“Hot” electrons in metallic nanostructures - non-thermal carriers or heating?

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Abstract

Determining the electron distribution in an illuminated metal is a fundamental problem in physics, and an essential step towards applications such as photo-catalysis for green fuels. It is particularly important to understand how different is this light-induced distribution from the distribution that ensues from just increasing the temperature, i.e., from heating. Here, we develop coupled Boltzmann-heat equations where the temperatures of the electrons and the phonons are determined uniquely by only requiring energy conservation and enforcing basic thermodynamics. We find that the electron and lattice temperatures are similar, justifying (for the first time, to our knowledge) the (classical) single temperature models. We also show that, surprisingly, the non-equilibrium distribution is dominated by holes above the Fermi level. Most importantly, we find that although the number of high energy non-thermal electrons is substantially larger than in equilibrium, the fraction of absorbed power that actually leads to their generation is extremely small; instead, almost all absorbed power causes mere heating. This finding also shows that the common ambiguity associated with assigning a temperature to the non-equilibrium electron system is remarkably small. Our formulation allows for the first time a unique quantitative comparison of theory and measurements of steady-state electron distributions in metallic nanostructures.
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, since the energy of the absorbed photons 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 [3–8] or artificial photosynthesis [9–11]; These processes have an immense importance in paving the way towards realistic alternatives for fossil fuels. Other applications include photodetection [12–15], up-conversion [14–15] 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 “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 include three channels of energy transfer (see Fig. 1(a)), namely (i) photon energy absorption by the electrons, (ii) electron-electron interactions (leading to thermalization), and (iii) electron-phonon interaction (leading to energy transfer from the electrons to the underlying lattice). Furthermore, the theory should take into account energy leakage from the lattice to the environment (e.g. a substrate or solution), and 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 is studied [16–21], focusing on an accurate description of the material properties, e.g., metal band structure...
and relaxation rates \cite{22,24}; some studies also accounted for the electron temperature dynamics \cite{19,21} and (to some extent) for the permittivity \cite{21} dynamics. On the other hand, the few pioneering theoretical studies of the steady-state non-equilibrium under CW illumination \cite{25,27} accounted for the electron distribution in great detail, but did not evaluate the rise in the electron and phonon temperatures accurately, nor describe the energy leakage to the ambient environment in detail.

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 unique value for the temperature, inherently an equilibrium property? \cite{28}. Yet, it is well-known that the temperature of metallic nanostructures does increase upon CW illumination, sometime to the degree of melting (or killing cancer cells); this process is traditionally described using classical, single temperature heat equations (see, e.g., \cite{29}).

Here, we suggest a unique self-contained theory for the photo-generation of non-equilibrium energetic carriers in metal nanostructures that reconciles this “paradox”. The framework we chose 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., \cite{16,19,21,30,35}. To the BE we add, in a self-consistent way, electron-phonon scattering - via conservation of energy - thus allowing for the electron and phonon (lattice) temperatures to rise above the ambient temperature and for the energy leakage to the environment to be quantified correctly. Furthermore, using a specific form for the electron-electron thermalization channel (see next section) allows us to determine the electron temperature without ambiguity. These aspects distinguish our calculation of the steady-state non-equilibrium from previous ones.

Using our theory, we show that the population of non-equilibrium energetic electrons and holes can increase dramatically under illumination, yet this process is extremely inefficient, as almost all 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 \cite{29}. 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. Detailed comparison to earlier work is presented throughout the main text and the SI.

Model
We start by writing down the Boltzmann equation in its generic form,

$$\frac{\partial f(\mathcal{E}, T_e, T_{ph})}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_{ex} + \left( \frac{\partial f}{\partial t} \right)_{e-e} + \left( \frac{\partial f}{\partial t} \right)_{e-ph}. \quad (1)$$

Here, $f$ is the electron distribution function at an energy $\mathcal{E}$, 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. Electron excitation due to photon absorption increases the electron energy by $\hbar \omega$, thus, generating an electron and a hole, see Fig. 1(a) and Fig. S1(a); it is described (via the term $\left( \frac{\partial f}{\partial t} \right)_{ex}$) using an improved version of the Fermi golden rule type form suggested in [17, 18, 21, 35] 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 (whose width is comparable to the Debye energy, $\hbar \omega_D$) near the Fermi energy, see Fig. 1(b) and Fig. S1(b). We adopt a general Bloch-Boltzmann-Peierls form for the $e-ph$ collisions [17, 30, 36].

Electron-electron ($e-e$) collisions lead to thermalization. They occur throughout the conduction band, but are strongly dependent on the energy - for electron energies close to the Fermi energy they are relatively slower than for electrons with energies much higher than the Fermi energy, which can be as fast as a few femtoseconds, see Fig. 1(c) and [19, 21, 37].

Traditionally, two generic models are used to describe these collisions. The exact approach invokes the 4-body interactions between the incoming and outgoing particles within the Fermi golden rule formulation, see e.g., [16, 19, 30, 33, 36] as well as SI Sections 1.b & 1.c. This approach has two main drawbacks - first, evaluation of the resulting collision integrals is highly time-consuming [18]; second, this approach obscures the physics - it is not clear what is the state into which the system wishes to relax.
An alternative is to adopt the so-called relaxation time approximation, whereby it is assumed that within an energy-dependent time scale $\tau_{e-e}(\mathcal{E})$, the non-equilibrium electron distribution relaxes to a Fermi-Dirac form $f^T(\mathcal{E}, T_e)$ \cite{16, 27, 30, 33} with a well-defined temperature $T_e$, 
\[
\left( \frac{\partial f(\mathcal{E})}{\partial t} \right)_{e-e} = -\frac{f - f^T(T_e)}{\tau_{e-e}(\mathcal{E})}.
\]

The electron temperature that characterizes that Fermi-Dirac distribution is the temperature that the electron subsystem will reach if the illumination is stopped and no additional energy leaks to the phonon subsystem. The relaxation time approximation is known to be an excellent approximation for small deviations from equilibrium (especially assuming the collisions are elastic and isotropic \cite{38}). In this approach, $e - e$ collisions are much simpler to compute, and the physical principle which is hidden in the full collision integral description, namely, the desire of the electron system to reach a Fermi-Dirac distribution, is illustrated clearly. Most importantly, the relaxation time approximation allows us to eliminate the ambiguity in the determination of the temperature of the electron subsystem.

