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Thermodynamics and transport properties in the transient regime

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Abstract. The nonequilibrium behaviour in the transient regime of metals excited by ultrashort optical pulses is investigated by means of a second order expansion of the Boltzmann equation. By definition, the transition range is located between the time necessary for the establishment of the electron temperature and the time where a description by the standard steady state equations is justified. Relaxation functions are derived for the electrical and thermal currents, and the relaxation times related to them are determined. It is shown that for the electrical transport the relaxation time corresponds to Drude's momentum scattering time whereas the corresponding time for the heat flow is identified as the electron temperature relaxation time. Further, expressions for the electrical and thermal conductivity are obtained in the case of a local thermal nonequilibrium between the electron and phonon subsystems in first and second order, respectively. Consequences for the determination of the temperature distributions inside metals are discussed. The solution of the Boltzmann equation is also used for the calculation of the time dependent energy distribution function of the electrons. The results are in good agreement with the experiment.

1. Introduction

In the past few years, the availability of lasers with a pulse duration well down into the femtosecond range has opened a wide field for theoretical investigations and experimental applications. For example, these new laser systems offer the possibility of structuring exposed material with high precision and minimal thermal stress. This is closely related to the appearance of new phenomena like the phase explosion or the existence of different temperatures for the electrons and phonons.

In the transient region where a steady state does not yet exist, the standard equations for the solid state lose their validity and have to be replaced by relaxation expressions governed by characteristic times. Some of these equations and times are derived in section 3.

Short laser pulses usually possess high power densities and an electron may absorb energies as high as some few eV between two scattering events. Consequently, the electron system can be driven far out of equilibrium and, hence, a description of its properties by a first order solution to the Boltzmann equation, still the standard approach in solid state physics, may become inappropriate. In this case, the application of the Fermi–Dirac function even with different temperatures for the electron and phonon subsystems may not be justified. One way to handle this difficulty is to seek higher order solutions to the Boltzmann equation. Section 4 is devoted to such a nonequilibrium approach. The consequences of nonequilibrium are illustrated in some few examples: for the electronic energy distribution function and for the thermal and electrical conductivity.

2. Nonequilibrium electron distribution

We will investigate processes related to the absorption of pico- and subpicosecond laser pulses in metals. For this reason, we separate the entire system into two subsystems. The establishment of a state of equilibrium is achieved in each of the two systems with different relaxation times, where $\tau_{ee} \ll \tau_{pp}$. Furthermore, it is reasonable to assume that in most cases the phonon system does not change essentially during the interaction with subpicosecond laser pulses, at least when the hierarchy of relaxation times meets the condition $\tau_{ee} \ll \tau_{ep} \ll \tau_{pp}$. While the phonon–phonon relaxation time in metals is always much longer than the characteristic time for energy exchange, τ_{ep} , the second inequality, τ_{ep} can be approximately of the same order of magnitude as τ_{ee} if the coefficient for the energy exchange is very large. Nevertheless, we can assume the establishment of a local electron temperature after the duration of some τ_{ee} . This assumption will, however, introduce a lower limit of about 100 fs for the investigations following below.

During the interaction of a strong laser field with metals, electrons absorb photons and transfer to states with the energy $E \pm \hbar\omega$. As a result, a nonequilibrium distribution is generated. Aiming to describe such an electron subsystem we start from the Boltzmann equation. For an electron gas interacting with laser radiation this kinetic equation may be written as

$$\frac{\partial f(\vec{k}, t)}{\partial t} + \vec{v} \frac{\partial f(\vec{k}, t)}{\partial \vec{r}} - e\vec{v}\vec{E} \frac{\partial f(\vec{k}, t)}{\partial E} = \int P(\vec{k}, \vec{k}', t)[f(\vec{k}', t) - f(\vec{k}, t)] d\vec{k}' - \nu G(f(\vec{k}, t)) \quad (1)$$

where all terms, except the last one, keep their usual meaning. This additional term represents the phonon-assisted absorption or emission of photons and is discussed in more detail below.

In our calculations we require that the following conditions are satisfied: (a) interband transitions are excluded, (b) the skin effect is normal and (c) the relaxation of the electron distribution is due to electron–electron and electron–phonon collisions. That means we consider a free electron system at not too low temperature and exclude additional scattering processes as caused, for example, by magnons.

3. Relaxation functions

Since we are mainly interested in the physics that occurs on short time scales we have to go, as mentioned above, beyond the steady state approach presented in most text books on solid state physics. For that purpose we introduce relaxation functions for the currents and calculate their characteristic relaxation times.

For times much larger than the corresponding relaxation times the derived equations must meet, of course, the standard steady state expressions such as the Fourier law for the heat flow j_Q and Ohm's law for the electrical current j_e . It depends, therefore, strongly on the ratio of the relaxation time belonging to the investigated quantity over the typical process time whether a relaxation function is necessary or not. That is, we have to compare in this paper the duration of the laser pulse with the distinct relaxation times. Since the latter can be different by orders of magnitude for various processes in the same material one has to check this condition for any physical quantity considered. This will be done in the next section for the electrical and thermal current.

3.1. Electrical current

Multiplying equation (1) by the product of the electronic charge times the velocity and integrating over the wave vector yields

$$\begin{aligned} -e \int \vec{v} \frac{\partial f(\vec{k}, t)}{\partial t} d\vec{k} - e \int \vec{v}^2 \frac{\partial f(\vec{k}, t)}{\partial \vec{r}} d\vec{k} + e^2 \int \vec{v}^2 \vec{E} \frac{\partial f(\vec{k}, t)}{\partial E} d\vec{k} \\ = -e \int \int \vec{v} P(\vec{k}, \vec{k}', t) [f(\vec{k}', t) - f(\vec{k}, t)] d\vec{k}' d\vec{k} + ev \int \vec{v} G(f(\vec{k}, t)) d\vec{k}. \end{aligned} \quad (2)$$

Let us examine the integrals in equation (2) step by step. The first one gives simply

$$-e \int \vec{v} \frac{\partial f(\vec{k}, t)}{\partial t} d\vec{k} = -\frac{\partial}{\partial t} \int e \vec{v} f(\vec{k}, t) d\vec{k} = \frac{\partial \vec{j}_e}{\partial t}. \quad (3.1)$$

For the evaluation of the second integral we have to replace $f(k, t)$ in the usual manner of perturbation theory by the Fermi–Dirac distribution (Ashcroft and Mermin 1976). Then we can integrate by parts using the property that $f(k, t)$ vanishes at $k = \pm\infty$ much faster than the energy can increase when the wave vector tends toward infinity. Considering the explicit time dependence of the temperature contained in f_0 we get an additional term. The evaluation yields

$$\begin{aligned} -e \int \vec{v}^2 \frac{\partial f(\vec{k}, t)}{\partial \vec{r}} d\vec{k} \Rightarrow e \int \frac{\vec{v}(E - \mu)(\vec{v}\nabla T + \dot{T})}{T} \frac{\partial f_0(\vec{k})}{\partial E} d\vec{k} \\ = e \int \frac{(E - \mu)(\vec{v}\nabla T + \dot{T})}{T} \frac{\partial f_0(\vec{k})}{\hbar \partial \vec{k}} d\vec{k} \\ = -\frac{e}{T} \int \left[\left(\frac{(E - \mu)}{m} + \vec{v}^2 \right) \nabla T + \vec{v} \dot{T} \right] f_0(\vec{k}) d\vec{k} = -\frac{e}{T} [(\vec{v}^2)_0] \nabla T \end{aligned} \quad (3.2)$$

where the integrals containing $(E - \mu)$ and \vec{v} , respectively, vanish.

To calculate the third integral we assume here and in the following a constant effective mass and then find after integration by parts

$$e^2 \int \vec{v}^2 \frac{\partial f(\vec{k}, t)}{\partial E} d\vec{k} \vec{E} = -e^2 \int \frac{2}{m} f(\vec{k}, t) d\vec{k} \vec{E} = -\frac{e^2 n}{m} \vec{E} \quad (3.3)$$

where n is the electron density.

