"Hot" electrons in metallic nanostructures - non-thermal carriers or heating?
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Abstract

Determining the electron distribution in a continuously illuminated metal is a fundamental problem in physics, and an essential step towards applications such as photo-catalysis for green fuels. This requires accounting for both non-equilibrium and heating, something which was not considered before for steady-state illumination. Here, we develop coupled Boltzmann-heat equations to show that the non-equilibrium distribution is dominated by holes, and that the electron and lattice temperatures are similar, justifying the (classical) single temperature models. Importantly, we find that most absorbed power causes heating, and only a small fraction actually leads to “hot” carrier generation, the number of which is nevertheless substantially larger than in equilibrium. Our formulation allows for the first quantitative comparison of theory and measurements of steady-state electron distributions in plasmonic systems.
What happens to electrons in a metal when they are illuminated? This fundamental problem is a driving force in shaping modern physics since the discovery of the photo-electric effect. In recent decades, this problem resurfaced from a new angle, owing to developments in the field of nano-plasmonics [1, 2], where metallic nanostructures give rise to resonantly enhanced local electromagnetic fields, hence, to controllable optical properties.

Even more recently, there is growing interest in controlling also the electronic and chemical properties of metal nanostructures, where the energy of optically-induced plasmons is transferred to the electrons in the metal, thus driving it out of equilibrium. These non-equilibrium energetic electrons - sometimes (ill)referred to as “hot electrons” - can be exploited to perform various chemical functions which require energetic electrons. The most attractive and widely-studied application is photo-catalysis, in which these energetic electrons are used to drive a chemical reaction such as hydrogen dissociation, water splitting [3–9] or artificial photosynthesis [10, 11]; These processes have an immense importance in paving the way towards realistic alternatives for fossil fuels. Other applications include photo-detection [12–14], up-conversion [15, 16] and more.

Motivated by the large and impressive body of experimental demonstrations of the above-mentioned applications, many theoretical studies address the question: how many non-equilibrium high energy (i.e., “hot”) electrons are generated for a given illumination. Naively, one would think that the answer is already well-known, but in fact, finding a quantitative answer to this question is a challenging task. A complete theory of non-equilibrium carrier generation should not only include a detailed account of the non-equilibrium nature of the electron distribution, but also the possibility of both the electrons and the underlying lattice to heat up (via non-radiative transitions). Furthermore, the theory should take into account that technologically important applications such as photo-catalysis are performed under continuous wave (CW) illumination, which drives the electron distribution into a non-equilibrium steady-state.

Quite surprisingly, to date, there is no comprehensive theoretical approach that takes all these elements into account. Typically, the transient electron dynamics are studied [17–22], focusing on an accurate description of the material properties, e.g., metal band structure and relaxation rates [23–25]; some studies also accounted for the electron temperature [20, 22] and (to some extent) for the permittivity [22] dynamics. However, it is not a-priori clear what can be learned from the transient case about the steady-state population of energetic
non-equilibrium electrons (i.e., under CW illumination). On the other hand, the few pioneering theoretical studies of the steady-state non-equilibrium under CW illumination [26–28] accounted for the electron distribution in great detail, but did not adjust the electron temperature, and ignored the possible heating of the phonons.

The fact that temperature effects were not treated in previous theoretical studies of “hot” electrons is not a coincidence. After all, the system is out of equilibrium, so how can one define a temperature, inherently an equilibrium property? [29] On the other hand, it is well-known and experimentally verified that the temperature of metallic nano-structures does increase upon CW illumination, sometime to the degree of melting (or killing cancer cells) [30]. How does one reconcile this paradox? Below, we suggest a unique solution, based only on energy conservation and basic thermodynamics, namely, the simple fact that the temperature of an electronic system appears only through the Fermi distribution.