What remains to be done is to determine $T_{ph}$ - it controls the rate of energy transfer from the electron subsystem to the phonon subsystem, and then to the environment. Recent studies of the steady-state non-equilibrium in metals relied on a fixed value for $T_{ph}$ (choosing it to be either identical to the electron temperature, or to the environment temperature) and/or treated the rate of $e - ph$ energy transfer using the relaxation time approximation with a fixed $e - ph$ collision rate. While phenomenologically correct, these approaches ignore the dependence of the energy transfer to the environment on the nanoparticle shape and on the thermal properties of the host material. Therefore, not only this phenomenological approach fails to ensure energy conservation, but also it fails to provide a correct quantitative prediction of the electron distribution near the Fermi energy (which is strongly dependent on $T_{ph}$) and provides incorrect predictions regarding the role of nanoparticle shape and host properties on the steady-state electron distribution and the temperatures.

In order to determine $T_{ph}$ self-consistently while ensuring energy conservation, one has to account for the “macroscopic” properties of the problem. Specifically, we multiply Eq. (1) 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 electronic distribution,
\[
\frac{dU_e}{dt} = W_{ex} - W_{e-ph}.
\]
Eq. (2) has a simple and intuitive interpretation: the dynamics of the electron energy
is determined by the balance between the heat that flows in due to photo-excitation
\[ W_{ex} \equiv \int \mathcal{E} \rho_e(\mathcal{E}) \left( \frac{\partial f}{\partial t} \right)_{ex} d\mathcal{E} \]
and the heat that flows out to the lattice \( W_{e-ph} \equiv -\int \mathcal{E} \rho_e(\mathcal{E}) \left( \frac{\partial f}{\partial t} \right)_{e-ph} d\mathcal{E} \), see SI, Section 1.b).

In similarity to Eq. (2), the total energy of the lattice, \( U_{ph} \), is balanced by the heat flowing in from the electronic system and flowing out to the environment, namely,
\[ \frac{dU_{ph}}{dt} = W_{e-ph} - G_{ph-env} (T_{ph} - T_{env}). \]  

Here, \( T_{env} \) 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. (1)-(3) provide a general formulation for the non-thermal electron generation, electron temperature and lattice temperature in any metal nanostructure under arbitrary illumination conditions; it includes no ad hoc assumptions. Once a steady-state solution for these equations is found, energy conservation is ensured - the power flowing into the metal due to photon absorption is exactly balanced by heat leakage to the environment. Within the relaxation time approach, there is only one pair of values for the electron and phonon temperatures for which this happens. Our “macroscopic” approach thus allowed us to determine the temperatures in a system which is out of equilibrium in a unique and unambiguous way.

The equations require as input the local electric field distribution from a solution of Maxwell’s equations for the nanostructure of choice, see SI, Section 2. 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. For concreteness, we chose parameters for Ag, taken from comparison to experiments of ultrafast illumination [17]; 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 [9, 39, 70], see Table S1; this configuration also justifies the neglect of interband transitions (see also SI, Section 1). As we demonstrate, this generic case leads to several surprising qualitative new insights, as well as to quantitative predictions of non-equilibrium carrier distributions.

**Results**
“Hot” electron distribution. Fig. 1 shows the deviation of the electron distribution from the distribution at the ambient temperature (i.e., in the dark), $\Delta f \equiv f(\mathcal{E}, T_e, T_{ph}) - f^T(\mathcal{E}, T_{env})$, as a function of electron energy for various local field levels. The distributions depend on the local field quantitatively, but are qualitatively similar, showing that the 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\[71\], see Fig. 2(a). This is in accord with the approximate (semi-classical) solution of the Boltzmann equation (see e.g., [30, 33]) and the standard interpretation of the non-equilibrium distribution (see e.g., [40, 41]). The minute deviation from equilibrium (see scale in Fig. 1d) justifies a-posteriori the assignment of the system with an electron and phonon temperature.

Non-thermal contribution to “hot” electron distribution. It is clear that the distributions $\Delta f$ 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, $\Delta f^{NT} \equiv f(\mathcal{E}, T_e, T_{ph}) - f^T(\mathcal{E}, T_e)$. 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 $f^T(\mathcal{E}, T_e)$ and $f^T(\mathcal{E}, T_{env})$ 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 [30, 33]) 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, compare Fig. 1(a)
and Fig. 1(b) with Fig. S1(b).

Second, further away from the Fermi energy, $\hbar \omega$-wide (roughly symmetric) shoulders 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 were so sought-after 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\[72\]. 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 non-thermal electron distributions we obtained look similar to those obtained by accounting only for photon excitation \[22, 23, 40, 41\]. However, as pointed out in \[22, 27\], the latter distributions are valid only immediately after illumination by an ultrashort pulse; they would be similar to the steady-state distributions only if all other terms in the BE were energy-independent, which is not the case (see SI, Section 1 and Fig. S1). More specifically, they do not predict correctly the electron distribution near the Fermi energy; this means that the total energy stored in the electron system is not correctly accounted for and that the contribution of inter-band transitions to the non-equilibrium cannot be correctly determined.