Utilizing the property of detailed balance for the scattering rates one can rewrite the fourth integral as

$$\begin{aligned} -e \int \int \vec{v} P(\vec{k}', \vec{k}, t) f(\vec{k}', t) d\vec{k}' d\vec{k} = -e \int \vec{v} f_0(\vec{k}) d\vec{k} \int P(\vec{k}, \vec{k}', t) \frac{f(\vec{k}', t)}{f_0(\vec{k})} d\vec{k}' \\ = -e \int \vec{v} f_0(\vec{k}) d\vec{k} \frac{1}{\zeta(\vec{k}, t)} = 0 \end{aligned} \quad (3.4)$$

where the k' -integration over the transition rate was replaced by a relaxation time $\zeta(k, t)$. The final expression, however, turns out to be zero since the current vanishes in the case of equilibrium if we assume a lifetime independent of k .

The fifth integration is straightforward and results in

$$e \int \int \vec{v} P(\vec{k}', \vec{k}, t) f(\vec{k}, t) d\vec{k}' d\vec{k} = e \int \vec{v} f(\vec{k}, t) \frac{1}{\xi(\vec{k}, t)} d\vec{k} = \frac{e}{\tau_e} \int \vec{v} f(\vec{k}, t) d\vec{k} = -\frac{1}{\tau_e} \vec{j}_e \quad (3.5)$$

where the relaxation time has been approximated by a constant.

Expanding the operator $G(f[k, t])$ into a series of increasing numbers of multiphoton absorption and emission processes, respectively, and taking, for example, only the lowest order, we obtain

$$\begin{aligned} e\nu \int \vec{v}G(f(\vec{k}, t)) d\vec{k} &= \frac{e\nu}{\hbar} \int \frac{\partial E}{\partial \vec{k}} G(f(\vec{k}, t)) d\vec{k} \\ &\sim \frac{e\nu}{\hbar} \int [f_0(E + \hbar\omega, t) - f_0(E, t) + H(E - \hbar\omega)(f_0(E - \hbar\omega, t) \\ &\quad - f_0(E, t))] dE = 0 \end{aligned} \quad (3.6)$$

where $H(x)$ is the Heaviside step function. The same will, of course, happen also for the higher order terms.

Section 4 below contains a more detailed treatment of this part of the nonequilibrium distribution (see especially equation (20)).

With equations (3.1)–(3.6), inserted into equation (2) and multiplied by τ_e , we arrive at the sought relaxation function for the electrical current

$$\tau_e \frac{\partial \vec{j}_e}{\partial t} + \vec{j}_e = \frac{ne^2\tau_e}{m} \vec{E} - \frac{e^2\tau_e}{T} \langle \vec{v}^2 \rangle \nabla T. \quad (4)$$

Since the term proportional to the electric field exceeds the second one by a factor of order $(\mu/k_B T)^2$, we can ignore the thermoelectric contribution and directly compare the right hand side of equation (4) with the Drude form of the electrical conductivity. This way we realize that the relaxation time of the electrical current can be identified with Drude's momentum scattering time, i.e., $\tau_e = \tau$. Consequently, after some few times τ a steady state behaviour is established. Using experimental data for the specific resistivity, the number of conduction electrons and the free electron mass m_0 , an estimate for τ gives values between some few and some tens of femtoseconds at room temperature (Ashcroft and Mermin 1976). A more accurate determination can be achieved by a band structure calculation of $(n/m)_{eff}$ (Allen *et al* 1986) or by using the 'exact' high temperature expression (Pinski and Allen 1981) (in practice, even $T > \Theta_D$ may be enough)

$$\tau_e = \frac{\hbar}{2\pi k_B T_{ph} \Lambda_{tr}} = \tau \quad (5)$$

with Λ_{tr} as the transport electron–phonon coupling constant. In most cases Λ_{tr} can be replaced by the usual electron–phonon coupling constant Λ . Although equation (5) is a good approximation in many situations, it should be borne in mind that the observed resistivity depends on both the electron–phonon and the electron–electron collisions. Equation (5), however, covers only the former mechanism. These distinctions will become clearer in section 4 where we will give a sketch of the derivation of the thermal conductivity for the general case of nonequilibrium between the electrons and phonons.

3.2. Thermal current

In order to repeat the calculation in view of the thermal current one has to multiply equation (1) by the product of the energy difference $(E - \mu)$ times the velocity

$$\begin{aligned} \int \vec{v}(E - \mu) \frac{\partial f(\vec{k}, t)}{\partial t} d\vec{k} + \int \vec{v}^2(E - \mu) \frac{\partial f(\vec{k}, t)}{\partial \vec{r}} d\vec{k} - e \int \vec{v}^2(E - \mu) \vec{E} \frac{\partial f(\vec{k}, t)}{\partial E} d\vec{k} \\ = \int \int \vec{v}(E - \mu) P(\vec{k}, \vec{k}', t) [f(\vec{k}', t) - f(\vec{k}, t)] d\vec{k}' d\vec{k} \\ - \nu \int \vec{v}(E - \mu) G(f(\vec{k}, t)) d\vec{k}. \end{aligned} \quad (6)$$

The first integration is similar to Eq. (3.1) and we get immediately the thermal analogy

$$\int \vec{v}(E - \mu) \frac{\partial f(\vec{k}, t)}{\partial t} d\vec{k} = \frac{\partial}{\partial t} \int \vec{v}(E - \mu) f(\vec{k}, t) d\vec{k} = \frac{\partial \vec{J}_Q}{\partial t}. \quad (7.1)$$

Again, due to the lack of knowledge of the temperature dependence of $f(k, t)$, we replace it in the next integral by the equilibrium distribution and obtain

$$\begin{aligned} \int [E(\vec{k}) - \mu] \vec{v}^2 \frac{\partial f(\vec{k}, t)}{\partial t} d\vec{k} &\Rightarrow \int [(E(\vec{k}) - \mu)(\vec{v} \nabla T + \dot{T})] \vec{v} \frac{\partial f_0(E)}{\partial T} d\vec{k} \\ &= - \int \frac{(E(\vec{k}) - \mu)^2 (\vec{v} \nabla T + \dot{T})}{T} \vec{v} \frac{\partial f_0(E)}{\partial E(\vec{k})} d\vec{k} \\ &= - \int \frac{(E(\vec{k}) - \mu)^2 (\vec{v} \nabla T + \dot{T})}{T} \frac{1}{\hbar} \frac{\partial E(\vec{k})}{\partial \vec{k}} \frac{\partial f_0(E)}{\partial E(\vec{k})} d\vec{k} \\ &= \int \left\{ \frac{2[E(\vec{k}) - \mu](\vec{v} \nabla T + \dot{T})}{T} \vec{v} + \frac{(E(\vec{k}) - \mu)^2 \nabla T}{Tm} \right\} f_0(E) d\vec{k} \\ &= \left\{ \frac{\langle E^2 \rangle_0 - 2\langle E \rangle_0 \mu + \mu^2}{Tm} \right\} \nabla T = \left\{ \frac{\langle E^2 \rangle_0 - \mu^2}{Tm} \right\} \nabla T. \end{aligned} \quad (7.2)$$

It should be noted that in the case of a local thermal nonequilibrium the temperature T refers to the temperature of the electrons and not to that of the phonons.

