Two-temperature relaxation and melting after absorption of femtosecond laser pulse

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Abstract

The theory and experiments concerned with the electron-ion thermal relaxation and melting of overheated crystal lattice constitute the subject of this paper. The physical model includes two-temperature equation of state, many-body interatomic potential, the electron-ion energy exchange, electron thermal conductivity, and optical properties of solid, liquid, and two phase solid-liquid mixture. Two-temperature hydrodynamics and molecular dynamics codes are used. An experimental setup with pump-probe technique is used to follow evolution of an irradiated target with a short time step 100 fs between the probe femtosecond laser pulses. Accuracy of measurements of reflection coefficient and phase of reflected probe light are 1% and ~ 1 nm, respectively. It is found that, firstly, the electron-electron collisions make a minor contribution to a light absorption in solid Al at moderate intensities; secondly, the phase shift of a reflected probe results from heating of ion subsystem and kinetics of melting of Al crystal during 0 < t < 4 ps, where t is time delay between the pump and probe pulses measured from the maximum of the pump; thirdly the optical response of Au to a pump shows a marked contrast to that of Al on account of excitation of d-electrons.

Key words: femtosecond laser ablation, pump-probe, optics of hot Al and Au

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1. Supersonic heating and melting

Figures 12 show diagrams of processes in pump femtosecond laser pulse (fsLP) action on metal. The three time slices "ei", m1,m2, and c1c2 in Fig. 1 correspond to the following non-equilibrium processes: (e-i) the electron-ion thermal relaxation, (m) the melting of an overheated crystal lattice, and (c) the cavitation decay of a metastable state. Duration of fsLP \( \tau_{fsLP} \approx 40 - 100 \) fs is shorter than characteristic times of these three processes. They have very various time scales from picoseconds to nanoseconds. The electron overheating (\( T_e \gg T_i \)) starts from ei when a fsLP arrives \( \tau_{fsLP} \) and disappears at ei2 when temperatures \( T_e, T_i \) equilibrate (\( \tau_{eq} = \tau_{eq} = 3 - 6 \) ps for Al at our intensities). The time is reckoned from the maximum of pump fsLP in Fig. 1. Since arriving of the pump to a target the conductivity electrons become much hotter than the ions.

Two-temperature (2T) matter with hot electrons transits to a peculiar state with thermodynamic and optical characteristics different from one-temperature (1T) case. In 2T there are appearance of excesses of electron energy and pressure above equilibrium 1T ones. Also there are changes in elastic moduli and band structure. In semiconductor lattice the binding forces become weaker with increase of \( T_e \), while in metals situation is opposite. Large changes in optics of Au at high \( T_e \) result from excitation of d-electrons. On account of the ion heat capacity \( C_i \) (thermal "inertia" of a lattice) the beginning of melting \( t_{m1} \approx C_i/T_m/\alpha T_e \) is delayed relative to the instant "ei1", where \( T_m \) and \( \alpha \) are the melting temperature and e-i energy exchange rate.

It has been known that:

(i) for metals and semiconductors the fluences \( F \) near the ablation threshold \( F_{abl} \) are significantly higher than the melting threshold \( F_m \). In this sense the Lennard-Jones (LJ) case is an exception [10]. LJ \( E_m/E_{coh} \) vacancy migration to cohesion energy ratio and \( T_3/T_e \) triple to critical temperature ratio are large in comparison with metals and semiconductors. While \( E_{abl}/E_{coh} \) is approximately the same for all three groups. Therefore it is not surprising that in the LJ case \( F_{abl} \approx F_{melt} \). In metals for \( F > F_{abl} \) the molten layer is approximately as thick as heated \( d_f \). When stretching stress overcome material strength a cavitation (fragmentation of liquid) begins inside molten metal at the instant \( c_1 \) shown in Fig. 1. In LJ near threshold \( F \approx F_{abl} \) spallation (fragmentation of solid) starts in

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2. 2T hydrodynamics and light reflection