On the other hand, these approaches can be used to provide a quantitative prediction of the electron distribution away from the Fermi energy, where $e-ph$ interactions are negligible; peculiarly, however, this was not attempted in \[22, 23, 40, 41\], and instead, only claims about the qualitative features of the electron distributions were made. The electron distributions we obtained are also different from the steady-state distributions obtained previously in \[20, 25, 27\]. The main reason for these differences is that these studies did not correctly account for the electron and phonon temperatures, hence, the energy flow from the thermal electrons to the lattice. This makes the total energy in the electron system in those studies incorrect.

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 SI, Section 2), 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., \[39, 42\]). Indeed, Fig. 2(b) shows that the non-thermal
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, $\Delta f \equiv f(E, T_e, T_{ph}) - f^T(E, T_{env})$, as a function of electron energy for various incoming field levels; the system is a bulk Ag illuminated by $\hbar \omega = 2.25 \text{eV}$ 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 $\Delta f$.

electron distribution has a quadratic dependence on the electric field ($\Delta f^{NT} \sim |E|^2$).

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 SI, Section 2). Since $G_{ph-env}$ is proportional to the thermal conductivity of the host and inversely proportional to the
FIG. 2: Non-thermal contribution to non-equilibrium. a: Comparison of the true non-equilibrium distribution $\Delta f^{NT} \equiv f(\mathcal{E}, T_e, T_{ph}) - f^T(\mathcal{E}, T_e)$ with $\Delta f$ within the energy range close to the Fermi energy for $|\mathbf{E}|^2 = 10^9 [V/m]$. 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 $f(\mathcal{E})$ of electrons at $\mathcal{E} = 1.8$ eV above the Fermi level (blue rectangles) and electrons at $\mathcal{E} = 2.5$ 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).

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. Since the temperature rise is also inversely proportional to $G_{ph-env}$ (see [43] and Fig. S2), the difference in the photo-catalytic rate between the TiO$_2$ and SiO$_2$ substrates (compare [39] and [44]) 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 [44].

Electron and phonon temperatures. 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 [29]. 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 and quantitative) justification, to the best of our knowledge, for the use of the single temperature heat equation in the context of metallic nanostructures under illumination [29]. Neverthe-
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.

less, we note that the temperature difference is proportional to the incoming intensity such that for high intensities, the single temperature model may not be sufficient.

**Efficiency.** 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), providing a way to evaluate the efficiency of the 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 \( W_{ex}^{NT} \equiv \int E \rho_e(\mathcal{E}) \left( \frac{\partial f}{\partial t} \right)_{ex} d\mathcal{E} \) is more than 10(!) orders of magnitude lower than the power invested in the heating of the electrons and phonons (which are accordingly 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. We emphasize that the above efficiency calculation requires the determination of the steady-state temperatures. It is thus the main result of the current study.

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 \[3, 4, 6, 8, 20, 40, 42\]. Indeed, a comparison with the pure thermal distribution of high energy electrons (Fig. 2) shows that the absolute electron popul-
lation 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 [23, 45], or optimizing the nanostucture geometry to minimize heating and maximize the local fields [46], e.g., using single nm particles [47] (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 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.
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 ($W_{eNT}^{ex}$ 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.

I. SUPPLEMENTARY INFORMATION - SOLUTION OF THE QUANTUM-LIKE BOLTZMANN EQUATION

We determine the electron distribution in the conduction (sp) band, $f(\mathcal{E}, T_e, T_{ph})$, in a metal nanostructure under continuous wave (CW) illumination by solving the quantum-like Boltzmann equation (BE). This model is in wide use for such systems [16, 19, 30, 31, 35, 38]; it is valid for nanoparticles which are more than a few nm in size (hence, not requiring energy discretization) [21, 27] and for systems where coherence and correlations between electrons are negligible. The latter assumption holds for a simple metal at room temperatures (or higher), as it has a large density of electrons and fast collision mechanisms. In order to include quantum finite size effects or quantum coherence effects, one can use the known relation between the discretized BE and quantum master equations [48, 49].

For simplicity, we consider a quasi-free electron gas such that the conduction band is purely parabolic (with a Fermi energy of $\mathcal{E}_F = 5.1$eV and total size of $\mathcal{E}_{max} = 9$eV, typical to Ag [31]). This allows to represent the electron states in terms of energy $\mathcal{E}$ rather than momentum. We also neglect interband ($d$ to $sp$) transitions - these have a small role when describing metals like Al illuminated by visible light, Ag for wavelengths longer than about
500nm or so, or Au for near infrared frequencies, where a dominantly Drude response is exhibited.

The resulting Boltzmann equation is

$$\frac{\partial f}{\partial t} \left( \mathcal{E}(\vec{k}); T_e, T_{ph} \right) = \left( \frac{\partial f}{\partial t} \right)_{\text{photon absorption}} + \left( \frac{\partial f}{\partial t} \right)_{e-\text{ph collisions}} + \left( \frac{\partial f}{\partial t} \right)_{e-e \text{ collisions}} ,$$  \hspace{1cm} (4)

where \( f \) is the electron distribution function at an energy \( \mathcal{E} \), 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. The first term on the right-hand-side (RHS) of Eq. (4) describes excitation of conduction electrons due to photon absorption, see SI Section IA below for its explicit form. The second term on the RHS of Eq. (4) describes energy relaxation due to collisions between electrons and phonons, see SI Section IB below for its explicit form. This interaction causes the electrons in our model to be only quasi-free. The third term on the RHS of Eq. (4) represents the thermalization induced by \( e-e \) collisions, i.e., the convergence of the non-thermal population into the thermalized Fermi-Dirac distribution, given by

$$f^T (\mathcal{E}; T_e) = \left( 1 + e^{(\mathcal{E}-\mathcal{E}_F)/k_B T_e} \right)^{-1},$$  \hspace{1cm} (5)

where \( k_B \) is the Boltzmann constant [74].

