Nonlinear absorption of ultrashort laser pulses in thin metal films

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Self-consistent simulations of the ultrafast electron dynamics in thin metal films are performed. A regime of nonlinear oscillations is observed, which corresponds to ballistic electrons bouncing back and forth against the film surfaces. When an oscillatory laser field is applied to the film, the field energy is partially absorbed by the electron gas. Maximum absorption occurs when the period of the external field matches the period of the nonlinear oscillations, which, for sodium films, lies in the infrared range. Possible experimental implementations are discussed. © 2022 Optical Society of America

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The recent progress in the study of metallic nanostructures is mainly due to the development of ultrafast spectroscopy techniques, which allow the experimentalist to probe the electron dynamics on a femtosecond (and, more recently, attosecond) time scale. Typical “pump-probe” experiments involve perturbing the system via a first stronger pulse, followed by a second weaker pulse that acts as a diagnostic tool. By modulating the relative amplitude of the signals, as well as the delay between the pump and the probe, it is possible to assess with great precision the dynamical relaxation of the electron gas.\textsuperscript{1-4}

In the present work, we focus on the ultrafast electron dynamics in thin metallic films. Several experiments have shown\textsuperscript{1,2} that electron transport in thin metal films occurs on a femtosecond time scale and involves ballistic electrons traveling at the Fermi velocity of the metal $v_F$. These findings were corroborated by accurate numerical simulations,\textsuperscript{5} which highlighted a regime of slow nonlinear oscillations corresponding to ballistic electrons bouncing back and forth on the film surfaces. These oscillations were recently measured in transient reflection experiments on thin gold films.\textsuperscript{6} The existence of this regime prompted us to analyze the possibility of boosting energy absorption in the film by optically exciting the electron gas at the frequency of the nonlinear oscillations.

In the rest of this Letter, time is normalized in units of the inverse plasmon frequency $\omega_{pe}^{-1}$, velocity in units of the Fermi speed $v_F$, and length in units of $L_F = v_F/\omega_{pe}$. For alkali
metals we have $L_F = 0.59 \left( \frac{r_s}{a_0} \right)^{1/2} \text{Å}$, $\omega_{pe}^{-1} = 1.33 \times 10^{-2} \left( \frac{r_s}{a_0} \right)^{3/2} \text{fs}$, $E_F = 50.11 \left( \frac{r_s}{a_0} \right)^{-2} \text{eV}$ and $T_F = 5.82 \times 10^5 \left( \frac{r_s}{a_0} \right)^{-2} \text{K}$, where $r_s$ is the Wigner-Seitz radius. We concentrate primarily on sodium films, for which $r_s = 4a_0$ ($a_0 = 0.529 \text{Å}$ is the Bohr radius).

We consider a system of electrons interacting via a Coulomb potential and confined within a slab of thickness $L$. The ion background is represented by a fixed density with soft edges, $n_i(x) = \overline{n}_i \left[1 + \exp \left(\left(\frac{|x| - L/2}{\sigma_i}\right)\right)\right]^{-1}$, where $\overline{n}_i = 3/(4\pi r_s^3)$ is the ion density of the bulk metal and $\sigma_i \ll L$ a diffuseness parameter. In this jellium model, the self-consistent electrostatic potential depends only on the coordinate normal to the surface (here noted $x$). Thus, the motion of an electron parallel to the surface of the film is completely decoupled from the motion normal to the surface and a one-dimensional (1D) model can be adopted.

The electrons are initially prepared in a Fermi-Dirac equilibrium at finite (but small) temperature. They are subsequently excited by imposing a constant velocity shift $\Delta v_x = 0.08v_F$ to the initial distribution. This scenario is appropriate when no linear momentum is transferred parallel to the plane of the surface (i.e., $q_\parallel = 0$) and is relevant to the excitation of the film with optical pulses. For $q_\parallel = 0$, only longitudinal modes (volume plasmon with $\omega = \omega_{pe}$) can be excited.