In Lagrangian variables the 2T hydrodynamics (2T-HD) equations \([\mathbf{3,4,7,12,13,14,16,17}]\) are
\[
\partial x(x',t)/\partial t = u, \quad \rho \partial x(x',t) = \rho^0 \partial x' \tag{1}
\]
for kinematics and mass conservation,
\[
\rho^0 \partial u/\partial t = -\partial p/\partial x',
\]
for a force balance, and two thermal equations
\[
\rho^0 \partial [E_c(\rho,T_e)/\rho]/\partial t = \frac{\partial}{\partial x'} \left[ \rho k(\rho,T_e,T_i) \partial T_e/\partial x' \right] - \frac{\partial}{\partial x'} p \alpha (T_e-T_i) + \frac{\rho^0}{\rho} Q, \tag{2}
\]
describing instant local electron and ion heat balances, where \(x\) is an Eulerian coordinate defined in Fig. \([\mathbf{2}]\). \(x(x',t)\) is the trajectory of material particle with Lagrangian coordinate \(x' = x(t = -5\tau_L)\) which is equal to \(x\) before the action of a pump fsLP. In 2T-HD simulation the pump intensity is \(I(t) = 0, t < -3\tau_L\), and \(I(t) = [F/(\tau_L \sqrt{\pi})] \exp(-t^2/\tau_L^2), t > -3\tau_L; \rho^0 = \rho(x,t = -3\tau_L)\) is the initial material density: 2.71 g/cm\(^3\) (Al) and 19.3 (Au), \(\rho, \rho\) are pressure and density, \(\kappa\) is a coefficient of a thermal heat conduction. \(Q(x,t) = [I(t)/\delta] \exp(-x/\delta)\), where \(\delta\) is the thickness of the skin-layer shown in Fig. \([\mathbf{2}]\) as "skin". Unknowns \(\rho, T_e, T_i, u\) are functions of the Lagrangian variables \(x', t\). When knowing the trajectories \(x(x',t)\), the variables \(\rho, T_e, T_i, u\) can be presented as the functions of the Eulerian coordinates \(x, t\): \(E_c, E_i\) are the internal electron and ion energies. \(Q\) is the absorbed power, \(\alpha(T_e - T_i)\) is the e-i energy exchange term.

From the profiles \(\rho, f, T_e, T_i, u\) as functions of \(x\), obtained from the Eqs. (1-3), one can find the corresponding profiles of the dielectric permittivity \(\epsilon(\rho, f, T_e, T_i) = \epsilon_i + i\epsilon_r\) and the complex index of refraction \(N = n + ik\), \(\epsilon = N^2\), where \(f\) is a volume fraction of liquid phase discussed below for case of solid-melt mixture. Next, for the \(x\)-profile \(\epsilon(x, t_{fsLP})\) at fixed time \(t_{fsLP}\) (velocity of light is taken to be infinite), Helmholtz equation
\[
\partial^2 F/\partial x^2 + sk^2 F = 0 \quad k = \omega/c \tag{4}
\]
is solved for amplitude \(F\) of the probe fsLP perpendicular to a target. Equation \([\mathbf{4}]\) describes a reflection of the probe light from target. Its solution gives the amplitude and phase of the reflected wave and correspondingly the time evolution \(R(t), \psi(t)\) of the reflectivity \(R\) and phase \(\psi\). They are compared with the experimental dependencies in Figs.\([\mathbf{3,13}]\). By contrast, the pump absorption is taken from the experiment \([\mathbf{5}]\). Equation \([\mathbf{4}]\) is evaluated by the \(2 \times 2\) transfer matrices method \([\mathbf{19}]\). In our experiments the chromium-forsterite laser with the pump \(\lambda_{pump} = 1240\) nm and probe \(\lambda_{prob} = 620\) nm (first and second harmonics) is used \([\mathbf{5,17}]\). A fsLP duration is 100 fs. Values \(R, \psi\) have been measured by microinterferometric technique described in \([\mathbf{3,7,17,20}]\).

3. 2T thermodynamics, collisions, and thermal transport

The values \(p_i, E_i(\rho, T_i)\) and \(p_e, E_e(\rho, T_e)\) in (1-3) are taken as in \([\mathbf{5}]\) from the wide range equation of state \([\mathbf{21}]\) and from Fermi model for the conduction electrons, \(p = p_i + p_e\) is the total pressure. The coupling factor \(\alpha\) and the heat capacity \(C_e\) are taken from \([\mathbf{6}]\). According to the Drude formula the electron heat conductivity \(\kappa\) in (2) is
\[
\kappa = (1/3)\nu^2 C_e/\nu, \quad \nu = (\nu_{deg}^2 + \nu_{pl}^2)^{-1/2}, \tag{5}
\]
\[ v = \sqrt{\nu_F^2 + 3k_BT_e/m_e}, \quad \nu_F = \frac{\sqrt{2E_F/m_e}}{E_F} = \frac{k_BT_F}{E_F} \text{ is Fermi energy.} \]