Note that our model does not require indicating what is the exact nature of the various collisions (Landau damping, surface/phonon-assisted, etc., see discussions in [37, 50]), but rather, it accounts only for their cumulative rate. Our model also does not account for electron acceleration due to the force exerted on them by the electric field (which involves a classical description, see SI Section IA below), nor for drift due to its gradients or due to temperature gradients; These effects will be small in the regime of intensities considered in our study, especially for few nm (spherical) particles (see also SI Section II below) [43]. We also ignore tunneling aspects, which have to be studied for the quantification of processes such as photo-catalysis, photo-detection etc. and secondary light emission processes (Raman scattering, fluorescence) which are weak. Similar simplifications were adopted in most previous studies of this problem, e.g., [21, 25, 26, 40, 51]). These neglected effects can be implemented in our formalism in a straightforward way.
FIG. 5: (Color online) (a) \( \left( \frac{\partial f}{\partial t} \right)_{ex} \) [12] as a function of electron energy for a local field of \( |\vec{E}| = 7 \cdot 10^3 \text{V/m} \). (b) The \( e - ph \) collision rate [13] as a function of electron energy for \( T_e - T_{ph} = 0.2^\circ \text{K} \). The inset shows the four competing phonon generation/absorption processes. (c) The \( e - e \) collision rate as a function of electron energy, as given by Fermi liquid theory, Eq. [14].

A. The quantum mechanical excitation term

Usually, the BE is regarded as a (semi-)classical model of electron dynamics. Indeed, several popular textbooks draw the links between the BE to the classical model of an electron motion in an electric field (e.g., [30, 31, 33]). In this case, the change of momentum of the electrons (acceleration) due to the force exerted on them by the electric field corresponds to a coherent excitation term, i.e., a term which is proportional to \( \frac{\partial}{\partial E} \frac{\partial \vec{E}}{\partial \vec{k}} \). However, since it relies on a classical field, this expression describes the photon-electron interaction correctly only if the energy imparted on the electron by the electric field is much greater than the energy of a single photon [34]. Since this is not the case, this term does not allow one to derive correctly the non-equilibrium dynamics; in fact, this failure to produce the experimental observation triggered Einstein to employ a quantized model for the photo-electric effect, and eventually led to the creation of quantum mechanics theory, as we know it.
In order to circumvent this problem within the BE, frequently the (semi-)classical (linear (∼ $\vec{E}$), coherent) excitation term is replaced by a quantum-like (∼ $|\vec{E}|^2$, incoherent) term derived from the Fermi golden rule [17–19, 21, 35, 40]. Early derivations of this term (e.g. [17]) did not supply a rigorous expression for its magnitude, but rather fit its magnitude to experimental results. Later studies attempted to link the magnitude of this term to the total absorbed power [19].

Here, we employ the simpler, elegant expression proposed in [35], namely, we define $A(E; \omega)$ such that

$$A(E_{\text{final}} = E; \omega) = \frac{n_A(\omega) \cdot D_J(E, E - \hbar \omega) \rho_J(E, E - \hbar \omega)}{N_A \int D_J(E, E - \hbar \omega) \rho_J(E, E - \hbar \omega) dE},$$

where $D_J(E_{\text{final}}, E_{\text{initial}})$ is the squared magnitude of a transition matrix element for the electronic process $E_{\text{initial}} \rightarrow E_{\text{final}}$; Further, $\rho_J$ is the population-weighted density of pair states,

$$\rho_J(E_{\text{final}}, E_{\text{initial}}) = [f(E_{\text{initial}}) \rho_e(E_{\text{initial}})] \frac{[1 - f(E_{\text{final}}) \rho_e(E_{\text{final}})]}{},$$

and $\rho_e = \frac{3 n_e}{2 \pi} \sqrt{\frac{\varepsilon}{2 \pi}}$ is the density of states of a free electron gas [31], $n_e$ being the electron density. Finally, $n_A(\omega)$ is the number density of absorbed $\hbar \omega$ photons per unit time between $\omega$ and $\omega + d\omega$ and $N_A = \int d\omega n_A(\omega)$ is the total number density of absorbed photons per unit time. For CW illumination, it is given by

$$N_A = \frac{\langle p_{\text{abs}}(\vec{r}, t) \rangle_t}{\hbar \omega},$$

where the absorbed optical power density (in units of $W/m^3$) is given by the Poynting vector [52], namely,

$$\langle p_{\text{abs}}(t) \rangle_t = \omega \varepsilon''(\omega, T_e, T_{ph}) \langle \vec{E}(t) \cdot \vec{E}(t) \rangle_t,$$

where the temporal averaging, $\langle \rangle_t$, is performed over a single optical cycle such that only the time-independent component remains. Note that the absorption lineshape arises naturally from the spectral dependence of the local electric field in Eq. (9); it depends on the nanostructure geometry and the permittivities of its constituents. This way, there is no need to introduce the lineshape phenomenologically as done in [35].
The absorption probability of a $\hbar \omega$ photon, $A (\omega)$, satisfies
\[
\int_0^\infty A(\mathcal{E}; \omega) d\mathcal{E} = \frac{n_A(\omega)}{N_A},
\]
and the net change of electronic population at energy $\mathcal{E}$ per unit time and energy at time $t$ due to absorption is $N_A \phi_A$, where
\[
\phi_A(\mathcal{E}; \omega) = \int_0^\infty d\omega [A(\mathcal{E}; \omega) - A(\mathcal{E} + \hbar \omega; \omega)],
\]
is a quantity describing the total (probability of a) population change at energy $\mathcal{E}$ per unit time and energy at time $t$.