To do so, we describe a self-contained theory for the photo-generation of non-equilibrium energetic carriers in metal nanostructures. The framework is the quantum-like version of the Boltzmann equation (BE), which is in regular use for describing electron dynamics in metallic systems more than a few nm in size, see e.g., [17–20, 22, 31–36]. To the BE we add, in a self-consistent way, electron-phonon scattering, such that - via conservation of energy - we allow the electron and phonon (lattice) temperatures in the plasmonic nanostructure to rise above the ambient temperature. This distinguishes our calculation of the steady-state non-equilibrium from previous ones. Indeed, we account for three energetic channels, namely, non-thermal electron energy, thermal electron and phonon energy, while previous studies treated only the first channel. We show that the population of non-equilibrium energetic electrons and holes [50] can increase dramatically under illumination, yet this process is extremely inefficient, as the majority of the absorbed energy leads to heating; the electron and phonon temperatures are found to be similar, thus, justifying, for the first time to our knowledge, the use of the (classical) single temperate heat model [30]. Somewhat surprisingly, we find that just above (below) the Fermi energy, the non-equilibrium consists of holes (electrons), rather than the other way around; we show that this behaviour is due to the dominance of $e-ph$ collisions. All these results are very different from those known for electron dynamics under ultrafast illumination, as well as from previous studies of the steady-state scenario that did not account for all three energy channels.
We start by writing down the Boltzmann equation in its generic form,
\begin{equation}
\frac{\partial f(E, T_e, T_{ph})}{\partial t} = \Phi_{ex}[f] + \left( \frac{\partial f}{\partial t} \right)_{e-ph} + \left( \frac{\partial f}{\partial t} \right)_{e-e}.
\end{equation}

Here, $f$ is the electron distribution function at an energy $E$, electron temperature $T_e$ and phonon temperature $T_{ph}$, representing the population probability of electrons in a system characterized by a continuum of states within the conduction band; finding it for electrons under (CW) illumination is our central objective. The right-hand side of the BE describes three central processes which determine the electron distribution, namely, photon absorption ($\sim \Phi_{ex}$), electron-phonon and electron-electron scattering. These processes, with their effect on the distribution, are schematically depicted in Fig. 1(a)-(c); their specific structure is detailed in the Methods section and in the SM, Section I.

The next step, which is the central novelty of this work, is the unique and self-consistent determination of the electron and phonon temperatures from both Eq. (1) and energy conservation arguments. In the spirit of the two temperature model [17, 18, 37], and specifically following [36], we split Eq. (1) into its thermal ($f^T$) and non-thermal ($\Delta f^{NT} \equiv f(E, T_e, T_{ph}) - f^T(E, T_e)$) parts, namely,
\begin{align}
\frac{\partial \Delta f^{NT}}{\partial t} &= \left[ \Phi_{ex}[f(E)] - \Phi_{ex}[f^T(E)] \right] \\
&\quad + \left[ \left( \frac{\partial f}{\partial t} \right)_{e-ph} - \left( \frac{\partial f^T}{\partial t} \right)_{e-ph} \right] + \left[ \left( \frac{\partial f}{\partial t} \right)_{e-e} - \left( \frac{\partial f^T}{\partial t} \right)_{e-e} \right],
\end{align}
\begin{equation}
\frac{\partial f^T}{\partial t} = \Phi_{ex}[f^T(E)] + \left( \frac{\partial f^T}{\partial t} \right)_{e-ph} + \left( \frac{\partial f^T}{\partial t} \right)_{e-e}.
\end{equation}

$f^T$ has the form of a Fermi distribution with the electron temperature $T_e$, which can differ from both the phonon temperature $T_{ph}$ and the temperature of the environment $T_{env}$. The sum of equations (2) & (3) gives Eq. (1), yet the separation into thermal and non-thermal parts has some direct implications: (i) photon absorption contributes to the non-thermal electron distribution but also the thermal distribution (first term in Eq. (3)). Indeed, it is intuitive to appreciate that once a photon is absorbed, the total energy of the electron system grows, such that it will aspire to relax to a Fermi distribution with a slightly higher temperature. This is a crucial difference with respect to previous work, since as we show below, most of the absorbed photon power goes to establishing the new thermal distribution, i.e., to heating, and not to pushing the electron system away from thermal distribution.
(ii) Distinguishing between collisions of phonons with thermal and non-thermal electrons ensures that the latter lead to a change of the phonon temperature, but leave the electron temperature unaffected. (iii) It ensures that the non-thermal energy “lost” due to $e-e$ collisions is “reinserted” into the thermal electron subsystem.