At \( T_e < T_F \) when electron degeneracy is significant the collision frequency is \( v \approx \nu_{\text{deg}} \) ("deg" stands for degenerate),

\[ \nu_{\text{deg}} = (\nu_{ei} + \nu_{ee})(\rho/\rho^*)^{-1.3}. \]

The Coulomb collisions \( \nu_{\text{pl}} \) in (5) is taken as \( \nu_{\text{pl}} = (E_F/h)(T_e/T_F)^{-3/2}((\nu^*)^2/\nu^2)^{3/2}. \) They dominate at very high \( T_e > T_F \) and limit \( \nu \) at \( T \sim T_F \) by an atomic frequency \( \nu_{at} \sim 10^{16} \text{s}^{-1} \) (saturation of the \( \nu \) increases with increasing \( T_e \)).

The electron-electron collisions \( \nu_{ee} \) in \( \nu_{\text{deg}} \) (5) is calculated separately for solid and liquid Al

\[ \nu_{ee}^{\text{sol}} = 4.2 \cdot 10^{14}(T_e/T_F)_3 \text{[s}^{-1}], \]
\[ \nu_{ee}^{\text{liq}} = 1.1 \cdot 10^{14}T_e/(130 + 0.0367T_e - 66700/T_e) \text{[s}^{-1}], \]

where \( T_3 = T_m(p = 0) = 933 \text{ K}, \) \( T_i \) in K. The coefficients in (5) approximate the quantum-mechanical MD heat conduction of the molten 1T Al [23]. The thermal conductivity is calculated with Kubo-Greenwood formula up to \( T = 10 \text{ K} \) [23]. Values for \( \kappa \) from [66] and for electric conductivity \( \sigma = n_e\epsilon^2/(m_e\nu_{ee}) \) with [3] describe well 1T reference data for solid Al between the Debye and triple point \( T_3 \) temperatures.

\[ \nu = \sqrt{\nu_F^2 + 3k_BT_e/m_e}, \quad \nu_F = \sqrt{2E_F/m_e}, \quad E_F = k_BT_F \text{ is Fermi energy.} \]

At \( T_e < T_F \) when electron degeneracy is significant the collision frequency is \( v \approx \nu_{\text{deg}} \) ("deg" stands for degenerate),

\[ \nu_{\text{deg}} = (\nu_{ei} + \nu_{ee})(\rho/\rho^*)^{-1.3}. \]

The factor \( (\rho/\rho^*)^{-1.3} \) in (6) approximates the quantum-mechanical molecular dynamic (MD) data [23] showing the drop of the electrical conductivity of Al with the density decrease in the temperature range under consideration. The electron-electron collision frequency is

\[ \nu_{ee} = b(E_F/h)(T_e/T_F)\nu. \]

\[ \nu_{pl} = (E_F/h)(T_e/T_F)^{-3/2}((\nu^*)^2/\nu^2)^{3/2}. \]

The Coulomb collisions \( \nu_{ei} \) in (5) is calculated separately for solid and liquid Al

\[ \nu_{ei}^{\text{sol}} = 4.2 \cdot 10^{14}(T_e/T_F)_3 \text{[s}^{-1}], \]
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4. Optical properties: collisions and interband excitations

The value \( \epsilon \) necessary for (4) is a sum of the Drude and the interband terms [4, 17, 24, 25]

\[ \epsilon = 1 - \frac{\omega_{\text{pl}}^2}{\omega^2 + \nu^2} \left( 1 - i \frac{\nu}{\omega} \right) + \Delta_{\text{bb}}, \]

where \( \omega_{\text{pl}}^2 = 4\pi n_e\epsilon^2/m_{\text{eff}}. \)

In Al \( m_{\text{eff}} = (1.2 - 1.7)m_e. \) In an Al crystal \( \Delta_{\text{bb}} \) results mainly from the transitions between parallel zones [18]. This term dominates at room temperatures. Its contribution increases the absorption more than by order of magnitude in comparison with pure Drude absorption. In a molten Al \( \Delta_{\text{bb}} \) disappears [25].