After the excitation is applied, the electron distribution function $f_e(x, v_x, t)$ starts evolving in time according to the semiclassical Vlasov equation

$$\frac{\partial f_e}{\partial t} + v_x \frac{\partial f_e}{\partial x} + \frac{e}{m_e} \frac{\partial \phi}{\partial x} \frac{\partial f_e}{\partial v_x} = 0,$$

where $m_e$ is the electron mass and $e$ denotes the absolute electron charge. The electrostatic potential is obtained self-consistently, at each instant, from Poisson’s equation

$$\frac{d^2 \phi}{dx^2} = \frac{e}{\varepsilon_0} \left[ n_e(x, t) - n_i(x) \right],$$

with $n_e = \int f_e dv_x$. As a reference case, we studied a sodium film with initial temperature $T_e = 0.008 T_F \simeq 300 \text{ K}$, diffuseness parameter $\sigma_i = 0.3 L_F$, and thickness $L = 50 L_F \simeq 59 \text{ Å}$. The time evolution of the thermal $E_{\text{th}}$ and center-of-mass $E_{\text{cm}}$ energies was analyzed (Fig. 1). During an initial rapidly-oscillating phase, $E_{\text{cm}}$ is almost entirely converted into thermal energy (Landau damping). After saturation, a slowly oscillating regime appears, with period equal to $50\omega_{pe}^{-1} \approx 5.3 \text{ fs}$. This period is close to the time of flight of electrons traveling at the Fermi velocity and bouncing back and forth on the film surfaces (further details are provided in our previous work).

The above nonlinear oscillations appear for all reasonable values of the physical parameters. Preliminary studies suggest that electron-electron collisions do not destroy this regime either, at least for relatively low excitation energies and short times. It is tempting, therefore, to investigate whether some kind of resonant absorption can be achieved when the system is externally excited at the same frequency of the nonlinear oscillations.
A similar scenario was investigated by Taguchi et al.\textsuperscript{9} (building on an idea due to Brunel\textsuperscript{10}) in order to simulate the interaction of an argon cluster with a strong laser field ($\approx 10^{15} - 10^{16}$ W/cm$^2$). In their simulations, the neutral cluster is quickly ionized by the laser field, which heats the electrons up to 10 eV. At these temperatures, the electrons behave classically and are initially described by a Maxwell-Boltzmann distribution. In that case, the electron transit velocity through the cluster is not clearly defined and depends on the intensity of the laser (indeed, in the classical case, there is no “natural” oscillatory regime like the one seen in Fig. 1). For a degenerate electron gas, the transit velocity is unambiguously given by the Fermi velocity of the metal and thus we expect an even neater resonance to occur.

Our conjecture can be tested in the following way. At time $\omega_{pe}t = 1000$ ($\approx 106$ fs for a sodium film), when the oscillatory regime is well established, we switch on a small external electric field, uniform in space and sinusoidal in time with period $T$: $E_{\text{ext}} = E_0 \sin(2\pi t/T)$, where $E_0$ is the (constant) field amplitude. The simulation is then continued with the external field on for another $4000\omega_{pe}^{-1} \approx 425$ fs. This situation corresponds to a laser pulse that is switched on very quickly and lasts for a duration longer than 425 fs.

For an electron transit velocity exactly equal to $v_F$, we would expect resonance for a laser period $T = 2L/v_F$ (= 100 in units of $\omega_{pe}^{-1}$). The factor 2 comes from the fact that the electric field must keep the same sign during a transit from one surface to the other, and reverse sign during the “return” transit. We note that the resonance is expected to fall in the infrared (IR) domain. Indeed, for a laser period $T = 100\omega_{pe}^{-1} = 10.6$ fs, the corresponding wavelength is $\lambda = 3.2 \mu$m.

The amplitude $E_0$ of the laser field can be estimated by noting that the total energy of the laser pulse is $U = (\frac{1}{2}\varepsilon_0 E_0^2) c \tau S$, where $c$ is the speed of light in vacuum, $\tau$ is the pulse duration, and $S$ is the surface of the laser spot. Typical values for IR lasers\textsuperscript{11} are $S = 0.01\text{mm}^2$ and $U = 1\mu$J, and by taking a pulse duration $\tau = 400$ fs (similar to the duration used in the simulations), we obtain an electric field $E_0 = 4.3 \times 10^8$ V/m. In the numerical simulations, the electric field is normalized to $\overline{E} = m_e v_F \omega_{pe}/e = 1.70 \times 10^{12}(r_s/a_0)^{-5/2}$ V/m, yielding $\overline{E} = 5.31 \times 10^{10}$ V/m for sodium films. Therefore, by taking a field amplitude $E_0 = 0.01\overline{E}$, we get a dimensional value that is realistic for an IR laser pulse. This external field amplitude is an order of magnitude smaller than the self-consistent electric field present at the film surfaces.

The results for the reference case ($L = 50L_F$) are shown in Fig. 2, where the electron thermal energy is plotted against time. We observe that the absorption is clearly enhanced for $\omega_{pe}T = 106$ and $\omega_{pe}T = 150$, whereas for larger or smaller values virtually no energy is absorbed. We also verified that the resonance does not depend on the phase of the external oscillating field.