Altogether, the change of population due to photon excitation is given by
\[
\left( \frac{\partial f}{\partial t} \right)_{ex} (\mathcal{E}) = \frac{N_A \phi_A(\mathcal{E})}{\rho_e(\mathcal{E})},
\]
so that electron number conservation is ensured, $\int d\mathcal{E} \rho_e(\mathcal{E}) \left( \frac{\partial f}{\partial t} \right)_{ex} (\mathcal{E}) \sim \int d\mathcal{E} \phi_A(\mathcal{E}) = 0$.

The functional form of Eq. (12) is shown in Fig. 5(a) - one can see a roughly flat, $\hbar \omega$-wide region of positive rate above the Fermi energy, and a corresponding negative regime below the Fermi energy. In that regard, the incoherent, quantum-like, $|\vec{E}|^2$ excitation term reproduces the predictions of the photoelectric effect. The slight asymmetry originates from the density of states $\rho_e(\mathcal{E})$.[75]. Some earlier papers, e.g., [41] (and potentially, also [40][76]) used excitation rates similar to those of Eq. (12) to qualitatively describe the steady-state “hot electron” density. However, such a qualitative estimate is appropriate only in case all other terms in the underlying equation are energy-independent. Clearly, from Fig. 5, this is not generically the case.

Note that in our approach, we effectively assume that momentum is conserved for all transitions. A more accurate description requires one to distinguish between the electron states according to their momentum, as done e.g., in [18] for a continuum of electron states and in [21][27] for discretized electron states. However, it was shown in [27] Figs. 4 & 5)) that these considerations have, at most, a moderate effect on the excitation rate for particles as small as 2nm, thus, justifying our approach. In that sense, our treatment provides a tight upper limit for efficiency of non-thermal generation.
B. The $e-ph$ collision term

In [17], the rate of change of $f$ due to $e-ph$ collisions is derived from the Bloch-Boltzmann-Peierls form [30, 36][77], giving

$$
\left( \frac{\partial f}{\partial t} \right)_{e-ph} = -\mathcal{X} \sqrt{\frac{m^*_\text{eff}}{2\pi \rho}} \frac{E_D}{\hbar v_{ph}} \int_0^{E_D} d\epsilon_{ph} \frac{\epsilon_{ph}^2}{\rho} \frac{\sqrt{2}}{\pi} \left\{ f(\epsilon) \left[ 1 - f(\epsilon + \epsilon_{ph}) \right] n(\epsilon_{ph}) + [1 - f(\epsilon - \epsilon_{ph})] \left[ n(\epsilon_{ph}) + 1 \right] \right\} 
$$

Here, $\mathcal{X} \sim 2\mathcal{E}_F/3$ [17] is the effective deformation potential, $\rho$ is the material density and $m^*_\text{eff}$ is the effective electron mass [78]. For simplicity, we further assume that the phonon system is in equilibrium, so that $n(\epsilon_{ph}) = n^T(\epsilon_{ph}) = \left( e^{\epsilon_{ph}/k_B T_{ph}} - 1 \right)^{-1}$ is the Bose-Einstein distribution function where $\epsilon_{ph}$ is the phonon energy and $T_{ph}$ is the phonon temperature; more advanced models that account also for the possible non-equilibrium of the lattice exist (see e.g., in [19, 53]) but are relatively rare. Eq. (13) relies on the Debye model [79], namely, a linear dispersion relation for the phonons is assumed, $\epsilon_{ph} = v_{ph} \hbar |q|$, where $v_{ph}$ is the speed of sound ($\approx 3650\text{m/s}$ in Ag) and $q$ is the phonon momentum. Beyond the Debye energy, $E_D = k_B T_D \approx 0.015\text{eV}$ for Ag, the density of phonon states vanishes. Previous work emphasized the insensitivity of the non-equilibrium dynamics to the phonon density of states and dispersion relations, thus, justifying the adoption of this simple model [17, 54] and the neglect of the phonon non-equilibrium.

The two terms associated with $f(\epsilon + \epsilon_{ph})$ describe phonon absorption, whereas the two terms associated with $f(\epsilon - \epsilon_{ph})$ describe phonon emission. Fig. 5(b) shows the energy dependence of these four different processes described by Eq. (13) for $T_e - T_{ph} = 0.2^\circ\text{K}$, neglecting the small non-thermal part of the distribution (justified a-posteriori). For this temperature difference, an estimate based on the relaxation time approximation for $e-ph$ collisions allows us to relate the magnitude of each term ($\sim 10^{12}/\text{sec}$) to a collision rate of $\sim 10\text{fs}$, in accord with the value sometimes adopted within this context [33]. However, since these four processes compete with each other, the resulting total change of the distribution due to $e-ph$ collisions is several orders of magnitude slower. Overall, one can see that (13) has a rather symmetric, $\sim \hbar \omega_D$-wide Lorentz-like lineshape. For $T_e > T_{ph}$, the rate is negative (positive) above (below) the Fermi energy, reflecting the higher likelihood of phonon emission processes, i.e., energy is transferred from the electrons to the phonons. In order to see this more clearly, we can calculate the rate of energy transfer between the electrons and
phonons by multiplying by $\mathcal{E} \rho_e(\mathcal{E})$ and integrating over all electron energies. The resulting integral, defined as $W_{e-ph} \equiv -\int_0^\infty \mathcal{E} \rho_e(\mathcal{E}) \left( \frac{\partial f}{\partial \mathcal{E}} \right)_{e-ph} d\mathcal{E}$, is hardly distinguishable from its thermal counterpart, $W_{e-ph}^T \equiv -\int_0^\infty \mathcal{E} \rho_e(\mathcal{E}) \left( \frac{\partial f}{\partial \mathcal{E}} \right)_{e-ph} d\mathcal{E}$, which is usually represented by $G_{e-ph}(T_e - T_{ph})$ \[36\]. For $T_e > T_{ph}$, the factor $\mathcal{E} \rho_e(\mathcal{E})$ weighs favourably the region above the Fermi energy, such that $W_{e-ph}$ and $W_{e-ph}^T$ are positive. In \[54\], an ab-initio, parameter-free derivation of the electron-phonon coupling coefficient based on density functional theory found $G_{e-ph} \sim 3 \cdot 10^{16} \text{W/m}^3 \text{K}$ for Ag, in agreement with values found in previous works \[17, 19, 36, 55–56\], and with a negligible temperature-dependence, up to about $3000^\circ \text{K}$.