Electron density of states (DOS) in Al is stable against melting and against \( T_e \) and against \( T_e \) in [26]. Therefore the iron charge \( Z = n_i/n_i \) and the electron effective mass \( m_{\text{eff}} \) defining \( \omega_{\text{pl}} \) weakly depend on melting and overheating of electrons. A phenomenological dependence of \( \Delta_{\text{bb}} \) on a total frequency \( \nu \) [24] has been proposed [4, 18]. At large \( \nu > \omega \) the term \( \Delta_{\text{bb}} \) becomes small as compared to the Drude term as it is in liquid.

5. Optics of mixtures

MD simulations show that in Al within the early (~ 0.1 - few ps) stage the solid-liquid mixture fragmentation space scale ~ 1 nm is small in comparison with \( \delta \). Therefore the \( \epsilon_{\text{mix}} \) can be defined by a volume fraction \( f \) of liquid in mixture: \( \epsilon_{\text{mix}}(f , \epsilon_{\text{sol}}, \epsilon_{\text{liq}}) \). For the weak mixtures \( (f \approx 0 \text{ or } f \approx 1) \) we have [28]

\[ \epsilon_{\text{mix}}^{\text{f=0}} = \epsilon^{\text{sol}} \left( 1 + 3f \frac{\epsilon_{\text{liq}}^{\text{sol}} - \epsilon_{\text{sol}}^{\text{sol}}}{\epsilon_{\text{liq}} + 2\epsilon_{\text{sol}}} \right). \]

An approximate interpolation for intermediate \( f \approx 1 \) of these linear in \( f \) solutions [14] is

\[ \epsilon_{\text{mix}}^{\text{f}} = \epsilon_{\text{mix}}^{\text{f=1}} f^4 + \epsilon_{\text{mix}}^{f=0}(1 - f^4). \]
Expressions (11) have been used in calculations shown in Figs. 3 and 4. At an early stage it is necessary to consider optics of a solid-liquid mixture given by these expressions because at this stage the thickness of a solid-liquid mixture layer is comparable with the thickness $\delta$ of a skin-layer – a penetration depth of a probe photon.

Values $e^{\text{sol}}(T = 300 \text{ K}) = -53.5 + 24.1 i$, $N^{\text{sol}} = 1.6 + 7.5 i$, $e^{\text{liq}}(T = 1200 \text{ K}) = -40 + 15.3 i$, $N^{\text{liq}} = 1.2 + 6.4 i$ [25] differ moderately. In this case, there is another approximation [28] 

$$(e^{\text{mix}})^{1/3} = e^{\text{1/3}}$$

nonlinear in $f$ but linear in small difference $e^{\text{sol}} - e^{\text{liq}}$. Comparison of this approximation with (11) shows that results differ small: the maximum deviation achieved at $f \approx 0.75$ is $\approx 1\%$ for $\text{Re} (e)$ and less than $3\%$ for $\text{Im} (e)$. As was said at early stage optics of solid-liquid mixture is significant. Let us mention that as it will be shown below at this stage there is non-equilibrium melting of an overheated crystal. At intermediate and late stage $c_1c_2$ shown in Fig. 1 exist. Vapor-liquid mixture can influence optical reflection if thickness of cavitation layer $\delta$ is less or comparable with $\delta$. The cavitation layer covers the undersurface vapor-liquid layer against probe photons.

6. Role of $\nu_{ee}$ in optics of aluminum

In an early stage the $T_e$ is high – then the $\nu_{ee}$ (7) dominates in the total frequency $v$ [5] as maximum $T_e$ for our fluences are smaller than 10 $K$ and the $\nu_{ee}$ collisions are less frequent. There are different coefficients $b^e$ and $b^f$ for the $\nu_{ee}$ (7) in expressions for $\kappa$ [5] and for optics – in the Drude and in the interband terms [10]. In crystals the $b^e$ includes normal and Umklapp processes while the $b^f$ in the solid Al may differ from zero as a result of the Umklapp effect (situation is different for gold, see below). In liquid Al the coefficient $b^f = 0$ – the e-e collisions do not contribute into optical absorption as the Umklapp is impossible. In Al a Fermi sphere is larger than in Au while the Brillouin zones are approximately equal (the lattice constants are $\approx 4 \text{ nm}$ for Al and Au both). Therefore the Umklapp effect is more significant in Al. E.g., it results in order of magnitude increase of the electron-ion energy exchange rate $\alpha$ [29]. Value of $b$ in (7) is a subject of discussions. Below the Debye temperature the $\nu_{ee} \propto T^3$ tends to zero strongly and becomes less than the $\nu_{ee} \propto T^2$. Then specific electrical resistance $r = 1/\sigma$ for very pure crystals is $r = AT^2 + CT^4$. The measurements [30] give $b^f = 15$. Here we suppose that $\nu_{ee}$ does not depend on frequency of electromagnetic field and the coefficient $b$ in (7) for resistance $r$ is equal to $b^f$. At the same time the theory [31] gives $b^f = 0.6$. For high $T_e$ the calculations [4] $b^f = b^f = 1$ is accepted.