The resonant period is close, but not exactly equal, to the predicted value $\omega_{pe}T = 100$
and the resonance displays a certain broadness. The latter can be explained by noting that a certain dispersion exists in the electron velocities around $v_F$, which generates a dispersion in the resonant period. If the period is $T = 2L/v$, then the resonance broadness should be $|\delta T| = (2L/v^2) \delta v$. In order to estimate the broadness, we plot, in Fig. 3, the variation of the velocity distribution at the center of the film: $\delta f(v_x) = |f_e(x = 0, v_x, \omega_{pe}t = 1000) - f_e(x = 0, v_x, t = 0)|$. The distribution is indeed modified around the Fermi velocity, as expected (see also Fig. 3 in Ref. 5). Note that $\delta f$ is not symmetric around $v_x = 0$, because the initial excitation was not symmetric either. On closer inspection, the peaks occur at a velocity slightly smaller (in absolute value) than $v_F$, roughly $|v_x| \approx 0.9v_F$. Their broadness can be estimated by assuming that a deviation of 2% (relative to the maximum $f_e = 1$) is significant. Then, $v$ varies in the interval $0.7v_F < v < 1.1v_F$ (and equivalently for negative velocities), so that $\delta v \approx 0.4v_F$. This yields a broadness $\omega_{pe}\delta T \approx 50$, with $90 < \omega_{pe}T < 140$. This estimate is compatible with the simulation results of Fig. 2, where the resonance has clearly disappeared at $\omega_{pe}T = 73$ and 230.

In order to test the robustness of this nonlinear resonance effect, we repeated the same numerical experiment with a thicker film, $L = 100L_F$ (the initial evolution for this case is shown in our previous work5). The resonant period is expected to scale linearly with the film thickness, and indeed we observed enhanced absorption for $\omega_{pe}T = 212$ and 250 (Fig. 4).

In contrast, we observed that the resonance virtually disappears for thicker films, $L = 200L_F$ or larger. We interpret this result by noticing that the existence of the resonance depends on nonequilibrium electrons traveling coherently through the film. The phase space portraits of the electron distribution function (see Fig. 3 in our previous work5) show a complex structure of traveling vortices. It is probable that, for thicknesses larger than a certain threshold, the necessary coherence is lost, so that the resonance cannot manifest itself.

The resonance also disappears for very small amplitudes of the external field. For the reference case $L = 50L_F$, the resonance is still observed for $E_0/E = 0.005$, but no longer for $E_0/E = 0.001$. This may be related to the fact that the absorbed energy at resonance $U_{abs}$ scales quadratically with the field amplitude: $U_{abs} \propto e^2 E_0^2 T^2/m_e$ (this formula becomes exact for the harmonic oscillator). For small fields, the resonance is thus very weak and other factors (e.g., Landau damping) can easily erase it completely.

In summary, we have shown the existence of a nonlinear absorption regime in the electron dynamics of thin metal films. This effect is generic and should not, in principle, depend on the nature of the metal. The resonance occurs in the IR domain and should be accessible via experiments employing ultrafast laser sources with standard specifications. This absorption mechanism could be used as an optical diagnostic technique to determine, for instance, the thickness of the film, or to obtain information on the electronic distribution.
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FIGURE CAPTIONS

**Fig. 1:** Initial time evolution of the thermal and center-of-mass energies for a film thickness \( L = 50L_F \).

**Fig. 2:** Time evolution of the thermal energy in the presence of an external electric field. The external field is switched on at \( \omega_{pe}t = 1000 \). (a) \( \omega_{pe}T = 27 \); (b) \( \omega_{pe}T = 73 \); (c) \( \omega_{pe}T = 106 \); (d) \( \omega_{pe}T = 150 \); (e) \( \omega_{pe}T = 230 \). The results are for a film of thickness \( L = 50L_F \).

**Fig. 3:** Variation of the electron velocity distribution with respect to the initial Fermi-Dirac equilibrium, at the center of the film, at time \( \omega_{pe}t = 1000 \).

**Fig. 4:** Same as Fig. 2 for a film of thickness \( L = 100L_F \). (a) \( \omega_{pe}T = 90 \); (b) \( \omega_{pe}T = 150 \); (c) \( \omega_{pe}T = 212 \); (d) \( \omega_{pe}T = 250 \); (e) \( \omega_{pe}T = 290 \); (f) \( \omega_{pe}T = 350 \).