We note that our approach accounts for the mutual effect $e-e$ collisions have on $e-ph$ collisions \[16\], since $e-ph$ collisions are treated by the $f$-dependent rate \[13\] (rather than within the relaxation time approximation).

C. The $e-e$ collision term

The rate of $e-e$ collisions at thermal equilibrium is usually slower than the $e-ph$ collision rate (order of picoseconds) since they involve only deviations from the independent electron approximation \[31\]. However, away from thermal equilibrium, the $e-e$ collision rates of high energy non-thermal electrons increase substantially and can become comparable to the $e-ph$ collision rate or even faster (see Fig. 5(c)). Specifically, by Landau’s Fermi liquid theory \[58\], the $e-e$ collision rate is given by

$$\tau_{e-e}^{-1}(\mathcal{E}) = K \left[ (\pi k_B T_e)^2 + (\mathcal{E} - \mathcal{E}_F)^2 \right],$$

(14)

where $K = m_{eff}^* / 8 \pi^4 \hbar^6 W_{e-e}$ is the characteristic $e-e$ scattering constant that contains the angular-averaged scattering probability $W_{e-e}$ and the effective mass of the electron, $m_{eff}^*$; for Au and Ag, $K = 2 \cdot 10^{14} / eV^2 \text{s} \[16\]$. Similar variations of this expressions within a continuum of states description were used e.g., in \[17, 19\] in the context of ultrafast illumination. The more recent calculations of the $e-e$ collision rate within a discretized electron energy description, e.g., in \[21, 37\] retrieved this expression. Experimental data obtained via two photon photo-emission measurements are found in excellent agreement with the Fermi liquid based expression (14), see discussion in \[19, 80\].

Since $e-e$ collisions are elastic (and within the approximation adopted here, also
isotropic) [38], we can adopt the relaxation time approximation, and write
\[(\Delta_{\tau} f)_{e-e} = \frac{f(\mathcal{E}, T_e, T_{ph}) - f^T(\mathcal{E}, T_e)}{\tau_{e-e}(\mathcal{E})}.\] (15)

However, we note that the regular $e-e$ term does not conserve the energy of the electron system as a whole (although it is supposed to, by the elastic nature of $e-e$ collisions). As a remedy, we introduce a term $\mathcal{F}_{e-e}(\mathcal{E})$, defined by the condition
\[
\int_{0}^{\infty} \mathcal{E} \rho_e(\mathcal{E}) [(\Delta_{\tau} f)_{e-e} + \mathcal{F}_{e-e}(\mathcal{E})] d\mathcal{E} = 0.
\]
It ensures that the electron energy, defined as $U_e \equiv \int_{0}^{\infty} \mathcal{E} \rho_e(\mathcal{E}) f(\mathcal{E}, T_e, T_{ph}) d\mathcal{E}$, is conserved. Such a term is regularly included in Boltzmann models of fluid dynamics, where it is known as the Lorentz term [59], but to our knowledge, was not employed in the context of illuminated metal nanostructures [81],[82].

Thus, overall, we have
\[
\left(\frac{\partial f}{\partial t}\right)_{e-e} = (\Delta_{\tau} f)_{e-e} + \mathcal{F}_{e-e}(\mathcal{E}).\] (16)

II. PRACTICAL CONSIDERATIONS

In order to avoid limiting the generality of our results, we did not indicate throughout the manuscript details of a specific nanostructure. In this SI Section, we discuss what needs to be done in order to apply our theory to a specific experimental configuration.

Throughout the manuscript, we treated $|\vec{E}|$ as a parameter representing the local field [83]. In order to evaluate the non-thermal carrier density for an actual nanostructure configuration and illumination pattern, one needs to solve the Maxwell equations for the given configuration (for example, $\vec{E} = \left[3\epsilon_h/(2\epsilon_h + \epsilon_m)\right] \vec{E}_{inc}$ for a small sphere illuminated uniformly) and apply our formulation locally, i.e., for each point in the nanostructure independently; this procedure was adopted in [27] and was complemented by surface/volume averaging. In that respect, the role of surface plasmon resonances in promoting “hot” carrier generation is obvious - at resonance, the local electric fields are enhanced, hence, the electron system is driven more strongly away from equilibrium.