Estimate of the upper limit for $b^f$ follows from the check of the Wiedemann-Franz law $\kappa/\sigma = LT$ done for melt Al in [23], where $L$ is Lorentz number. In Drude approximation we have $\kappa/\sigma = LT/(1 + \nu_{ee}/\nu_{ee})$ because in melt umklapp is absent and $\nu_{ee}$ (7) does not contribute to electric conductivity $\sigma = 1/r$. Relative deviation $\varepsilon$ of the ratio $\kappa/(\sigma T)$ from $L$ in [23] is less than 10%. This means that electrons in Al remain degenerate up to temperature $T = 10 \text{ K}$ achieved in [23]. The limit $\varepsilon < 0.1$ impose restriction on value $b^f < 1.5 - 2$. It is obtained from $\nu_{ee}/\nu_{liq} < \varepsilon$ where expressions (7) and (9) was used. On the other hand, the value $b^f$ is important at early stage because it influences heat propagation into bulk when the propagation is supersonic. To achieve thickness $d_T \approx 110 \text{ nm}$ at Al ablation threshold the values $b^f$ should be near this restriction $b^f \approx 1.5 - 2$. The thickness $d_T \approx 110 \text{ nm}$ is necessary to reproduce experimentally defined crater depth $45 - 50 \text{ nm}$. For smaller $b^f$ the simulated crater is deeper and fluence threshold is higher than the experimental ones.

Performed optical measurements shown in Figs. 3, 4 together with simulations give additional information about $b^f$. The interesting sharp narrow "well" at the theoretical $R(t)$ in Fig. 3 corresponds to $b^f = 1.7$. Its minimum is achieved when $T_e$ and hence $\nu_{ee}$ have the largest amplitudes (at the end of the pump). This well might be very useful for diagnostics. The left wing of the well follows the history of electron heating while the right wing reflects the kinetics of melting because the gradual phase transformation from crystal state to melt in a skin-layer progressively suppresses optical contribution of the e-e collisions (7). Unfortunately the well is not observed. Density of experimental points at the time axis in Figs. 3, 4 is large enough to exclude missing of the well between the two successive points. The accuracy of experimental measurements of a relative reflection (≈ 1%) is sufficient to catch the well. Analysis of our simulation runs in a fluence range $1 < F/F_{abl} < 4$ shows that it is necessary to have the $b^f$ below 0.2-0.5 to meet the measurements; for Al the calculated and measured thermomechanical ablation threshold is $F_{abl} = 0.5 J/cm^2$, $F_{abl} = 65 \text{ mJ/cm}^2$ [5].

7. Melting and decrease of phase angle

Simulations show that the phase evolution $\psi(t)$ presented in Fig. 4 contains important information concerning the kinetics of melting. The base for this is the difference commented in Fig. 5 between the defined in Section 4 $e^{\text{sol}}$ and $e^{\text{liq}}$. As a result of attenuation of the band-band transition during melting the value $n = Re(N)$ becomes smaller. This is why the $\psi_{liq}^0$ in Al is 2.2 nm differing from solid in the direction of the phase rotation to the crater. The value 2.2 nm corresponds to the case
of a Fresnel reflection from homogeneous semispace. Remarkably that this small difference is measurable by the pump-probe interferometry. The sign of rotation directions in Fig. 5 defines the sign of the phase difference $\Delta \psi$ in Fig. 4. Detection of ultrafast melting of semiconductors [31] is possible due to the same liquid-solid phase difference $\Delta \psi$. But in this case the melting transforms semiconductor into a metallic state – therefore $\Delta \psi$ is significantly larger (e.g., $\Delta \psi = 12.4$ nm for GaAs, $\lambda = 620$ nm) – and this transformation can be detected easily.