Since the difference of the mean energy and the Fermi energy, $\langle E \rangle - \mu$, calculated by means of $f(k, t)$ is not necessarily zero as in equation (3.2) one obtains for the thermoelectric contribution

$$\begin{aligned} -e \int \vec{v}^2 (E - \mu) \frac{\partial f(\vec{k}, t)}{\partial E} d\vec{k} \vec{E} &= -e \int \vec{v}(E - \mu) \frac{\partial f(\vec{k}, t)}{\hbar \partial \vec{k}} d\vec{k} \vec{E} \\ &= e \int \left[\vec{v}^2 + \frac{(E - \mu)}{m} \right] f(\vec{k}, t) d\vec{k} \vec{e} = e \left[\langle \vec{v}^2 \rangle + \frac{\langle E \rangle - \mu}{m} \right] \vec{E}. \end{aligned} \quad (7.3)$$

Because the thermal current is also zero in the equilibrium the next integral vanishes in analogy with equation (3.4) if we make the same substitutions:

$$\begin{aligned} \iint [E(\vec{k}) - \mu] \vec{v} P(\vec{k}', \vec{k}, t) f(\vec{k}', t) d\vec{k}' d\vec{k} \\ &= \iint [E(\vec{k}) - \mu] \vec{v} f_0(\vec{k}) d\vec{k} \int P(\vec{k}, \vec{k}', t) \frac{f(\vec{k}', t)}{f_0(\vec{k})} d\vec{k}' \\ &= \iint [E(\vec{k}) - \mu] \vec{v} f_0(\vec{k}) d\vec{k} \frac{1}{\zeta(\vec{k}, t)} = 0. \end{aligned} \quad (7.4)$$

For the calculation of the fifth integral it is convenient to separate off the integration over k' and then to define a relaxation time for the heat flow, such that

$$\begin{aligned} - \iint [E(\vec{k}) - \mu] \vec{v} P(\vec{k}', \vec{k}, t) f(\vec{k}, t) d\vec{k} d\vec{k}' &= - \int [E(\vec{k}) - \mu] \vec{v} f(\vec{k}, t) d\vec{k} \int P(\vec{k}', \vec{k}, t) d\vec{k}' \\ &= - \int [E(\vec{k}) - \mu] \vec{v} f(\vec{k}, t) \frac{1}{\xi(\vec{k}, t)} d\vec{k} = - \frac{1}{\tau_Q} \int [E(\vec{k}) - \mu] \vec{v} f(\vec{k}, t) \\ &= - \frac{1}{\tau_Q} \vec{J}_Q. \end{aligned} \quad (7.5)$$

To make the calculation of the last term containing the phonon-assisted photon processes as simple as possible we again restrict ourselves to the lowest order, as in equation (3.6)

$$\begin{aligned}
 -v \int \vec{v}(E - \mu) G(f(\vec{k}, t)) &= -v \int \vec{v}(E - \mu) \{f_0(E + \hbar\omega) - f_0(E) \\
 &\quad + H(E - \hbar\omega)[f_0(E - \hbar\omega) - f_0(E)]\} d\vec{k} \\
 &\sim -v \left\{ \int \frac{1}{\hbar} (E - \mu) \{f_0(E + \hbar\omega) - f_0(E) \right. \\
 &\quad \left. + H(E - \hbar\omega)[f_0(E - \hbar\omega) - f_0(E)]\} dE \right\} = 0.
 \end{aligned} \tag{7.6}$$

The vanishing of the whole expression can be most easily seen by a transformation of $E \pm \hbar\omega$ into E' followed by a subdivision of the integrand into $(E' - \mu)$ and ω .

The differential equation of the thermal current is obtained immediately if one inserts the solutions (7.1)–(7.6) into equation (6) and then multiplies the whole equation by τ_Q

$$\tau_Q \frac{\partial \vec{j}_Q}{\partial t} + \vec{j}_Q = -\tau_Q \frac{\langle E^2 \rangle_0 - \mu^2}{mT} \nabla T \tag{8}$$

where we have neglected the small contribution of equation (7.3). This is no restriction for s-polarized waves or for laser radiation parallel to the normal of the surface because in both cases the electric field is perpendicular to the heat flow and, therefore, cannot contribute.

For the determination of the relaxation time τ_Q , we match the right hand side of equation (8) with the Fourier law. Within the framework of Eliashberg's theory the high temperature thermal resistivity ($T > \Theta_D$) can be written as an integral involving the coupling function $\alpha^2 F(\Omega)$ (Grimvall 1986)

$$\frac{1}{\lambda} = \frac{3m}{\pi k_B \hbar n} 2 \int_0^{\Omega_{max}} d\Omega \frac{\alpha^2 F(\Omega)}{\Omega} = \frac{3m\Lambda}{\pi k_B \hbar n}. \tag{9}$$

From equations (8) and (9) we obtain for τ_Q

$$\tau_Q = \frac{mT_e}{\langle E^2 \rangle_0 - \mu^2} \lambda = \frac{T_e}{\langle E^2 \rangle_0 - \mu^2} \frac{\pi \hbar k_B n}{3\Lambda} \tag{10}$$

where we stress by the additional index 'e' that T belongs to the electron subsystem. After rewriting, in the high- T limit the mean square of the energy density stored in the electron system is given by

$$\langle E^2 \rangle_0 - \mu^2 = n\hbar \frac{2}{\Lambda} \int d\Omega \alpha^2 F(\Omega) \Omega = n\hbar^2 \langle \Omega^2 \rangle. \tag{11}$$

After insertion of equations (10) and (11) into (8) we finally find that the relaxation time of the heat flow corresponds to the electron temperature relaxation time

$$\tau_Q = \frac{\pi k_B \gamma_e T_e}{3\hbar \langle \Omega^2 \rangle \Lambda \gamma_e} = \frac{c_e(T_e)}{h_{ex}} = \tau_T \tag{12}$$

first derived by Allen (1987). The amount of the relaxation time τ_Q is primarily determined by the coefficient of the heat exchange h_{ex} . This important quantity manifests the interaction between the electron and phonon subsystems. It depends on the coefficient of the specific heat of the electrons γ_e , the electron–phonon coupling constant Λ , also called the mass enhancement coefficient, and the averaged square of the phonon frequency. The present definition of the relaxation time τ_Q differs from Maurer's (1969) derivation especially by the temperature dependence. In his theory it is inversely proportional to the temperature. The difference can be traced back to the treatment of the electron system. In Maurer's approach, there is no coupling to the phonons and the relaxation takes place only in the electron system.

For the differential function of the thermal current it follows by substitution of equation (10) into equation (8)

$$\tau_Q \frac{\partial \vec{j}_Q}{\partial t} + \vec{j}_Q = -\lambda \nabla T. \quad (13)$$

This is known as the Maxwell–Cattaneo equation (Joseph and Preziosi 1989). Considering the integral version of equation (13)

$$\vec{j}_Q(t) = -\frac{1}{\tau_Q} \int_{-\infty}^t e^{-(t-t')/\tau_Q} \lambda \nabla T(t') dt' \quad (14)$$

we recognize that the heat flow described by equations (13) or (14) is nonlocal in time. Both expressions state that the heat flow at time t consists of the sum of flows at earlier times weighted by an exponential that accounts for temperature relaxation caused by the coupling to the phonon bath. It is worth noting that in the limit of vanishing relaxation time both converge into Fourier's law. From this we can conclude that the Fourier law is well defined if τ_Q is much smaller than any time relevant for the process. On the other hand, an arbitrarily small time constant is certainly unphysical since a many-body property like the heat flow needs a finite period of time for its development.

The generalized equation for the heat flow in the electron system, equation (14), forms the basis of the extended two-temperature model (ETTM) (Hüttner and Rohr 1996, 1998) whereas the phonons are taken into account in the usual manner as, e.g., in the two-temperature model (TTM) (Anisimov *et al* 1974). On short time scales, in the order of τ_Q , both models predict completely different behaviour. In the ETTM the electron temperature possesses a damped wavelike behaviour in contrast to the diffusive one expected by the TTM. In thin films, however, also the phonon temperature can display a nondiffusive distribution due to the time evolution of the spatially varying electron temperature caused by the back scattering of the temperature wave from the rear side.

