having an effective temperature defined through a distribution function, Fermi-Dirac for the electrons and Bose-Einstein for the nuclei. But in the sub-picosecond regime the electrons are far from equilibrium, the distribution function has a form different from the Fermi-Dirac one and no temperature can be defined.

In contrast to optical measurements of transmission and reflection that rely on dynamic changes in macroscopic optical constants, TR-2PPE provides a direct measurement of the temporal evolution of the nonequilibrium electron distribution. Photoemission experiments made on a gold film [13–15] put into evidence the departure of the hot electron distribution from the Fermi-Dirac one, corresponding to the thermal equilibrium. In a first experiment [13] a polycrystalline gold film was irradiated by a 1.84 eV laser pulse of 400 fs duration. The electron energy distribution was measured with a probe laser of 5.52 eV laser of duration of 700 fs. Since the work function of gold is 5.1 eV, the 5.52 eV probe photons are able to produce photoelectrons to be measured by single-photon photoemission. The experimental distribution can be fitted by a Fermi-Dirac function at an elevated temperature, calculated within the TTM model, except within 800 fs of the heating pulse, when a clear departure from this distribution is observed. As a result, an electron temperature cannot be defined in this phase of the process and hence the TTM, commonly used to analyze laser-heating experiments, fails on the subpicosecond time scale.

TR-2PPE [16–23] is also a high resolution spectroscopic tool for studying empty states below the vacuum level. Hot electron dynamics was studied in Cu [16–22], Ag [17, 18, 23], Au, W, Rh [17], Co, Fe, Ni [23]. In the TR-2PPE technique, the number of electrons at a given kinetic energy is monitored as function of the time delay between the pump and the probe pulses. Deconvoluting the measured signal from the laser pulse autocorrelation curve one obtains the lifetime of the intermediate state (the state where the electron arrives after the excitation by the pump laser). For the experimental lifetimes obtained for noble metals a clearly departure from the Fermi liquid theory is seen. Recent results [17, 23] have shown that these values, higher than the Fermi liquid ones, may represent the lifetime of secondary electrons resulting from Auger deexcitation of primary holes created in the sp band.

In this paper we will propose a simple model for the ballistic transport for thin metal surfaces and subpicosecond time scales where the ballistic transport was proved experimentally to be more important than the diffusive one [2, 5]. We

completely disregard the band structure of the metal like the presence of band gap and band dispersion. Inclusion of band structure effects requires a much higher level of sophistication. Such a calculation has been done for current distribution in a very thin metallic layer (less than 100 A°) for electron injected by a ballistic electron emission microscope (BEEM) [26]. Here we are interested by higher film thickness up to 500 A° where the developed theory is hard to extend. Also, in BEEM the electrons are injected in the metal by a tip and have a well defined and greater momentum than have the photoexcited electrons due to the negligible photon momentum [27].

2. BALLISTIC ELECTRON DISTRIBUTION

The electrons excited by the laser pulse are not uniformly distributed in the bulk. Because of the metal absorption, the laser light penetrates into the metal only on a short distance called the skin depth. Thus even the excitation process produces an anisotropic spatial distribution of the excited electrons. Ballistic and diffusive transport will further change this initial distribution. Because the laser beam diameter is usually much larger than the optical skin depth, the radial diffusion is also negligible within the time scale of interest.

In the following, we shall present a simple model for the hot electron distribution perpendicular to the surface (along the z axis) determined by the ballistic transport. We suppose that hot electrons are excited by a very short laser pulse (pulse of δ type). We consider that the excited electrons behave as a free gas, moving without collision and with equal probability in all directions. In doing this, we neglect completely the band dispersion and the lack of available states for some electron wavevector values. Also we neglect electron-electron or electron-phonon collisions. For some times and photon energies this might be a good approximation because of longer specific time for electron-electron and electron-phonon relaxation. For example, for excited gold electrons of 1.4 eV above Fermi level the lifetime is of 30 fs [17]. During this time the electron can be supposed not to undergo any collision.

Because of the work needed to extract them, the electrons are confined in the metal and undergo total elastic reflection at the two boundaries of the thin metal film. To excite an electron at a given position, the photon position is well defined but, by the uncertainty relation $\Delta \vec{r} \Delta \vec{k} \geq \dfrac{1}{2}$, its momentum is not well defined. So, after the excitation by the photon, the electron will have a momentum arbitrarily orientated and accordingly will move with equal probability in all directions. For a one-dimensional model this reduces to the motion in both directions of the z axis, the axis perpendicular to the metal surface. As usual laser sources have the width in

the micrometer range, the lateral motion (in the x and y directions) in the femtosecond time scale can be neglected.

The initial distribution at $t = 0$, just after laser excitation, is

$$g(z,t) = \exp\left(-\frac{z}{\lambda_{ph}}\right),$$ (1)

where λ_{ph} is the mean free path of the photon in the metal.