The phase $\Delta \psi(t)$ obtained from 2T-HD equations is compared with experimental data in Fig. 6. Expansion movement of reflecting boundary should increase $\Delta \psi$ but at the early time it decreases as a result of gradual melting of skin-layer. Agreement between data and theory indicates that theory given below properly describes the melting.

Figure 6 illustrates the heating of ions by hot electrons in 2T-HD model. In MD simulation atoms are heated by the space-time distributed thermostat power source with the temperature distribution taken from 2T-HD. This MD approach is similar to one developed in [2, 32], see also [34] where phenomenological terms describing non-equilibrium melting are added to 2T-HD equations. Particular mechanism of heating (heat flow from electrons or thermostat) has no action upon the kinetics of melting if we suppose that elastic moduli do not depend on $T_e$ as in the case of Al [27]. In Fig. 6 the 2T-HD and MD $T_i$ profiles are approximately the same. Some difference results from equilibrium and non-equilibrium description of melting. The arrows in Fig. 6 mark the slice of melting from equilibrium 2T-HD. The kinks at the ends of this slice result from hidden fusion energy. In MD the degradation of crystal symmetry during the fast heating and melting is distributed in wider range beyond the liquidus/solidus positions. Crystal beyond solidus is in overheated state [2, 32].

Phase transformation and propagation of melting into bulk is shown in Fig. 7. The profiles of the symmetry index $s$ are presented. The index $s$ is defined as a number of crystal axis passing through an atom and averaged over atoms within a x-slab, and $s = 6$ in a cold fcc lattice. One can see how quickly the rather thick (thicker than $\delta$) layer of mixture is formed. Later the layer of pure melt (the plateau at the instant $t = 4$ ps $s$-profile in Fig. 7) appears. Much later the narrow melting front with small overheating separating a melt from a crystal is formed. Maximum thickness of the molten layer for the fluence $F_{abs} = 65$ mJ/cm$^2$ is $\approx 100$ nm.

8. Gold optical response and $d$-electrons

Absorption of pump fsLP causes sharp changes in optical properties at very early time – during the pulse $\tau_e$. They are shown in Fig. 8. Bulk gold targets are used. This response is caused by fast heating of electrons. If we compare Figs. 3, 4 (Al) and Fig. 8 (Au) having similar relative temperatures $T_e/T_F$ at 2T stage and similar final $T_i = T_e$ temperatures after e-i relaxation we will see obvious large differences. They are related to the differences in the band structures of Al and Au [27].

Estimates of heating history from the maximum $T_e$ to e-i thermalization give for the main seven thermal parameters $F_{inc}^{abs}$, $F_{inc}$ J/cm$^2$, $F_{abs}$ mJ/cm$^2$, $E_{elmax}$ MJ/kg, $T_{elmax}$ K, $Z = N_e n_{e6p}$, $T_{elmax}$ kK the values: (0.5, 0.7, 50, 1, 1.5, 1.2, 0.8), (1, 1.3, 140, 3, 2.5, 1.5, 2.5), (2, 2.9, 500, 10, 5, 2.4, 8) for the three cases shown in Figs. 8 where $F_{inc}^{abs} = (1.3 - 1.4)$ J/cm$^2$. A thermomechanical ablation threshold, $E_{elmax}$, $T_{elmax}$ are electron thermal energy and temperature at the end of a pump. $Z$ is number of electrons exited from the 5d to the 6s,6p band at the maximum $T_{elmax}$. $T_{elmax}$ is maximum ion temperature achieved after e-i relaxation. An expression
$E_e(T_e) = 45.74997T_e^2 - 119.7567T_e^{2.1} + 105.4197T_e^{2.2} - 30.9551T_e^{2.3}$. for electron thermal energy at fixed density $\rho = 19.3 \text{ g/cm}^3$ approximates data obtained from the ABINIT [33] simulations up to $T_e = 10 \text{ eV}$, here $E_e$ is in MJ/kg, and $T_e$ in K. Our curve is above the standard parabola $E_e = \gamma T_e^2$ because we include exciting of the $d$-electrons. But it is below the curve [8] where a red-shift of the $d$-band with $T_e$ was not considered. Experimental and theoretical values for the density of a crater at a threshold $F_{inc,lab}$ is 110 nm [7]. The first case with the smallest $F_{inc}$ is near a melting threshold for bulk Au. Our three cases cover a range of energy densities obtained in [15, 34, 35, 36, 37] for ultrathin (25-30 nm) freestanding Au films. Here we consider bulk targets and use different techniques of measurements.