For weak electric fields, like used in the current work, the distribution and temperatures can then be readily determined. For small spherical metal nanoparticles, the temperature(s) are uniform [13]. The majority of previous theoretical studies relied on these same assumptions (e.g., [21],[25],[40]) and many experimental studies of non-thermal carrier generation indeed used small metal spheres (e.g., [39],[44]).
For more complicated geometries, or for bigger nanostructures, the field may not be uniform. Nevertheless, the gradients of the electric fields are usually assumed to have a small effect on the electron distribution. The non-uniformity of the temperature is negligible, due to the relatively high thermal conductivity of the metal [43]. Due to these reasons, these gradients were neglected in all previous studies; we adopt the same approach here. For higher fields, the optical and thermal properties of the metal may change due to the rise in temperature, requiring a fully self-consistent solution of the coupled Maxwell, Boltzmann and heat equations. Such a treatment is left to a future study.

The size of the particle affects the field relatively weakly for sufficiently small size (for which the quasi-static approximation holds). However, as well-known [43], the nanoparticle temperature depends strongly on the particle size; for example, for nano-spheres, it grows quadratically with the radius $a$. In our formulation, this effect is accounted for via the value of the phonon-environment coupling, $G_{ph-env}$, which is usually calculated from first principles via molecular dynamics simulations, see e.g., [60–63]. Overall, it scales inversely with the surface area [18]; this is equivalent to assuming the total heat conductance to the environment is proportional to the particle surface area.

As pointed out in the main text, we have carried out additional calculations to demonstrate the dependence of electron distribution and temperatures on the particle size via $G_{ph-env}$. The original results (appearing in the main text figures (5nm; $G_{ph-env} = 5 \times 10^{14}$ W/m³K [64])) can now be compared to results for a particle which is 10 times bigger (50nm; $G_{ph-env} = 5 \times 10^{12}$ W/m³K). In Fig. 6(a) we plot the electron and phonon temperatures as a function of intensity for these two cases. As can be observed, the electron temperature rise is much larger for the larger particle (compare to Fig. 3) - about 30K. However, the difference between the electron and phonon temperatures is roughly the same; indeed, it can be shown analytically to be proportional to the incoming intensity which is the same for both sets of simulations.

In Fig. 6(b) we plot the electron non-equilibrium distribution (specifically, the absolute value of the deviation of the electron distribution from the Fermi distribution, $|\Delta f|$) for the two particle sizes and for two illumination levels, $|E|^2 = 10^5, 10^7$(V/m)$^2$. It is readily seen that the only deviations between the large and small particle cases are at the vicinity of the Fermi energy, but the non-thermal parts of the distributions (i.e., further away from $\varepsilon_F$, where $\Delta f^{NT} \sim \Delta f$) are insensitive to the particle size. In particular, we find that
the efficiency of non-thermal electron generation is roughly independent of particle size, but the overall heating scales as \(a^2\), in agreement with the single temperature (classical) heat equation. Such correspondence is absent in the simulations in \[27\], where the temperature was not adjusted for particles of different sizes\[84\]. This also means that smaller particles give rise to a higher relative efficiency of non-thermal carrier generation. This prediction should motivate a careful, single particle study that will enable one to verify this prediction vs. potentially contradicting claims based on measurements from macroscopic nanoparticle suspensions.

![Figure 6](image.png)

**FIG. 6:** (a) Electron (yellow) and phonon (blue) temperatures as a function of \(|\vec{E}|^2\), for a system with a host thermal conductivity \(G_{ph-env} = 5 \times 10^{12} \text{ W/m}^3\text{K}\), two orders of magnitude smaller than that employed in the simulations shown in Figs. 1-4. Correspondingly, the temperature rise is much larger, as well as the difference between the electron and phonon temperatures. (b) Deviation of the full non-equilibrium distribution from the thermal distribution for low host thermal conductivity and two intensities, \(|\vec{E}|^2 = 10^6, 10^8\text{(V/m)}^2\) (green and yellow dashed lines, respectively). On top of them are the distributions from the high \(G_{ph-env}\) values used in Fig. 1 (solid lines).

The results of Fig. 6(b) can be also interpreted in terms of the dependence of the non-thermal distribution on the host thermal conductivity. Indeed, the rate of energy density transfer to the environment \(G_{ph-env}\) is also proportional to the thermal conductivity of the host \[18\]. Thus, the different curves in Fig. 6(a) can be also associated with a system with a host thermal conductivity which is two orders of magnitude lower than the one presented in the main text. As for the larger nanoparticle, the electron temperature rise and the difference between the electron and phonon temperatures, are higher, as expected - indeed,
the heat flows away from the nanoparticle much more slowly for the larger nanoparticle. This shows, as stated in the main text, that if “hot” electrons play a dominant role in some experiment (say in photo-catalysis), then, these results should be unaffected by a change of host. Conversely, if the results are affected by a change of host material (as observed e.g., in [39, 44]), then it is not likely that the reason for that is the number of ”hot” electrons, but rather due to a thermal effect, or another chemical effect.

If one is interested in even smaller nanoparticles, then, within the energy state continuum description used in the current work, it may be necessary to account also for $e^{-}\text{surface}$ collisions (the so-called “quantum size effects”), as noted as early as in [65]. As this effect does not involve conservation of electron momentum, it can be accounted for in our formulation by adding a relaxation time like term, $(f_f^T)/\tau$, where $\tau$ is the time scale for these collisions which can be as fast as a few hundreds of femtoseconds in the case of a metal surface with atomic roughness [66]; accordingly, it is practically negligible with respect to the $e-e$ and $e-ph$ collision rates. Depending on the nature of the $e^{-}\text{surface}$ collisions, one may want to include/exclude them from the conservative term, $\mathcal{F}_{e-e}(\mathcal{E})$.