After some time the electron generated by the photon at z has left and the electrons from two other positions called z^+ and z^- (+, – index comes from the motion in the two directions of the z axis, having the origin at the surface and being positive in the metal; $z^+ > z$ and $z^- < z$) are now at the z position, contributing equally to the electron distribution. We consider that the electrons that move in the x and y directions are completely lost because the crystal film is considered infinitely extended in those directions. As the excited electron moves in the metal with a velocity greater than the Fermi velocity, even the lowest energy electron may experience many reflections in the z direction in its lifetime (the time between two collisions when its motion is free). Thus, the expressions for z^- and z^+ may be deduced counting the number of reflections at the two surfaces. For this reason we deduced general formulae that include a great number of reflections. Depending on the reflection number n_r being even or odd (which means that after the final reflection the electron arrives in z from the negative (–) or the positive (+) directions of the z axis), z^+ and z^- read as:

$$z^- = z - v_e t + n_r z_{max}, \ n_r \ \text{even}; \ z^- = v_e t - z - (n_r - 1)z_{max}, \ n_r \ \text{odd}$$ (2)

$$z^+ = z + v_e t - n_r z_{max}, \quad n_r \ \text{even}; \ z^+ = -(z + v_e t) + (n_r + 1)z_{max}, \ n_r \ \text{odd}$$ (3)

where z_{max} is the thickness of the metal film, v_e is the electron velocity, corresponding to a specific energy level E above E_f, $v_e = \sqrt{2E/m}$ and t is the traveling time between the excitation and the arrival at z. At time t the distribution function of the electrons will be:

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{z^-}{\lambda_{ph}}\right) + \exp\left(-\frac{z^+}{\lambda_{ph}}\right)\right)$$ (4)

This function has an oscillatory behavior in time that reflects the oscillatory motion of the electron in the metal when other collisions are neglected. The eqs. (2) and (3) are general, but because of the even/odd difference, one has to consider differently the cases when $v_e t$, the distance traveled by the electron at time t, is $v_e t \in (2k z_{max}, (2k + 1)z_{max})$ or $v_e t \in ((2k + 1)z_{max}, (2k + 2)z_{max})$. In the first case n_r can have the values $2k$ or $2k + 1$ while in the second case it can be $2k + 1$ or $2k + 2$.

Also, the conditions that z^+ and z^- must be positive and less than z_{max} result in specific expressions for the distribution function.

For $v_e t \in (2k z_{max}, (2k + 1/2) z_{max})$:

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{v_e t - z - 2k z_{max}}{\lambda_{ph}} \right) + \exp\left(-\frac{v_e t + z - 2k z_{max}}{\lambda_{ph}} \right) \right),$$

$$\text{if} \quad z \leq \left(vt - 2k z_{max} \right) \tag{5}$$

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{z - v_e t - 2k z_{max}}{\lambda_{ph}} \right) + \exp\left(-\frac{v_e t + z - 2k z_{max}}{\lambda_{ph}} \right) \right),$$

$$\text{if} \quad \left(v_e t - 2k z_{max} \right) \leq z \leq \left((2k + 1) z_{max} - v_e t \right) \tag{6}$$

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{z - v_e t - 2k z_{max}}{\lambda_{ph}} \right) + \exp\left(-\frac{(2k + 2) z_{max} - v_e t - z}{\lambda_{ph}} \right) \right),$$

$$\text{if} \quad \left((2k + 1) z_{max} - v_e t \right) \leq z \tag{7}$$

For $v_e t \in ((2k + 1/2) z_{max}, (2k + 1) z_{max})$:

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{v_e t - z - 2k z_{max}}{\lambda_{ph}} \right) + \exp\left(-\frac{v_e t + z - 2k z_{max}}{\lambda_{ph}} \right) \right),$$

$$\text{if} \quad z \leq \left((2k + 1) z_{max} - v_e t \right) \tag{8}$$

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{v_e t - z - 2k z_{max}}{\lambda_{ph}} \right) + \exp\left(-\frac{(2k + 2) z_{max} - v_e t - z}{\lambda_{ph}} \right) \right),$$

$$\text{if} \quad \left((2k + 1) z_{max} - v_e t \right) \leq z \leq \left(v_e t - 2k z_{max} \right) \tag{9}$$

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{z - v_e t - 2k z_{max}}{\lambda_{ph}} \right) + \exp\left(-\frac{(2k + 2) z_{max} - v_e t - z}{\lambda_{ph}} \right) \right),$$

$$\text{if} \quad \left(2k z_{max} - v_e t \right) \leq z. \tag{10}$$

For $v_e t \in ((2k + 1) z_{max}, (2k + 3/2) z_{max})$:

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{z - v_e t + (2k + 2) z_{max}}{\lambda_{ph}} \right) + \exp\left(-\frac{(2k + 2) z_{max} - z - v_e t}{\lambda_{ph}} \right) \right),$$

$$\text{if} \quad z \leq \left(v_e t - (2k + 1) z_{max} \right) \tag{11}$$

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{v_e t - z - 2k z_{\max}}{\lambda_{ph}} \right) + \exp\left(-\frac{(2k+2)z_{\max} - v_e t - z}{\lambda_{ph}} \right) \right), \quad (12)$$

$$\text{if } \left(v_e t - (2k+1)z_{\max} \right) \le z \le \left((2k+2)z_{\max} - v_e t \right)$$