The values of $Z$ presented above have been defined using the ABINIT [33] code, the normalization condition for the number of electrons, and the expression for the amount of electrons in the 6$p$ band. The ABINIT has been used as in [27] for calculation of the $T_e$ dependent DOS at different $T_e$ supposing that density is equal to $\rho^p$ (isochoric heating). For given $T_e$ the DOS of the $5d$ band obtained from ABINIT has been approximated by a rectangular, and the DOS of the $6s, 6p$ band has been described as the function $g(\varepsilon) \propto \sqrt{\varepsilon}$ in order to calculate $Z$. At a given $T_e$ a root $\mu$ of the normalization condition

$$11 \sqrt{\frac{2}{\pi}} \frac{m^3}{h^3} \frac{n_{atom}}{n_{electron}} \int_0^\infty \sqrt{x} \frac{\sqrt{x} dx}{e^{x^2/h^2} + 1} + L, \quad (13)$$

where $L = \frac{10}{(E_1 - E_2)} \ln(1 + e^{(\mu - E_1)/kT_e})/(1 + e^{(\mu - E_2)/kT_e})$, defines a chemical potential $\mu(T_e)$, here $E_1, E_2$ are edges of the $5d$ band relative to the bottom point of the $6s, p$ bands. The first and the second terms correspond to the numbers of electrons in the $6s, p$ and $5d$ bands, resp. At room temperature these numbers are $Z = 1$ and 10. It is known that for Au difference between this approach and calculation of $\mu(T_e)$ with exact DOS is small [38]. The exact function $\mu(T_e)$ is obtained together with the DOS in the ABINIT simulation. The excitation degree $Z$ is given by an expression $Z(T_e) = 11 - L$, where $L$ stands for the second term in (13) but now with known $\mu(T_e)$. To estimate possible influence on the value of $Z$ of position of the bottom point of the $6s$ band this position was varied in the range $\pm 2 \text{ eV}$ relative to its position at $T_e = 0$.

The values of $Z$ and collision frequency $\nu$ are necessary for the Drude estimates of $\varepsilon$. Growth of them is responsible for the rise of $|\sigma_{ei}|, \varepsilon_i$ in Fig. [9]. At room temperature $\nu/\omega_{prob}$ is small: 1.2% from electrical and thermal conductivities or 3.3% from optical data [39]. $\omega_{prob} = 2 \text{ eV}$. Heating of an electron subsystem in our conditions rises $\nu$ to large values: $\nu/\omega_{prob} \sim 1$. There are three candidates responsible for the growth of $\nu$: (i) an enhancement of $\nu_{ei}$ in solid or liquid Au with $T_e \gg T_i$ in comparison with $T_e = T_i$ case, (ii) $\nu_{ee}$ and Umklapps in crystal Au, and (iii) the e-e collisions between electrons from the $d$ and the $sp$ bands in solid or liquid Au. Let’s consider these cases.