Now, the electron temperature can be determined self-consistently and uniquely from the thermal part of the electron distribution by multiplying Eq. (3) by the product of the electron energy $\mathcal{E}$ and the density of electron states $\rho_e(\mathcal{E})$ and integrating over the electron energy. The resulting equation describes the dynamics of the energy of the thermal part of the electronic distribution,

$$\frac{dU^T_e}{dt} = W^T_{e-e} - W^T_{e-ph} + W^T_{e-e}.$$  \hspace{1cm} (4)

Eq. (4) has a simple and intuitive interpretation: the dynamics of the energy of the thermal electrons is determined by the balance between the heat that flows in due to photoexcitation ($W^T_{e-e} \equiv \int \mathcal{E} \rho_e(\mathcal{E}) \Phi_{ex}[f^T(\mathcal{E}, T_e)]d\mathcal{E}$) and from the decay of non-thermal (“hot”) electrons ($W_{e-e} \equiv \int \mathcal{E} \rho_e(\mathcal{E}) \left( \frac{\partial f^T}{\partial t} \right)_{e-e} d\mathcal{E}$), and the heat that flows out into the lattice ($W^T_{e-ph} \equiv -\int \mathcal{E} \rho_e(\mathcal{E}) \left( \frac{\partial f^T}{\partial t} \right)_{e-ph} d\mathcal{E}$, see SM, Section I.B).

In similarity to Eq. (4), the phonon temperature is determined by noting that the total energy of the lattice is balanced by the heat flowing in from the electronic system and flowing out into the environment, namely,

$$\frac{dU_{ph}}{dt} = W_{e-ph} - G_{ph-env}(T_{ph} - T_{env}).$$  \hspace{1cm} (5)

Here, $W_{e-ph} \equiv -\int \mathcal{E} \rho_e(\mathcal{E}) \left( \frac{\partial f}{\partial t} \right)_{e-ph} d\mathcal{E} \quad (\neq W^T_{e-ph})$ is the power flow from both thermal and non-thermal electrons to the phonons, $T_{env}$ is the temperature of the environment far from the nanostructure and $G_{ph-env}$ is proportional to the thermal conductivity of the environment; it is strongly dependent on the nanostructure geometry, exhibiting inverse proportionality to the particle surface area.

Eqs. (2)-(5) provide a general formulation for the non-thermal electron generation, electron temperature and phonon temperature in any metal nanostructure under arbitrary illumination conditions. Unlike previous attempts to define an “effective” temperature (see e.g., [20, 22]), we determine the temperatures uniquely using two of the most basic concepts in physics - conservation of energy and fermion statistics. The equations require as input the local electric field distribution from a solution of Maxwell’s equations for the nanostructure.
of choice, see SM, Section II. In what follows, we numerically search for the steady-state \((\partial/\partial t = 0)\) solution of these (nonlinear) equations for the generic case of CW illumination see Methods section. For concreteness, we chose parameters for Ag, taken from comparison to experiments of ultrafast illumination; the photon energy is chosen to coincide with the localized plasmon resonance of a Ag nano-sphere in a high permittivity dielectric, in similarity to many experiments [10, 38][51], see Table S1; this configuration also justifies the neglect of interband transitions (see also SM Section I). As we demonstrate, this case leads to several surprising qualitative new insights, as well as to quantitative predictions of non-equilibrium carrier distributions.