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{z - v_e t - 2k z_{\max}}{\lambda_{ph}} \right) + \exp\left(-\frac{v_e t + z - (2k+2)z_{\max}}{\lambda_{ph}} \right) \right), \quad (13)$$

$$\text{if } \left((2k+2)z_{\max} - v_e t \right) \le z.$$

Finally, for $v_e t \in ((2k+3/2)z_{\max}, (2k+2)z_{\max})$:

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{z - v_e t + (2k+2)z_{\max}}{\lambda_{ph}} \right) + \exp\left(-\frac{(2k+2)z_{\max} - z - v_e t}{\lambda_{ph}} \right) \right), \quad (14)$$

$$\text{if } z \le \left((2k+2)z_{\max} - v_e t \right)$$

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{z - v_e t + (2k+2)z_{\max}}{\lambda_{ph}} \right) + \exp\left(-\frac{z + v_e t - (2k+2)z_{\max}}{\lambda_{ph}} \right) \right), \quad (15)$$

$$\text{if } \left((2k+2)z_{\max} - v_e t \right) \le z \le \left(vt - (2k+1)z_{\max} \right)$$

$$g(z,t) = \frac{1}{2}\left(\exp\left(-\frac{v_e t - z - 2k z_{\max}}{\lambda_{ph}} \right) + \exp\left(-\frac{v_e t + z - (2k+2)z_{\max}}{\lambda_{ph}} \right) \right), \quad (16)$$

$$\text{if } z \ge \left(vt - (2k+1)z_{\max} \right).$$

Calculating the ballistic distribution function one obtains also an oscillatory distribution in time as can be seen in Fig. 1.

3. APPLICATION OF THE BALLISTIC MODEL

The ballistic electron distribution in gold is represented in Fig. 1. The figure illustrates the result obtained using eqs. (5–16), for different time delays after the excitation by the δ laser pulse. The calculations were performed for an electron of energy $E - E_F = 1.4$ eV in a gold film of 500 A° thickness. The energy of the Fermi level is $E_F = 5.53$ eV and $\lambda_{ph} = 150$ A°. For this level the velocity is $v_e = 15.6$ A°/fs. The result is strongly modified by the value of the film thickness. The above mentioned oscillations are very clear. So, in the absence of collisions or other relaxation processes, this model predicts an oscillating electron population at

the surface of a thin solid film. Also, one can see that after 30 fs nearly all carriers are swept out of the probing depth. This obviously contradicts the experimental findings and the reason of that contradiction is the neglection of the secondary electrons that are also measured. Our result compares well with the data published by [18] for a copper film but not with the [17] ones.
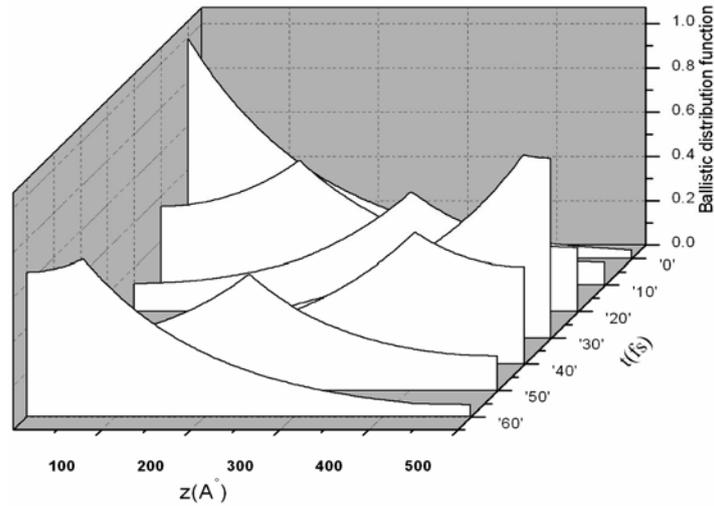

Fig. 1 – Ballistic distribution function at different times after the application of the δ laser pulse calculated for a gold film of 500 A° and an electron energy $E = E_f + 1.4$ eV.

5. CONCLUSIONS

In this paper we calculated the distribution of the hot electrons produced only by the ballistic transport that is important for short times and thin films. It is strongly influenced by the film thickness and becomes less important with the increasing thickness. Ballistic transport, calculated neglecting the band structure, predicts only an oscillating electron population. It gives a hint only about the spatial organization of the electrons. A complete hot electron distribution function must take into account other parameters characterizing the electrons like energy and $\overrightarrow{k_{//}}$ (the wave vector of the motion parallel to the surface). For such a complete description of electrons one has to consider, even for short times (less than 1 ps), the band structure, multiphoton excitation, inelastic electron-electron collisions, inelastic collisions with defects impurities or grain boundaries for polycrystalline samples and contribution of secondary electrons. For times greater than 1 ps or for energies close to Fermi level, electron-phonon interaction should also be considered. Despite many attempts to

obtain such a complete distribution function [28–31] there is no simple working model that includes all these interactions.

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