Depending on the magnitude of the coefficient of electron–phonon energy exchange, the time τ_Q can be much larger than the momentum relaxation time τ even for $T_e = T_{ph}$. For a crude estimate we combine equations (5) and (12) to

$$\frac{\tau_Q}{\tau} = \frac{2\pi^2 k_B^2 T^2}{3\hbar^2 \langle \Omega^2 \rangle} \approx 12 \frac{T^2}{\Theta_D^2} \quad (15)$$

where $\langle \Omega^2 \rangle$ can be approximated in the Debye model by $\frac{1}{2} \Omega_D^2$. As can be seen from table 1, the values of τ_Q calculated by the simple equation (15) with $\tau = \tau_D$ are not far away, perhaps except for Sn and Pb, from those evaluated by the more sophisticated equation (12).

Although the differential equations for the electrical and thermal current possess the same mathematical structure we conclude from the relaxation times listed in table 1 that one must

Table 1. Relaxation times for the heat flow as calculated from equations (12) and (15), respectively, at $T = 300$ K; also given is the Drude scattering time, the Debye temperature and the coefficient of electron–phonon energy exchange.

Metal	$\tau(300 \text{ K})$ (fs)	Θ_D (K)	h_{ex} (GW cm ⁻³ K ⁻¹)	τ_Q (fs) (12)	τ_Q (fs) (15)
In	3.5	112	87	357	297
Sn	2.1	170	145	227	78
Pb	1.3	88	122	393	180
Nb	4.0	277	2912	74	56
Ag	36.8	215	25	780	859
Au	27.6	170	26	784	1030

Table 2. The theoretical coefficient of heat exchange as calculated by equation (12) with the values from columns 2, 4 and 5; the fitted values result from columns 2 and 3. Data for γ_e are taken from Ashcroft and Mermin (1976); the other values from Brorson *et al* (1990) if not otherwise stated.

Metal	$\gamma_e \times 10^{-5}$ (J cm ⁻³ K ⁻²)	$\Lambda \langle \omega^2 \rangle_{fit}$ (meV ²)	$\Lambda_{lit.}$	$\langle \omega^2 \rangle_{lit.}$	$h_{ex,fit}$ (GW cm ⁻³ K ⁻¹)	$h_{ex,theo.}$ (GW cm ⁻³ K ⁻¹)
Au	6.7	23	0.15	178	26	30
Ag	6.5		0.12 ^a	344 ^b	35 ^c	46
Cu	9.7	29	0.10	377	94	123
Nb	71.7	320	1.04	275	3888	3475
Pb	16.0	45	1.55	31	122	130
Ti	8.5	350	0.54	601	1207	1711
V	117.7	280	0.82	352	5571	5741
W	13.7	112	0.26	425	259	256

^a Allen (1987).

^b $\langle \omega^2 \rangle = 0.5 \langle \omega_D^2 \rangle$.

^c Groeneveld *et al* (1990).

use equation (13) for a description of short time experiments in the thermal case whereas the steady state approximation, $j = \sigma E$, should usually be sufficient in the electrical one.

This is an important outcome since equation (13) leads to a hyperbolic differential equation for the electron temperature with the above discussed wavelike properties in contrast to the diffusive nature of the often used two-temperature model.

As a consequence, the experimental determination of the coefficient of heat exchange should not be based on fitting the measured electron temperature to the TTM but to a solution of the hyperbolic equation of heat conduction (HHCE). Since both approaches formally agree in the limit of τ_Q equal to zero one expects different values, especially for metals with small coefficient of heat exchange or large τ_Q . Physically speaking the TTM would postulate a faster heat transport than the ETTM. Consequently, the fitting of the experimental temperature data to a solution of the TTM could be leading to too small coefficients of heat exchange. This conjecture is supported by comparing the theoretical values evaluated by means of equation (12) with the experimental ones fitted to the electron temperature calculated by means of the TTM (Brorson *et al* 1990) in table 2.

Before concluding this section we have yet to discuss an important point. The statement above, that the ETTM merges with the TTM in the limit of τ_Q equal to zero, is not quite correct. The time τ_Q can vanish if either the electronic specific heat is zero or the coefficient of heat exchange becomes extremely large. The first possibility is obviously unphysical because an electron gas cannot be heated up if the coefficient of specific heat is zero. On the other hand, the second possibility implies that the coupling strength between the electron and phonon subsystems tends to infinity but then both systems have the same common temperature at any time. Consequently, a consideration of two temperatures becomes meaningless and, hence, the two-temperature model as well. In this respect, Fourier's law together with the energy balance would manifest the entire physics and the calculation of the temperature distribution ($T_e = T_{ph} = T$) could be done by standard methods (Carslaw and Jäger 1959). As a result the reduction of the ETTM to the TTM by taking the temperature dependent relaxation time τ_Q equal to zero is not possible, for physical reasons, in a strict sense.

Furthermore, it is worthwhile noting that the temperature dependence of the theoretically derived τ_Q as predicted in equation (12) is supported also by the experiments (Schoenlein *et al* 1987) for not too high intensities. Necessary corrections for high values were introduced and discussed for gold in Wang *et al* (1994).

4. Solution of the Boltzmann equation and thermal conductivity

It is well known that first order solutions of the Boltzmann equation are restricted to the physics near the equilibrium. Accordingly, only steady state properties can be deduced. Here we are interested especially in the interaction of short laser pulses with metals where a steady state behaviour cannot be assumed *a priori*. Hence, in this section we investigate the transient regime and deal, for this reason, first with a perturbation treatment of the Boltzmann equation up to the second order.

This will be followed by a discussion of the nonequilibrium distribution function with special regard to the role of the photon operator $G(f)$. In conclusion, based on the derived nonequilibrium distribution function the thermal and electrical conductivities are calculated.

4.1. Solution of the Boltzmann equation

We seek a solution of equation (1) by expanding f into a power series for the small parameter, $p = \nu\tau$, defined by

$$p(t) = \nu(t)\tau = \frac{I(t)\tau}{n\hbar\omega\delta} \quad (16)$$

where $I(t)$ is a time-dependent laser intensity and δ is the optical absorption depth. Physically speaking p is an estimate of the number of photons absorbed between two scattering events. Since p must be smaller than unity our approach is restricted to not too high intensities. This condition means that the deviation of the electron distribution from the equilibrium as caused by laser-induced processes is relatively small and that, for this reason, one can consider the light action as a perturbation. The expansion reads

$$f = \sum_{n=0}^m p^n f_n = f_0 + pf_1 + p^2 f_2 + \dots \quad (17)$$

where the unperturbed part f_0 corresponds to the Fermi–Dirac function that governs the electrons before the interaction starts. By insertion of equation (17) into equation (1) and by using the relaxation time approximation we find listed in increasing order of p for the first order terms

$$p \frac{\partial f_1}{\partial t} + (\vec{v}\nabla T + \dot{T}) \frac{\partial f_0}{\partial T} - e\vec{v}\vec{E} \frac{\partial f_0}{\partial E} = -\frac{pf_1}{\tau} - \nu G(f_0) \quad (18)$$

and for the second order ones

$$p^2 \frac{\partial f_2}{\partial t} + (\vec{v}\nabla T + \dot{T}) \frac{p\partial f_1}{\partial T} - e\vec{v}\vec{E} \frac{p\partial f_1}{\partial E} = -\frac{p^2 f_2}{\tau} - \nu G(pf_1) \quad (19)$$

where we have again taken into account in equations (18) and (19) the explicit time dependence of the local temperature. Before one can integrate the distribution functions it is necessary to specify the expression $\nu G(f)$. This function was introduced in Zinoviev (1980) for the description of the photoemission of electrons as a result of the irradiation of metals with short laser pulses. To this end, the authors have been required that the laser pulse length is much longer than the scattering time of the electrons. In practice, $\tau_L > 100$ fs should be long enough. That corresponds to our supposed lower boundary necessary for the establishment of the temperature. Under these conditions they derived for a Gaussian temporal profile

$$pG(f) = \sum_{s=1}^{\infty} \left[\frac{I_0 e^{(t^2/\tau_L^2)} \tau}{n\hbar\omega\delta} \right]^s [f_0(E + \hbar\omega) - f_0(E) + H(E - \hbar\omega)(f_0(E - \hbar\omega) - f_0(E))]^s \quad (20)$$

with $H(E - \omega)$ as the Heaviside step function to ensure the positiveness of the energy value. For the sake of simplicity, we restrict ourselves to one-photon processes ($s = 1$) in the following. This approximation is justified by the dependence of the expansion parameter p on the intensity I_0 . Typical upper values of I_0 are of the order of 10^{12} – 10^{13} W cm $^{-2}$ where higher order processes are not important yet.