Fig. 1 shows the deviation of the electron distribution from the distribution at the ambient temperature (i.e., in the dark), \(\Delta f \equiv f(E, T_e, T_{ph}) - f^T(E, T_{env})\), as a function of electron energy for various local illumination levels. The distributions depend on the local field quantitatively, but are qualitatively similar, showing that resonant plasmonic near-field enhancement can indeed be used to increase the number of photo-generated “hot” electrons, as predicted and observed experimentally. The change of population is largest near the Fermi energy, and takes the regular thermal form, namely, it is identical to the population difference between two thermal distributions; specifically, \(\Delta f > 0 (< 0)\) above (below) the Fermi energy [52]. This is in accord with the approximate (semi-classical) solution of the Boltzmann equation (see e.g., [31, 34]) and the standard interpretation of the non-equilibrium distribution (see e.g., [39, 40]).

However, it is clear that the distributions in Fig. 1 mix the two components of the electron distribution, namely, the thermal and non-thermal parts. To highlight the non-thermal contribution, one should consider the deviation of the electron distribution from the distribution at the steady-state temperature, \(\Delta f^{NT} \equiv f(E, T_e, T_{ph}) - f^T(E, T_e)\). Simply put, this is the “true” non-thermal part of the steady-state electron distribution, loosely referred in the literature as the “hot electron distribution”.

Since the differences between \(f^T(E, T_e)\) and \(f^T(E, T_{env})\) occur mostly around the Fermi energy, it is instructive to study \(\Delta f^{NT}\) in two energy regimes. First, Fig. 2(a) shows that near the Fermi energy, the population change is now about an order of magnitude smaller and of the opposite sign (in comparison to \(\Delta f\), Fig. 1(d)). This is a surprising result, which means that the non-thermal distribution just above (below) the Fermi energy is characterized by the presence of non-thermal holes (electrons). This result could only be obtained when the
explicit separation of the three energy channels are considered, allowing $T_e$ to increase above $T_{env}$. Notably, this is the exact opposite of the regular interpretation of the non-equilibrium distribution (as e.g., Fig. 1 and standard textbooks [31, 34]) which do not account for the increase of the total energy of the electron system, i.e., for the electron temperature rise. From the physical point of view, this change of sign originates from $e - ph$ collisions, as it has the same energy-dependence as the Bloch-Boltzmann-Peierls term, see Fig. 1(b) and Fig. S1(b).

Second, further away from the Fermi energy, $\bar{\hbar}\omega$-wide (roughly symmetric) pedestals are observed on both sides of the Fermi energy (Fig. 1(d)), corresponding to the generation of non-thermal holes ($\Delta f^{NT} < 0$) and non-thermal electrons ($\Delta f^{NT} > 0$). It is these high energy charge carriers that are so valuable for the catalysis of chemical reactions.

For energies beyond $\hbar\omega$ from the Fermi energy, the non-thermal distribution is much lower, as it requires multiple photon absorption [53]. This implies that in order to harvest the excess energy of the non-thermal electrons, one has to limit the harvested energy to processes that require an energy smaller than $\hbar\omega$.

The low density of non-thermal electrons and its scaling with the incoming intensity and particle size can be understood from rather simple arguments. Indeed, in standard atomic systems, significant population inversion (the analogue of the non-thermal population in the current case of a continuum of electron states) is obtained when the excitation rate ($\sim \sigma_{abs}I_{inc}$) is comparable to the relaxation rate. For the typical few nanoseconds relaxation time of atomic systems, this requires intensities in the range of $MW/cm^2$, the so-called saturation intensity. In analogy, since the relaxation rate in metals is only a few femtoseconds long, then, assuming the absorption cross-section of a molecule and a metal atom are comparable, one can expect the non-thermal electron generation to be efficient for intensities which are $\sim 6$ orders of magnitude higher than in atomic systems. This simple estimate is in good agreement with a (naive) linear extrapolation of our findings (Figs. 1-2). This “atomistic” argument also shows that, to leading order, one should not expect the non-thermal electron generation efficiency to depend strongly on the particle size.