(i) The frequency $\nu_{ei}$ and the e-i exchange rate $\alpha$ are coupled, $\dot{E}_{ei} = \alpha(T_e - T_i) \approx \alpha T_e - n_i \Delta E_{ei} \nu_{ei}(T_e)$, $T_e \gg T_i$, [40], where $\Delta E_{ei} \sim (m_e/M_i)E_F$ is an energy transfer from a light electron to a heavy ion in one e-i collision, $\nu_{ei}(T_e) \sim a^2(T_e/\theta) \nu_{ei}/(n_i \Delta E_{ei})$. If $\alpha = \text{const}$ as in Al [8, 29], then $\nu_{ei} = \nu_e(T_i) \propto T_i$ as usual. But in gold there is significant dependence on $T_e$, $\alpha = \alpha(T_e)$. An approximation of calculation of $\alpha \propto \int f(\varepsilon)\gamma(\partial f/\partial \varepsilon) d\varepsilon$ with DOS $g(\varepsilon)$ from ABINIT [33] (including the shift of the $d$-band with $T_e$) is $\alpha(T_e) = (0.23 + 4.37 \varepsilon_e^2/(1 + T_e^2) + 0.97 \varepsilon_e^2)^1/2 \text{ W/m}^2/\text{K}$. It is valid up to $T_e = 10 \text{ eV}$, here $f(\varepsilon)$ is Fermi distribution [8]. The $\alpha(T_e)$ begins to grow at $T_e = 3 \text{ kK}$ from $\alpha(T_e < 3 \text{ kK}) = 0.23 \cdot 10^{17} \text{ W/m}^2/\text{K}$ and saturates at the
value ten times larger ≈ 2 · 10^{17} \text{ W/m}^3/\text{K} \ [41]. This means that 
\nu_\text{e}(T_\text{e}, T_\nu) \propto (\alpha(T_\nu)/T_\nu n_\text{e} \Delta E_\text{e}) \text{ is enhanced if } T_\nu \gg T_\text{e}, T_\nu > 3 \text{ K. There is }$
\nu_\text{e}(T) = 1.2 \cdot 10^{11} \text{ T s}^{-1}, \nu_\text{p}(T) = 3.3 \cdot 10^{14} + 1.5 \cdot 10^{14} \text{ T in } \text{IT gold, } T \text{ in } \text{K. For } T_\nu = 2 \text{ kK we have }$
\nu_\text{p}(T) \approx 6.3 \cdot 10^{14} \text{ s}^{-1}. If } T_\nu > 2 \text{ eV as in two cases shown in Figs. 20 then the enhancement due to increase of } T_\nu \text{ gives large frequency}$
\nu_\text{e}(T_\nu = 2 \text{ kK}, T_\nu = 2 \text{ eV}) \approx 6 \cdot 10^{15} = 2 \nu_\text{prob}. 
(ii) In Al \nu_\text{e}(T) \text{ is small, Sec.5. As was said, the Umklapp processes are weaker in Au as the result of smaller Fermi/Brillouin ratio. Therefore it seems plausible that this candidate is less important than two other candidates. 
(iii) Electrons from } d \text{ versus } sp \text{ bands have different angular momentum and effective mass. Therefore photons are absorbed in collisions between them. Corresponding frequency } \nu_\text{p}\text{ is given by (7) with possible dependence } b(T_\nu). \text{ The } \nu_\text{p}\text{ may be }$
\nu_\text{prob} \approx \omega_\text{prob} \text{ at } T_\nu \sim T_\text{F.} 
From imaginary and real parts of expression (10) we obtain$
\nu = \sqrt{\alpha_\text{prob}} = (\varepsilon_\text{r} - \Delta_\text{r})/[1 - (\varepsilon_\text{r} - \Delta_\text{r})] \text{ and } Z/m_\text{eff} = (1 + \nu^2)(\varepsilon_\text{r} - \Delta_\text{r})/20.6/\nu. \text{ The mass } m_\text{eff} / m_e = 0.95 - 1.15 \text{ at room temperatures [23] remains approximately the same with increase of } T_\nu. \text{ This follows from our ABINIT simulations. According to [23] in 2T Au } E_\nu > \nu_\text{prob} = 2 \text{ eV, where } E_\nu \text{ is an absorption edge of the } d\text{-band. If we neglect the band-term } \Delta_\text{bb} = \Delta_\nu + i\Delta_\nu \text{ in (10), } \Delta_\nu = 0, \Delta_\nu = 0, \text{ then } (Z; \nu) = (0.9; 0.5), (1.7; 0.9), (3.3; 1.3) \text{ at the maximum } |\varepsilon_\text{r}|, \varepsilon_\text{r} \text{ in the three cases shown in Fig. 9.} 
Our data shown in Fig. 9 agree with data from [23] in } \varepsilon_\text{r} \text{ but give larger } \varepsilon_\text{r} \text{ and have a maximum at the time dependence } |\varepsilon_\text{r}(t)| \text{ while the dependence } \varepsilon_\text{r}(t) \text{ from [23] saturates. Perhaps the last difference results from the conductive cooling absent in ultrathin films. Let’s mention that data [23] contain the useful dependence } \varepsilon(\omega) \text{ but may be less accurate at a particular frequency. } (Z; \nu) = (1.2; 0.4) \text{ for the maximum of the dependence } \varepsilon(\omega) \text{ from [23] shown in Fig. 9 as the solid curves. As a result of smaller } \varepsilon_\text{r}\text{ these values are below our values (1.7; 0.9) for the case with approximately the same energy } E_\nu. \text{ Nevertheless there are appreciable excitation } Z \text{ and frequent collisions. Therefore we can conclude that measurements confirm the theoretical findings presented above that a pump irradiation creates an excited population } (Z > 1) \text{ rising } \omega_\text{pl} \text{ and transfers gold into the state with strongly collisional widened energy levels.} 
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