

## 2. Optical properties of gold

The non-resonant optical properties of gold can be described through the free-electron model, where electrons are considered to be free charges moving in response to an optical field  $\text{Re}[\vec{E}_0 e^{-i\omega t}]$  oscillating at angular frequency  $\omega$ . In this model, the dielectric response of the plasma can be derived directly from the non-relativistic single-particle equation of motion:  $\epsilon_{\text{intra}}(\omega) = 1 - \omega_p^2/(\omega^2 + i\gamma\omega)$ , where  $\omega_p = \sqrt{ne^2/\epsilon_0 m_e}$  is the plasma frequency,  $\epsilon_0$  is the vacuum permittivity,  $n$  is the electron number density,  $e$ ,  $m_e$  are the electron charge and mass and  $\gamma$  is a characteristic frequency accounting for electron–electron collisions. This model is justified by the fact that for metals the Fermi energy lies within the conduction band and many accessible states exist for the electrons. From a quantum perspective, free-electron motion only accounts for *intra*band transitions. For wavelengths in the far infrared, the free-electron model provides very good quantitative agreement with experimental data [33]. For the free-electron calculations we use the parameters  $\omega_p = 1.1515 \times 10^{16} \text{ rad s}^{-1}$ ,  $\gamma = 8.9890 \times 10^{13} \text{ s}^{-1}$ , obtained by fitting  $\epsilon''_{\text{intra}}(\omega)$  to the experimental data for long wavelengths in the far infrared. At optical frequencies and in the near infrared, the susceptibility of gold is more involved and the non-resonant model is not sufficient to explain the experimental measurements. Indeed, *inter*band transitions between the *d*-band and the conduction band become important and cannot be neglected. The presence of interband transitions enriches the variety of physical processes and lies behind the strong temperature dependence of the dielectric susceptibility. At optical frequencies, the gold dielectric susceptibility measured in experiments [33] deviates significantly from the predictions of the free-electron model as a consequence of two intense interband absorption peaks at  $\lambda = 300$  and  $410 \text{ nm}$ . Thus, the actual dielectric constant of gold can be expressed as the sum  $\epsilon_m(\omega) = \epsilon_{\text{intra}}(\omega) + \epsilon_{\text{inter}}(\omega)$ .

Gold is characterized by a face centered cubic lattice structure, where the Wigner–Seitz primitive cell is a rhombic dodecahedron. The reciprocal lattice is a body centered cubic where the Wigner–Seitz primitive cell is a truncated octahedron. At optical frequencies, the interband absorption is resonant around the points *X* and *L* in reciprocal space [28], which correspond, respectively, to the centers of the square and hexagonal facets of the truncated octahedron. Notably, such points are highly symmetric and around them the lattice vector  $\vec{k}$  can be expressed as the sum  $\vec{k} = \vec{k}_\perp + \vec{k}_\parallel$ , where  $\vec{k}_\perp$  lies on the square (*X*) or hexagonal (*L*) facets and  $\vec{k}_\parallel$  is perpendicular to them. In addition, the Fermi surface has cylindrical symmetry around the *X*, *L* points and the valence and conduction bands can be approximated in  $(k_\perp, k_\parallel)$  space by elliptic and hyperbolic paraboloids [28]:

$$E_v(\vec{k}) = E_{0v} - \frac{\hbar^2 k_\perp^2}{2m_{v\perp}} - \frac{\hbar^2 k_\parallel^2}{2m_{v\parallel}}, \quad E_c(\vec{k}) = E_{0c} + \frac{\hbar^2 k_\perp^2}{2m_{c\perp}} - \frac{\hbar^2 k_\parallel^2}{2m_{c\parallel}}, \quad (1)$$

where *v*, *c* indicate the valence and conduction bands. The values of the constants  $E_{0v}$ ,  $E_{0c}$ ,  $m_{v\perp}$ ,  $m_{c\perp}$ ,  $m_{v\parallel}$ ,  $m_{c\parallel}$  for the *X* and *L* transitions that we use in our calculations are known in the literature [28]. Note that, as a consequence of the cylindrical symmetry of the Fermi surface, the conduction and valence bands around the *X*, *L* points do not depend on the direction of  $\vec{k}_\perp$ , but only on its modulus  $k_\perp$ . The Fermi level  $E_F$  lies in the conduction band  $E_c(\vec{k})$  and for the sake of simplicity (and without loss of generality) we perform a constant shift of all energies and assume that  $E_F = 0$ . Note that the paraboloid approximation made in (1) is accurate only if  $k_\perp, k_\parallel \ll k_\Gamma$ , where  $k_\Gamma$  is the distance between the *X*, *L* points and the center of the Brillouin zone. The quantum states of electrons in the valence and conduction bands are Bloch