However, it should be noted that in more advanced models where the energy states are discretized (such that $e^{-}\text{surface}$ collisions are accounted for inherently), e.g., [21, 27], the electronic states and the phononic states are extended throughout the bulk, and no ”surface states” appear. One thus expects that in such calculations there will be no separate contribution from $e^{-}\text{surface}$ collisions. In fact, in [21, 37] it was shown that the electron collision time is independent of the nanoparticle size. All these results indicate that unlike previous claims [47] “quantum size effects” have at a marginal effect on the non-thermal carrier generation efficiency.

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TABLE I: Parameters used in the simulations; values chosen for (low quality \[67\]) 5nm Ag sphere.

| parameter               | parameter symbol | value                       |
|-------------------------|------------------|----------------------------|
| photon wavelength       | $\lambda$        | 2.25eV                     |
| photon wavelength       | $\lambda$        | 2.25eV                     |
| metal permittivity      | $\epsilon_{Ag}(\lambda)$ | $-8.5 + 1.8i$ \[67\]     |
| host permittivity       | $\epsilon_d$     | 4.25                       |
| Fermi energy            | $E_F$            | 5.1eV                      |
| conduction band width   | $E_{max}$        | 9eV                        |
| chemical potential      | $\mu$            | 5.1eV                      |
| ph-env coupling         | $G_{ph-env}$     | $5 \cdot 10^{14}W/m^3\cdot K$ |
| electron density        | $n_e$            | $5.86 \cdot 10^{28}m^{-3}$ |
| speed of sound          | $v_{ph}$         | 3650 m/s                   |
| ambient temperature     | $T_{amb}$        | 297K                       |
| electron mass           | $m_e$            | $9.1 \cdot 10^{31} \text{ kg}$ |

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[68] Negative values of the deviation from thermal equilibrium \( f - f^T \), see below) are referred to as holes, regardless of their position with respect to the Fermi energy. This nomenclature is conventional within the literature [32].

[69] We neglect the deviation of the phonon system from thermal equilibrium. This is an assumption that was adopted in almost all previous studies on the topic; accounting for this deviation can be done in a similar way to our treatment of the electron non-equilibrium, see e.g., [19, 53].

[70] 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 SI, Section II.

[71] 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.

[72] Observing the expected multiple step structure, as in [19], is numerically very challenging.

[73] In fact, the numerical results in [27] show that quantization effects are weak even for a 2nm particle! Indeed, the analytical result (red lines in figs 4 and 5 of [27]) for the high-energy carrier generation rate, obtained by taking the continuum state limit, is very similar to the exact discrete calculation; peculiarly, this similarity in the results seem to be in contrast to their interpretation! Moreover, the higher non-thermal electron generation in a dimer of spherical metals particles or in a cubic particle is seen to be associated almost completely with the higher average field enhancement and better resonance quality, both, purely classical aspects. Note, however, that the interpretation of these results in [27] was different. This shows that neglecting the possibility of momentum mismatch (which is the effective meaning of avoiding the energy state quantization, as essentially done in our calculations) provides a rather tight upper limit estimate.

[74] Note that we ignore here the difference between the Fermi energy and the chemical potential; we verified in simulations that the difference between them is truly negligible in all cases we studied.
This asymmetry may grow if the energy dependence of $D_J$ will be taken into account.

In that paper, a similar calculation was done, namely, of the “hot electron” excitation rate (rather than their density); however, the results were not shown on a logarithmic scale, hence, it is difficult to observe the similarity.

This expression does not include Umklapp collisions.

In our simulations, we used the values for these parameters as given in [17]. However, it should noted that the value they quote for $\rho$ might have involved a typo, which in turn, might have been adjusted via the value of $\mathcal{X}$. Either way, the overall value obtained for the cumulative $e-ph$ term ($G_{e-ph}$) is found to be in excellent agreement with the value computed in several other studies.

This is justified for noble metals, such as Ag, where only acoustic phonons are present. Assuming that these phonon modes are distinct and excluding Umklapp processes, only the longitudinal phonon acoustic mode is coupled to the electron gas.

It should be noted, however, that some earlier studies (e.g., [16]) employed a different expression for $\tau_{e-e}$ which incorporates a strong asymmetry with respect to the Fermi energy, based on the famous expression derived in [32, Pines & Nozieres]. However, Coleman [58] showed that the Pines & Nozieres expression is, in fact, unsuitable for our purposes and that the symmetric parabolic dependence of the collision rate on the energy difference with respect to the Fermi energy (as in [21, 27, 37]) is in fact the correct one. Indeed, the Pines & Nozieres traces the relaxation dynamics of a single electron, rather than the relaxation dynamics of the distribution as a whole; in other words, it accounts for scattering of electrons from a certain electronic state, but ignores scattering into an energy $\mathcal{E}$, a process which cancels out the dependence of the scattering rate on the Fermi function.

Note, however, that the more general $e-e$ scattering integrals do enforce energy conservation explicitly; see examples in the context of ultrafast illumination in e.g., [17, 19].

However, we note that in models that rely on the complete $e-e$ scattering integral (e.g., [16-19]), the electron energy is conserved, so that the Lorentz term is not necessary.

Also note that throughout the manuscript we avoid specifying the local intensity, as it is a somewhat improper quantity to use when discussing metals. Indeed, the negative real part of the permittivity causes the fields within the metal to be evanescent, hence, not to carry energy (such that the Poynting vector, hence, intensity vanish, at least in the absence of absorption).
Instead, we use the local density of electromagnetic energy, by specifying the local electric field, which is easy to connect to the incoming field.

[84] Worse, in [27], the electron temperature was fixed arbitrarily to $1300K$, whereas the single temperature (classical) calculation for this configuration shows that the temperature rise should be $< 1K$. 