The non-thermal electron distributions we obtained are very different from those obtained by accounting only for photon excitation [23, 24, 39, 40]. As pointed out in [23], such distributions are valid only immediately after illumination by an ultrashort pulse; they would have been similar to the steady-state distributions only if all other terms in the BE
were energy-independent, which is not the case (see SM, Section I and Fig. S1). Therefore, distributions such as those in [23, 24, 39, 40] should not be used in the assessment of the steady-state population of “hot” electrons. The electron distributions we obtained are also different from the steady-state distributions obtained previously in [21, 26–28]. The main reason for these differences is that these studies did not correctly account for the electron and phonon temperatures, the energy flow from the thermal electrons to the lattice, hence, the total energy in the electron system, are also inaccurate [54].

To allow for a quantitative prediction of the efficiency of applications such as photocatalysis, photo-detection etc., one needs to account for the actual nanostructure geometry (as noted, to allow linking the incident and local fields, see SM, Section II), the metal band structure and the specifics of the catalyzed process (chemical reaction etc.). However, we can already say that if the catalytic rate is linearly proportional to the number of high energy electrons, then, our results show a catalytic enhancement which is proportional to $|\vec{E}|^2$, in line with experimental data (see e.g., [38, 41]). Indeed, Fig. 2(b) shows that the non-thermal electron distribution has a quadratic dependence on the electric field ($\Delta f^{NT} \sim |\vec{E}|^2$).

As pointed above, our approach allows a quantitative estimate of both electron and phonon temperatures. In Fig. 3, these are plotted as a function of the local field. As seen, both temperatures grow quadratically with the local field, as in the classical (single temperature) approach [30]. This is a nontrivial result, since the underlying equations exhibit an implicit nonlinear dependence on the temperatures. Fig. 3 also shows that $T_e$ is only slightly higher than $T_{ph}$. This provides the first (qualitative) justification, to the best of our knowledge, for the use of the single temperature heat equation in the context of metallic nanostructures under illumination [30]. However, the temperature difference is proportional to the incoming intensity so that for high intensities, the single temperature model may not be sufficient.

Our calculations also show that the number of photo-generated high energy electrons $\Delta f^{NT}$ is independent of $G_{ph-env}$ (see Fig. S2 and discussion in SM, Section II). Since $G_{ph-env}$ is proportional to the thermal conductivity of the host and inversely proportional to the particle surface area, this implies that if a specific application relies on the number of high energy electrons, then, it will be relatively insensitive to the thermal properties of the host and the particle size; this is in agreement with the “atomistic” argument described above. Since the temperature rise is also inversely proportional to $G_{ph-env}$ (see [42] and
Fig. S2), the difference in the photo-catalytic rate between the TiO$_2$ and SiO$_2$ substrates (compare [38] and [43]) could be a result of a mere temperature rise, but is not likely to be related to the number of photo-generated high energy electrons. This result complements the chemistry-based arguments used in [43].

Our approach allows us to deduce how the power density pumped into the metal by the photons splits into the non-thermal electrons and into heating the electrons and the phonons (see Fig. 4). This provides a way to evaluate the efficiency of non-thermal electron generation. Remarkably, one can see that the overall efficiency of the non-thermal electron generation is truly abysmal: At low intensities, the power channeled to the deviation from equilibrium is more than 10(!) orders of magnitude lower than the power invested in the heating of the electrons and phonons (which are found to be nearly similar). This is in correlation with the results of Fig. 1: most absorbed power leads to a change of the electron distribution near the Fermi energy, rather than to the generation of high energy electrons, as one would desire. This shows that any interpretation of experimental results which ignores electron and phonon heating should be taken with a grain of salt.