Also using a Gaussian distribution for $I(t)$ integration of equation (18) yields

$$pf_1 = e^{(t/\tau)} \int_{-\infty}^t dt' e^{(t'/\tau)} \left\{ \left(-e\vec{v}\vec{E}_0 e^{-i\omega t'} e^{(t'^2/2\tau_L^2)} - (E - \mu) \left[\vec{v} \frac{\nabla T}{T} + \frac{\dot{T}}{T} \right] \right) \left(-\frac{\partial f_0}{\partial E} \right) + \nu_0 e^{(t'^2/\tau_L^2)} G(f_0) \right\} \quad (21)$$

in which the notations of the explicit time dependences of the electron temperature and the scattering time are omitted for brevity. The abbreviation ν_0 follows from equation (16) when $I(t)$ is replaced by I_0 . Provided $\tau_L \gg \tau$, it is allowed to extract from the integral as constants those terms that vary slowly with the time, i.e., the Gauss functions, the temperature and its gradient. These conclusions result from the fact that electron temperature cannot increase faster than the laser intensity. This is not true for the time derivative of the temperature which may be a rapid function of time. Nevertheless, integrals containing the derivative of the temperature with respect of time vanish if the condition $\tau_L \gg \tau$ is fulfilled. This can be easily seen when we integrate by parts

$$\begin{aligned} \int_{-\infty}^t e^{(t'/\tau)} \dot{T}(t') dt' &= e^{(t/\tau)} T(t) - \int_{-\infty}^t e^{(t'/\tau)} \frac{T(t')}{\tau} dt' \\ &\cong e^{(t/\tau)} T(t) - T(t) \int_{-\infty}^t e^{(t'/\tau)} \frac{1}{\tau} dt' = 0. \end{aligned} \quad (22)$$

With the abbreviation $p_0 = \nu_0 \tau$ we finally obtain for the first order term pf_1

$$pf_1 = - \left\{ \frac{e\tau\vec{v}\vec{E}_0}{1 - i\omega\tau} e^{-i\omega t - (t^2/2\tau_L^2)} + (E - \mu)\vec{v}\tau \frac{\nabla T}{T} \right\} \left(-\frac{\partial f_0}{\partial E} \right) + p_0 e^{(t^2/\tau_L^2)} G(f_0) \quad (23.1)$$

using a time-independent relaxation time.

The next order is obtained by insertion of equation (23.1) into equation (19)

$$p^2 f_2 = -e^{-(t/\tau)} \int_{-\infty}^t dt' e^{(t'/\tau)} \left\{ \vec{v}\nabla T \left(\frac{\partial(pf_1)}{\partial T} \right) - e\vec{v}\vec{E} \left(\frac{\partial(pf_1)}{\partial E} \right) - \nu_0 G e^{-(t'^2/\tau_L^2)} (pf_1) \right\}. \quad (23.2)$$

In the general case, due to the energy and temperature dependence of the relaxation time τ , the solution of the integral becomes rather long. It is therefore more convenient to calculate only the terms relevant for a special investigated problem. For example, the electric current is proportional to $\sum v f$ and, therefore, terms containing odd powers of v vanish upon integration over the k -space.

We will now apply the solutions (23.1) and (23.2) to some special problems. As a first one, we investigate the energy relaxation of the nonequilibrium electron distribution. In the case of one-photon processes we obtain for this distribution function from equations (17) and (23.1)

$$f(E) = f_0(E) + \tau\nu_0 e^{-(t^2/\tau_L^2)} \{ f_0(E + \hbar\omega) - f_0(E) + H(E - \hbar\omega) [f_0(E - \hbar\omega) - f_0(E)] \} \quad (24)$$

where the relaxation time τ is not yet specified. Under the interaction with a laser field the electrons are excited to states above the Fermi energy with roughly $E_F + \hbar\omega$. Under the

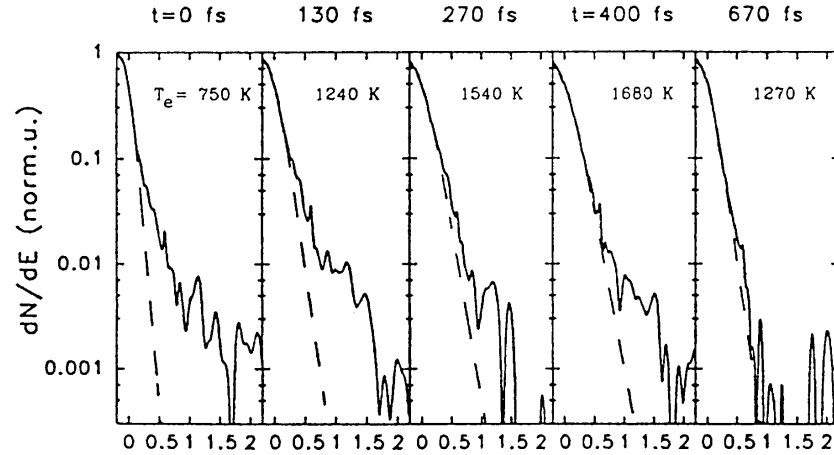


Figure 1. Experimental electron energy distribution function taken from Fann *et al* (1992)

random phase approximation of the Fermi-liquid theory the lifetime of a nonthermal electron due to both elastic and inelastic electron–electron collisions is given by (Pines and Nozieres 1966)

$$\tau_e^{-1} = \tau_T^{-1} + \tau_E^{-1} = \beta(4\pi^2 T_e^2 (eV) + [E - \mu_0]^2) \quad (25)$$

where β (Parkins *et al* 1981) is an experimental parameter. Under usual conditions when the intensity is not very low, especially the electron temperature changes considerably during the duration of the laser pulse and can be strongly time dependent. Nevertheless, it is justified to assume that the scattering time is not explicitly time dependent as can be seen from the following conservative estimate. Neglecting any time delay of the electron temperature and assuming an exponential increase, $T_e = T_0 \exp(t/\tau_L)$, we obtain

$$\frac{\partial \tau_e}{\partial t} = \frac{\partial \tau_e}{\partial T_e} \frac{\partial T_e}{\partial t} = -\frac{2\tau_e^2}{\tau_T \tau_L} < \frac{2\tau_e}{\tau_L} < 1$$

in agreement with our lower boundary.

The time evolution of the distribution function of a thin gold film was measured by Fann *et al* (1992). Figure 1 shows their data for a fluence of $300 \mu\text{J cm}^{-2}$ at a photon energy of 1.84 eV and a pulse length of $\tau_L = 180$ fs. The theoretical curves in figure 2 are calculated from equations (24) and (25) with the same data as used in the experiment and show a satisfying agreement.