wavefunctions  $\psi_{v,c} = \Omega^{-1/2} u_{\vec{k},v,c}(\vec{r}) \exp(i\vec{k} \cdot \vec{r})$ , where  $\Omega$  is the primitive cell volume,  $\vec{k}$  is the Brillouin wavevector and  $u_{\vec{k},v,c}(\vec{r})$  are the unit cell wavefunctions. By using the Fermi golden rule and following the procedure reported in [27, 28, 32], it is possible to calculate the imaginary part of the dielectric constant due to the  $X, L$  interband transitions

$$\epsilon''_{\text{inter}}(\omega, T_e) = \frac{\pi e^2}{3\epsilon_0 m_e^2 \omega^2} [|\vec{p}_{c,v}^X|^2 J_{c,v}^X(\omega, T_e) + |\vec{p}_{c,v}^L|^2 J_{c,v}^L(\omega, T_e)], \quad (2)$$

where  $\vec{p}_{v,c} = -i(\hbar/\Omega) \int_{\Omega} d^3r [u_{\vec{k},v}^*(\vec{r}) \nabla u_{\vec{k},c}(\vec{r})]$  is the dipole matrix element and  $J_{c,v}(\omega, T_e)$  is the joint density of states (JDOS)

$$J_{c,v}(\omega, T_e) = \frac{2}{(2\pi)^3} \int_{\text{BZ}} d^3k \{ \delta[E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega] f[E_v(\vec{k}), T_e] (1 - f[E_c(\vec{k}), T_e]) \}. \quad (3)$$

In the equation above,  $T_e$  is the electronic temperature and  $f(E, T_e)$  is the Fermi–Dirac occupation number. Note that the conservation of energy and the Pauli exclusion principle for every  $v \rightarrow c$  direct transition are carefully considered in the expression for  $J_{c,v}$ . Indeed, the factor  $f[E_v(\vec{k}), T_e]$  accounts for the probability that the  $\vec{k}$ -state in the valence band is occupied, while the factor  $1 - f[E_c(\vec{k}), T_e]$  accounts for the probability that the  $\vec{k}$ -state in the conduction band is empty. The real part of the dielectric constant can then be obtained directly from (2) using the Kramers–Kronig relation

$$\epsilon'_{\text{inter}}(\omega, T_e) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} \frac{\epsilon''_{\text{inter}}(\omega', T_e)}{\omega' - \omega} d\omega', \quad (4)$$

where  $\mathcal{P}$  represents the principal value of the integral. If the conduction electrons are taken out of equilibrium by light-induced heating, the interband absorption is affected by the so-called *Fermi smearing effect* [28]. Increasing temperature broadens the electron distribution around the Fermi energy, modifying the effective optical properties of gold. In order to understand the temperature dependence of  $\epsilon''_{\text{inter}}$ , contained in the  $X, L$  JDOSs, one needs to compute numerically the thermo-derivatives  $\partial_{T_e} J_{c,v}^{X,L}(\omega, T_e)$ . For the dipole matrix elements  $|\vec{p}_{c,v}^X|^2, |\vec{p}_{c,v}^L|^2$  we have used the values  $g_L |\vec{p}_{c,v}^L|^2 = 1.6015 \times 10^{-47} \text{ J kg}$ ,  $g_X |\vec{p}_{c,v}^X|^2 = 0.321 \times g_L |\vec{p}_{c,v}^L|^2$ , where  $g_L = 8$ ,  $g_X = 6$  [28, 34]. The resulting interband dielectric thermo-derivative can be fitted to a series of five Lorentzian functions:

$$\partial_{T_e} \epsilon''_{\text{inter}}(\omega) = \sum_{j=1}^5 \frac{\mathcal{F}_j \omega_p^2}{(\omega - \omega_j)^2 + \gamma_j^2}, \quad (5)$$

where  $\omega_p$  is the plasma frequency of gold. The fit parameters are given in table 1. The calculation of the real part  $\partial_{T_e} \epsilon'_{\text{inter}}$  through the integration of the Kramers–Kronig relation given by (4) is straightforward:

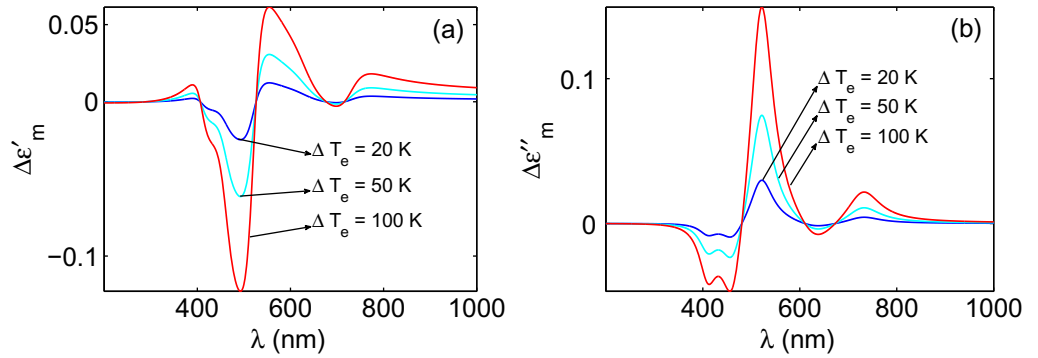
$$\partial_{T_e} \epsilon'_{\text{inter}}(\omega) = \sum_{j=1}^5 \frac{\mathcal{F}_j \omega_p^2 (\omega_j - \omega)}{\gamma_j (\omega - \omega_j)^2 + \gamma_j^3}. \quad (6)$$

As light impinges on the gold surface, the electrons in the conduction band are heated and the dielectric constant is modified by the amount  $\Delta\epsilon_m(\omega) = \partial_{T_e} \epsilon_{\text{inter}}(\omega) \Delta T_e$ .

Note that this thermo-modulational process is intrinsically nonlinear, since the increase of temperature depends on the absorbed optical power  $\Delta T_e(P_A)$ . The spectral dependence of the

**Table 1.** Fit parameters for the thermo-derivative  $\partial_{T_e} \epsilon''_{\text{inter}}(\omega)$ , given by (5).  $\omega_p = 1.1515 \times 10^{16} \text{ rad s}^{-1}$  is the plasma frequency of gold, which has been calculated by fitting the experimental data in the far infrared with the free-electron model.

| $j$                         | 1       | 2       | 3       | 4       | 5       |
|-----------------------------|---------|---------|---------|---------|---------|
| $\mathcal{F}_j \times 10^7$ | -1.6969 | -2.9413 | +5.0681 | -1.0016 | +0.4045 |
| $\omega_j/\omega_p$         | 0.3982  | 0.3541  | 0.3140  | 0.2587  | 0.2238  |
| $\gamma_j/\omega_p$         | 0.0217  | 0.0216  | 0.0173  | 0.0217  | 0.0130  |



**Figure 1.** Thermo-modulation of the dielectric constant of gold. (a) Real and (b) imaginary corrections to the dielectric constant  $\Delta\epsilon_m = \partial_{T_e} \epsilon_{\text{inter}}(\omega, T_0)(T_e - T_0)$  ( $T_0 = 300 \text{ K}$ ). Blue, cyan and red curves correspond to the electronic temperatures  $T_e = 320, 350$  and  $400 \text{ K}$ , respectively.

complex correction  $\Delta\epsilon_m(\omega)$  is plotted in figures 1(a) and (b) for several values of temperature variation  $\Delta T_e = 20, 50, 100 \text{ K}$  (blue, cyan and red curves, respectively). Note that the spectral dependence of both the real and imaginary parts  $\Delta\epsilon'_m(\omega)$ ,  $\Delta\epsilon''_m(\omega)$  is non-trivial and they can be either positive or negative; hence the optical absorption can increase or decrease, depending on the wavelength  $\lambda$ .

### 3. Electron temporal dynamics and the two-temperature model

An optical beam impinging on a metal surface modifies the effective interband susceptibility by heating the electrons in the conduction band. This light-induced electron heating can be described through the TTM, which takes into account the energy balance between the conduction electrons and the lattice. The electrons have a relatively small heat capacity and so thermalize through electron–electron collisions with a characteristic time of order  $\tau_{\text{th}} \approx 300 \text{ fs}$ . If one wishes to describe the temporal electron dynamics for ultrashort optical pulses ( $\tau_0 \approx 100 \text{ fs}$ ), it is necessary to include also the energy contribution of the non-thermalized electrons in the energy balance. This can be calculated directly from the Boltzmann equation in the relaxation time approximation [31]. A phenomenological description of the electron temporal dynamics can be obtained by separating the electron distribution of energy into thermalized and