In spite of the low efficiency of high energy electron generation, our results do leave room for optimism regarding the potential usefulness of plasmonic-assisted “hot-electron” generation, as originally envisioned [3, 4, 6–9, 21, 39, 41]. Indeed, a comparison with the pure thermal distribution of high energy electrons (Fig. 2) shows that the absolute electron population can be many orders of magnitude higher compared to the thermal distribution at the steady-state temperature. Furthermore, we can identify several pathways towards significant improvements of the efficiency of photo-generation of non-thermal electrons. In particular, as can be seen from Fig. 4, as the local field is increased, the power fraction going to non-equilibrium increases to $10^{-5}$. This improvement motivates the study of the non-thermal electron distribution for higher intensities. Such study, however, will require extending the existing formulation by extracting also the metal permittivity from the non-equilibrium electron distribution $f$, self-consistently (like done above for the electron temperature). Other pathways for improved “hot electron” harvesting may rely on interband transitions due to photons with energies far above the interband threshold [24, 44], or optimizing the nanostructure geometry to minimize heating and maximize the local fields [45], e.g., using single nm particles [1] (which support the same number of non-thermal carriers but lower heating levels).
Finally, the formulation we developed serves as an essential first step towards realistic calculations of the complete energy harvesting process, including especially the tunneling process, and the interaction with the environment, be it a solution, gas phase or a semiconductor. Our formulation enables, for the first time, a quantitative comparison with experimental studies of all the above processes and the related devices. Similarly, our formulation can be used to separate thermal and non-thermal effects in many other solid-state systems away from equilibrium, in particular, semiconductor-based photovoltaic and thermo-photovoltaic systems.

METHODS

Below, we describe briefly the expressions of the terms in Eq. (1) and the underlying assumptions of our model. More details can be found in SM Section I.

Electron excitation due to photon absorption increases the electron energy by $\hbar \omega$, thus, generating an electron and a hole, see Fig. S1(a); it is described (via the term $\Phi_{ex}[f]$) using an improved version of the Fermi golden rule type form suggested in [18, 19, 22, 36] which here also incorporates explicitly the absorption lineshape of the nanostructure, see Eq. (S9).

Electron-phonon ($e-ph$) collisions cause energy transfer between the electrons and lattice; they occur within a (narrow) energy window (width comparable to the Debye energy, $\hbar \omega_D$) near the Fermi energy, see Fig. S1(b); they are described by the Bloch-Boltzmann-Peierls form [18, 31, 46].

Electron-electron ($e-e$) collisions are responsible for conversion of the non-thermal energy to thermal energy, i.e., to proper heat generation. These collisions are described within the framework of Fermi liquid theory [47] (see Fig. S1(c)), and are separated into a relaxation-type scattering term, $(\Delta_T f)_{e-e}$, and a term $F_{e-e}(E)$. The latter is defined by the condition

$$\int_0^{\infty} E \rho_e(E) \left[(\Delta_T f)_{e-e} + F_{e-e}(E)\right] dE = 0,$$

which ensures that the electron energy, defined as $U_e \equiv \int_0^{\infty} E \rho_e(E) f(E,T_e,T_{ph}) dE$, is conserved. Such a term is regularly included in Boltzmann models of fluid dynamics, where it is known as the Lorentz term [48], but to our knowledge, was not employed in the context of illuminated metal nanostructures. Within this approximation, a simple form for the $e - e$ terms in Eqs. (2)-(3) is found, namely

$$\left[\left(\frac{\partial f}{\partial t}\right)_{e-e} - \left(\frac{\partial f_T}{\partial t}\right)_{e-e}\right] = (\Delta_T f)_{e-e},$$
\[
\left( \frac{\partial f^T}{\partial t} \right)_{e-e} = \mathcal{F}_{e-e}(\mathcal{E}).
\]

(6)

We emphasize that our treatment (Eq. (1)) intentionally avoids the extensive discussions on the origins of the collisions rates (see e.g., [22, 24, 49]); this allows us to treat the electron states in terms of their energy (rather than momentum). Further, interband transitions are neglected in Eq. (1). We also neglect any considerations associated with charge carrier transport due to drift or various inhomogeneities (field, temperature etc.); such inhomogeneities are weak, especially for (spherical) nanoparticles of a few nm size. Similar simplifications were adopted in most previous studies of “hot” electron generation, e.g., [22, 26–28, 39]). These neglected effects can be implemented in our formalism in a straightforward way.