It should be noted that our explanation of the time dependence of the relaxation of the nonequilibrium energy distribution is more general than that proposed by Fann *et al* (1992). In their model, the electron distribution function is divided into thermal and nonthermalized parts. A solution is given for the latter by assuming an unknown nascent distribution under the additional approximation of instantaneous excitation at $t = 0$ fs. Further, the temperature dependence of the scattering time is neglected. For the Gaussian laser function of our approach, a solution is derived for the complete electron system characterized by an energy and temperature dependent scattering time. In addition, the time dependence of the electron temperature at the surface was calculated by means of the ETTM for a 30 \AA Au film. As can be seen in figure 3, a second temperature increase appears after around 0.5 ps due to the hyperbolic equation and the concomitant reflection of the temperature wave from the rear side. We are not able to decide here whether the differences between the temperature at longer times

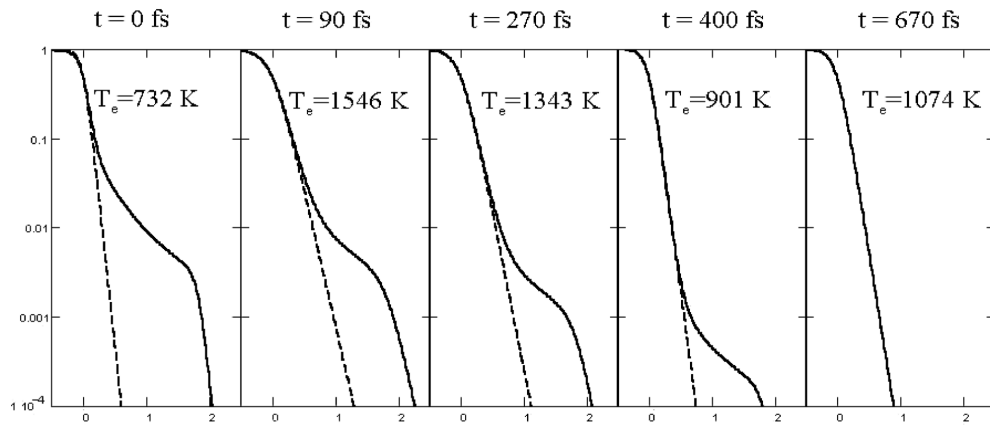


Figure 2. Theoretical electron energy distribution function against energy with $300 \mu\text{J cm}^{-2}$ absorbed laser fluence at five time delays. The dashed line is the Fermi-Dirac function and the corresponding electron temperature T_e is shown.

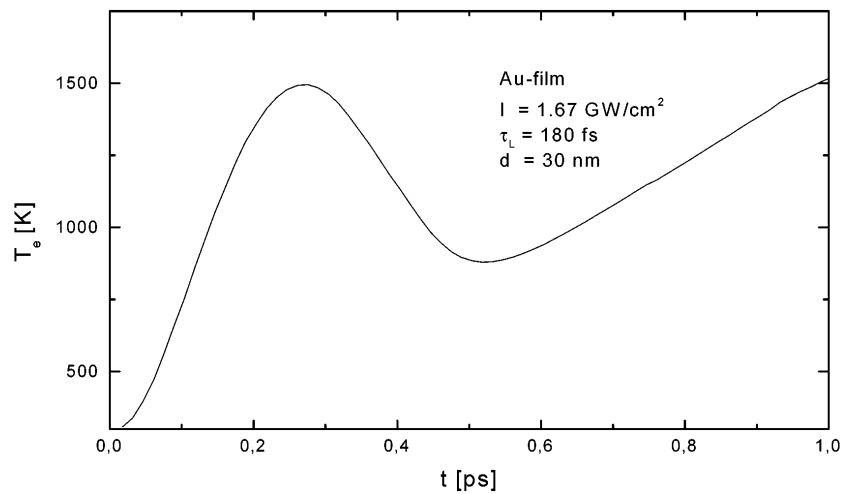


Figure 3. Electron surface temperature as a function of time for an Au film with thickness of $d = 30 \text{ nm}$.

are coming from a weakness of the ETTM model or whether they could be traced back to the relatively large experimental uncertainty of 30% in the absorbed fluence.

The corresponding change of the phonon temperature, not plotted here, is only 9 K from $T = 300$ to 309 K at $t = 1 \text{ ps}$ in agreement with the experimental finding of Groeneveld *et al* (1990).

An unambiguous resolution of such a wavelike property (figure 3) is not possible by a pump and probe experiment due to the unavoidable spatial and temporal averaging. We can, however, interpret the maximum of the electron temperature at $t = 400 \text{ fs}$ in their fit, i.e., long after the laser pulse, as an indication. Such behaviour cannot occur in a diffusive model, for example, the TTM.

Since the choice of time $t = 0 \text{ fs}$ is somewhat arbitrary we have selected it in such a way that the ratio of the calculated temperatures at $t = 0 \text{ fs}$ and $t = 130 \text{ fs}$ is roughly the same as

the ratio of the values found in the experiment. That is, $t = 0$ fs in figure 2 corresponds to $t = 100$ fs in figure 3.

In a second example, we use our nonequilibrium distribution function for a short derivation of the thermal conductivity. A more detailed treatment based, however, only on the first order term, equation (23.1), but including the thermoelectric contributions is reported in Hüttner (1998).

The heat flow is defined by $q = -\lambda \nabla T$ if the thermal gradient is a well defined quantity. This depends on the condition that the mean free path is much smaller than the characteristic length of the thermal gradient, i.e., $L_{mfp} \ll T/|\nabla T|$. This may be not valid in the case of short laser pulses. Nevertheless, in the following we assume that the condition is fulfilled. Furthermore, we take into account that, on short time scales, the electron temperature can be much higher than the phonon temperature and expand, therefore, the chemical potential as a function of the electron temperature up to the second order. Under these circumstances the thermal conductivity reads

$$\lambda = - \sum (E - \mu[T]) \bar{v} f (\nabla T)^{-1} \quad (26)$$

with $\mu(T) = \mu_0[1 - (\pi^2/12)x^2 - (7\pi^4/360)x^4]$ (Ashcroft and Mermin 1976, p 47) and $x = T_e/\mu_0$ where μ_0 is the chemical potential at zero kelvin. For a heat flow perpendicular to the surface, an approximation especially appropriate for short laser pulses as shown by many authors, we obtain from equation (23.1) for laser radiation parallel to the surface normal

$$\lambda = \sum \frac{(E - \mu[T_e])^2}{T_e} v^2 \tau(E, T_e, T_{ph}) \left(- \frac{\partial f_0}{\partial E} \right). \quad (27)$$

The inverse of the transport scattering time $\tau(E, T_e, T_{ph})^{-1}$ consists of the sum of the electron–phonon scattering rate and of the electron–electron one. Using equation (25) we can write for it

$$\tau^{-1} = \tau_{ph}^{-1} + \tau_{e-e}^{-1} = \tau_{ph}^{-1} + \tau_T^{-1} + \tau_E^{-1} = \tau_{ph}^{-1} + 4\pi^2 \beta T_e^2 + \beta(E - \mu)^2. \quad (28)$$

Its explicit form can be rewritten as

$$\tau(E, T_e, T_{ph}) = \frac{\tau_{ph}(T_{ph})}{1 + z(T_e, T_{ph}) + \tau_{ph}(T_{ph})\beta(E - \mu(T_e))^2} \quad (29)$$

where the function $z(T_e, T_{ph})$ is defined by the ratio of the electron–phonon scattering time over the temperature dependent part of the electron–electron scattering time

$$z(T_e, T_{ph}) = \frac{\tau_{ph}(T_{ph})}{\tau_T(T_e)} = 4\pi^2 \beta T_e^2 (eV) \tau_{ph}(T_{ph}). \quad (30)$$

Converting the sum into an integral and using the free electron density of states we obtain after integration

$$\lambda_1 = \lambda_{LTE} \frac{T_e}{T_{ph}(1 + z(T_e, T_{ph}))} \left\{ \sqrt{G(T_e)} - \frac{1}{\sqrt{G(T_e)}} \left[\frac{\pi^2 T_e^2}{24\mu_0^2} + \frac{7\pi T_e^4}{240\mu_0^4} \right] \right\} \quad (31)$$

where the conductivity λ_{LTE} is related to the case of local thermal equilibrium, i.e., $T_e = T_{ph} = T$. It contains only the electron–phonon scattering and reads

$$\lambda_{LTE} = \frac{\sigma_D \pi^2 k_B^2 T_{ph}}{3e^2}. \quad (32)$$

The function $G(T_e)$ is defined by

$$G(T_e) = 1 - \frac{\pi^2 k_B^2 T_e^2}{12\mu_0^2} - \frac{7\pi^4 k_B^4 T_e^4}{360\mu_0^4}. \quad (33)$$

Equation (32) is, of course, nothing other than the Wiedemann–Franz law with the dc electrical conductivity.

When local thermal equilibrium can be assumed then $G(T_e) \cong 1$, since μ_0 is typically of the order of some ten thousands of kelvin, and λ_1 becomes similar but not identical to the standard expression $\lambda = \lambda_{LTE}$. Nevertheless, even in this case the correction due to $z(T_e, T_{ph})$ may not be negligible depending on the absolute value of β as can be seen in figure 4.

The second order term of the Boltzmann equation, equation (23.2), is handled in the same way. One can greatly reduce the evaluation of this expression by formally interchanging the time integration with the integration over the k -space and observing that after multiplication with the velocity only even powers can contribute. Taking this into account we find for the distribution function

$$g_2 = 2\tau^2 \vec{v} \nabla T G \left(\frac{\partial f_0}{\partial T} \right). \quad (34)$$

Insertion into equation (27) leads to the second order correction

$$\lambda_2 = \sum \frac{v^2 \tau 2p}{T_e} \left\{ [E - \mu - \omega]^2 \left(-\frac{\partial f_0(E - \mu - \omega)}{\partial E} \right) + [E - \mu + \omega]^2 \left(-\frac{\partial f_0(E - \mu + \omega)}{\partial E} \right) - 2[E - \mu]^2 \left(-\frac{\partial f_0(E - \mu)}{\partial E} \right) \right\}. \quad (35)$$

After a straightforward but cumbersome computation one obtains for λ_2

$$\begin{aligned} \lambda_2 = \lambda_{LTE} \frac{T_e}{T_{ph}} 2\hat{p}_0(T_{ph}, \omega, t) & \left\{ \frac{\sqrt{G(T_e) + \hbar\omega/\mu_0}}{N(T_e, T_{ph}, \omega)^3} \left[N(T_e, T_{ph}, \omega) + \frac{z\hbar\omega}{12\mu_0} + \frac{7\pi^4 z\hbar\omega k_B^2 T_e^2}{120\mu_0^3} \right] \right. \\ & + \frac{\sqrt{G(T_e) - \hbar\omega/\mu_0}}{N(T_e, T_{ph}, \omega)^3} \left[N(T_e, T_{ph}, \omega) - \frac{z\hbar\omega}{12\mu_0} - \frac{7\pi^4 z\hbar\omega k_B^2 T_e^2}{120\mu_0^3} \right] \\ & - \frac{\pi^2}{N(T_e, T_{ph}, \omega)^2} \left(\frac{1}{\sqrt{G(T_e) + \hbar\omega/\mu_0}} + \frac{1}{\sqrt{G(T_e) - \hbar\omega/\mu_0}} \right) \\ & \times \left[\frac{k_B^2 T_e^2}{24\mu_0^2} + \frac{7\pi^2 k_B^4 T_e^4}{120\mu_0^4} \right] - \frac{1}{\sqrt{G(T_e)}(1 + z(T_e, T_{ph}))^2} \\ & \left. \times \left[\frac{\hbar\omega}{2\mu_0} + \frac{\pi^2 k_B^2 T_e^2}{48\mu_0^2} + \frac{7\pi^4 k_B^4 T_e^4}{480\mu_0^4} \right] \right\} \quad (36) \end{aligned}$$

where $G(T_e)$ was introduced in equation (33) and the abbreviation $N(T_e, T_{ph}, \omega)$ has the following meaning

$$N(T_e, T_{ph}, \omega) = 1 + z(T_e, T_{ph}) + \frac{z(T_e, T_{ph})\hbar^2\omega^2}{4\pi^2 k_B^2 T_e^2}. \quad (37)$$

Furthermore, we have rewritten $p_0(t)$ with the aim of extracting the expression from the energy integral by multiplying the numerator and the denominator by τ_{ph} , respectively. It then reads

$$\hat{p}_0 = v(t)\tau_{ph} = \frac{I_0\tau_{ph}}{n\hbar\omega\delta} e^{-(t-\tau_L)^2/\tau_L^2}. \quad (38)$$

It is worthwhile noting that λ_2 is explicitly dependent on the photon frequency and on the time and not merely implicitly from the latter due to $T_e(t)$ and $T_{ph}(t)$ like λ_1 and λ_{LTE} . The contribution of λ_2 to the thermal conductivity is effected by the magnitude of the laser intensity which, however, is subjected to some restriction in our model caused by the necessary smallness of the expansion parameter p .

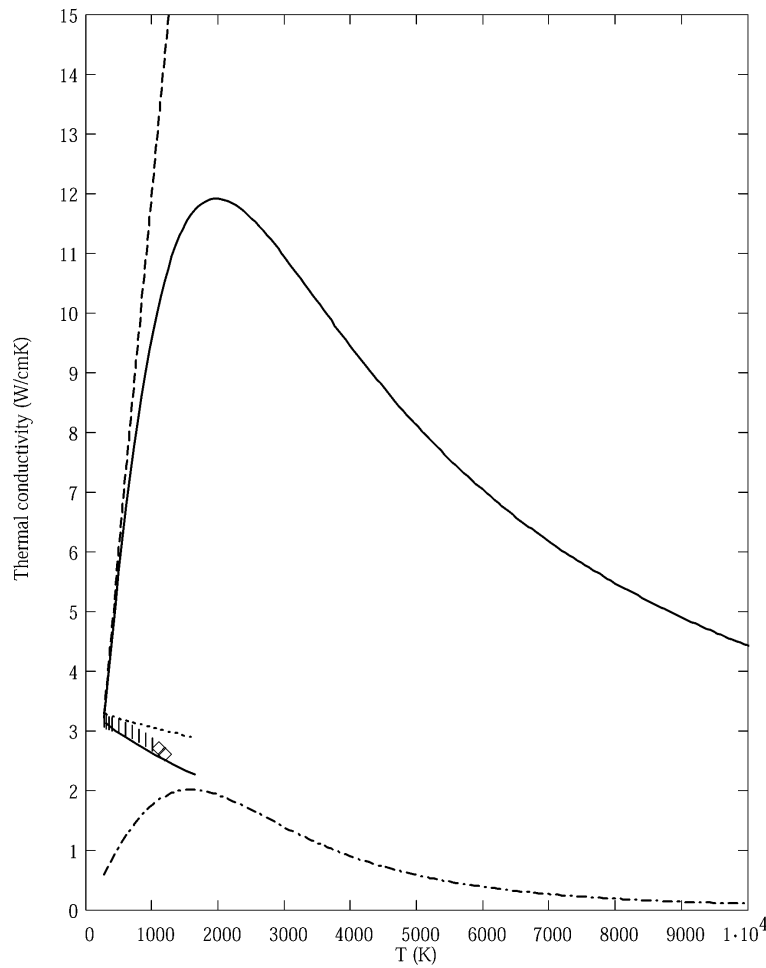


Figure 4. Thermal conductivity of Au for the case of nonlocal thermal equilibrium at fixed $T_{ph} = 300$ K: solid upper curve $\lambda_1 + \lambda_2$, dashed curve equation (39), dashed-dotted curve λ_2 , and for the local thermal equilibrium $T_e = T_{ph} = T$: solid curve λ_1 , dotted curve λ_{LTE} , \diamond experimental data taken from Weast (1982); for the laser parameter used cf text.

In figure 4 are shown plots of the complete thermal conductivity and of λ_2 for gold in the standard way, that is as a function of the temperature, as well as in the case of nonlocal thermal equilibrium at a fixed temperature of $T_{ph} = 300$ K, and for $T_e = T_{ph} = T$ evaluated for the fluence $F = 50 \text{ mJ cm}^{-2}$, $\tau_L = 500 \text{ fs}$, $\omega = 1 \text{ eV}$ and $\beta = 2.4 \times 10^{13} \text{ s eV}^{-2}$. Although the assumed constancy of the phonon temperature is only an approximation it is not a strong restriction as mentioned above.