The steady-state solution of Eq. (1) was attained by writing the (thermal) electron and phonon energies as the product of the corresponding heat capacities and temperatures and letting the system evolve naturally to the steady state by ramping up slowly the electric field. Table SI shows the values of all parameters used in our simulations. We observe that the results are insensitive to the initial conditions and choice of various parameter values.

Finally, we emphasize that the results shown in the main text are not sensitive to the details of the general model (Eqs. (1)-(3)). In fact, our procedure can be made more system specific; for instance, the metal band structure can be taken into account [24, 49], few nm nanoparticles can be studied by writing the BE in momentum space and discretizing it [22], and further quantum effects may be considered by going from the BE to a quantum master equation [26–28]. We do not expect any such change to have more than a moderate quantitative effect on the results shown below.

Author contribution: Both authors were involved in all stages of the research and paper writing.


Negative values of $f - f^T$ referred to as holes, regardless of their position with respect to the Fermi energy. This nomenclature is conventional within the literature [33].

In particular, the local field in this configuration gives a plasmonic near-field enhancement, of at least an order of magnitude, depending on the geometry and material quality. Our approach applies to any other configuration just by scaling the local field appropriately, see SM, Section II.

We note that since $\Delta f$ (and $\Delta f^{NT}$ below) are not distributions, but rather, differences of distributions, they can attain negative numbers, representing holes.

Observing the expected multiple step structure, as in [20], is numerically very challenging.

Note that the failure to account for the electron temperature means that they slightly over-estimate the relaxation rate of the electron system.
FIG. 1: **Full non-equilibrium electron distribution under illumination.** The steady-state of the system is determined by the balance of three processes, shown on the background of the thermal distribution (Grey). 

**a:** absorption of photons by an electron, with an energy quanta $\hbar \omega$. 

**b:** electron (red) - phonon (green) scattering, which leads to lattice heating. 

**c:** electron-electron scattering, which leads to thermalization and electron heating. In addition, the excess thermal energy from the lattice can be transferred to the environment. 

**d:** Deviation from the equilibrium distribution at the ambient electron temperature, namely, $\Delta f \equiv f(E, T_e, T_{ph}) - f(T, T_{env})$, as a function of electron energy for various incoming field levels; the system is a bulk Ag illuminated by $\hbar \omega = 2.25$eV photons, see all parameters values in Table S1. Non-thermal hole densities, which correspond to $\Delta f < 0$, are shown for simplicity in opposite sign. The dashed vertical line represents the Fermi energy. The various dips are artifacts of the semilogarithmic scale - they represent sign changes of $\Delta f$. 
FIG. 2: Non-thermal contribution to non-equilibrium. a: Comparison of the true non-equilibrium distribution $\Delta f^{NT} \equiv f(E, T_e, T_{ph}) - f^T(E, T_e)$ with $\Delta f$ within the energy range close to the Fermi energy for $|\vec{E}| = 10^4[V/m]$. The true non-equilibrium is smaller and of opposite sign, indicating the presence of non-thermal holes (electrons) above (below) the Fermi energy. b: The populations $f(E)$ of electrons at $E = 1.8$ eV above the Fermi level (blue rectangles) and electrons at $E = 2.5$ eV ($> \hbar \omega$) above the Fermi level (yellow triangles), all as a function of local field, showing a quadratic dependence between illumination field and hot carrier population (with a similar slope).

FIG. 3: Temperature rise under illumination. The electron (blue) and lattice (orange) temperatures extracted from the data of Figs. 1-2 as a function of the local field (semilogarithmic scale). The inset shows the behaviour also at lower intensities on a linear scale, showing the linear dependence more clearly.
FIG. 4: Power density and its distribution between the different channels. Power densities going into the thermal electron and lattice systems ($W_{e-e}$ in green diamonds and $W_{e-ph}$ in orange triangles, respectively), compared with the power going to the non-thermal electrons ($W_{eNTex}$ in blue squares), all as a function of local field. The power fraction that flows into the thermal channels (i.e. to heat the systems) is substantially larger than that going into generating non-thermal electrons.