Additionally the often used expression for the dependence of thermal conductivity on the electron temperature is plotted

$$\lambda(T_e) = \lambda_0 \frac{T_e}{T_0} \quad (39)$$

where T_0 is an arbitrary reference temperature. Although this approximation results from equation (31) for $z \ll 1$ and $k_B T_e \ll \mu_0$ it has to be used with care since already at fairly low electron temperatures, for gold about 2000 K, the true behaviour is completely different. By

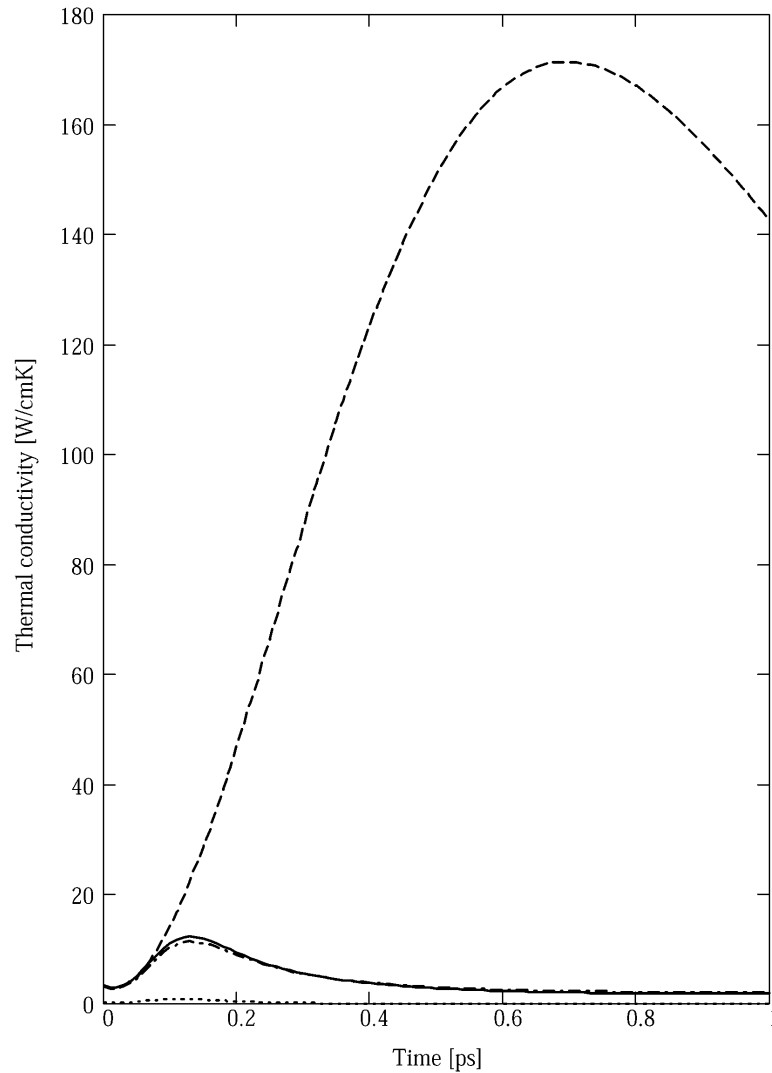


Figure 5. Thermal conductivity of Au as a function of time: solid curve $\lambda_1 + \lambda_2$, dashed–dotted curve only the expression in front of the opening curly bracket in equation (31), dotted curve λ_2 , dashed curve equation (39).

further increasing the electron temperature the thermal conductivity starts decreasing roughly inversely proportional to T_e instead of pursuing the postulated linear dependence. Without doubt, such changed behaviour must have consequences on the calculations of the electron and phonon temperature distribution in metals irrespective of the model selected (ETTM or TTM). Since the thermal diffusivity, the ratio of the thermal conductivity over the electronic specific heat, and, therefore, the transport of the heat inside the metal is reduced at higher temperatures one anticipates an increase of the temperatures to higher values near the surface. Work in this direction is in progress and will be reported elsewhere.

Due to the explicit time dependence of λ_2 it cannot be correctly described as a simple function of the temperature. With the aim to give at least an estimate of its contribution we

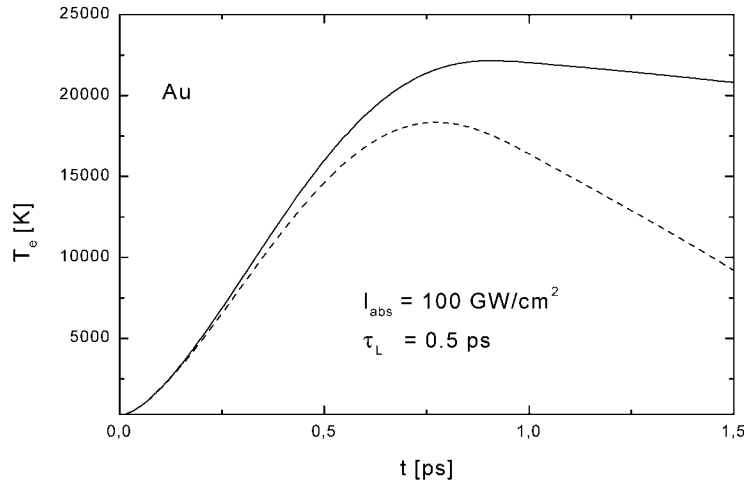


Figure 6. Temperature of the electrons at the surface calculated by means of the ETTM: with the main part of equation (31) (solid curve) (see text) and with λ given by equation (39) (dashed curve).

have set the time t equal to the laser pulse length τ_L for an evaluation. This approach is justified by figure 5 where the thermal conductivity is given as a function of time. To find these curves we have determined with the above parameters the approximate time dependence of electron and phonon temperature at the surface by means of our ETTM and used these data as the input quantities for the calculation of the conductivities. This is not a completely self-consistent evaluation since only the main part of λ_1 , the expression in front of the opening curly bracket in equation (31), was taken into account in the temperature calculation. Figures 6 and 7 present the used electron and phonon temperatures as a function of time. As expected, for the case of linear temperature dependence of the thermal conductivity the electron temperature reaches lower values and decreases faster than for the more exact expression. The phonon temperature seems to be opposite but this is caused by the assumed constancy of the coefficient of heat exchange. Taking into account the above mentioned correction for h_{ex} at high electron temperatures we would find τ_Q reduced by a factor of 2–3 (Wang *et al* 1994) and, therefore, some slightly faster relaxation. We have not done this in the calculation of figures 6 and 7 because both the coefficient of heat exchange and the coefficient of the specific heat of the electrons have to be modified in the ETTM. To be consistent, one has to do this from the beginning and not in the final formula. Such extensions would, however, require a complete recalculation of the ETTM.

Concluding this section, we discuss the consequences of the different electron and phonon temperatures on the frequency dependent electrical conductivity. This point is especially significant for the calculation of the optical properties of metals (Hüttner 1994, 1995). Using equation (17) the electrical current is given by

$$\vec{j}_e = \sigma \vec{E} = -e \sum \vec{v} [f_0 + p f_1 + p^2 f_2]. \quad (40)$$

Restricting to the first order term and taking into account that odd powers of the velocity vanish we obtain from equation (23.1) for the current

$$\vec{j}_e = e \sum_{\vec{k}} \frac{\vec{v}^2 e \tau}{(1 - i\omega\tau)} \vec{E}_0 e^{-i\omega t} e^{-(t^2/2\tau_L^2)} \left(-\frac{\partial f_0}{\partial E} \right) + e \sum (E - \mu) \vec{v}^2 \tau \frac{\nabla T}{T} \left(-\frac{\partial f_0}{\partial E} \right). \quad (41)$$

Since both the electron–phonon and electron–electron scattering processes contribute to the specific resistivity we have to insert for the scattering time the expression supplied by

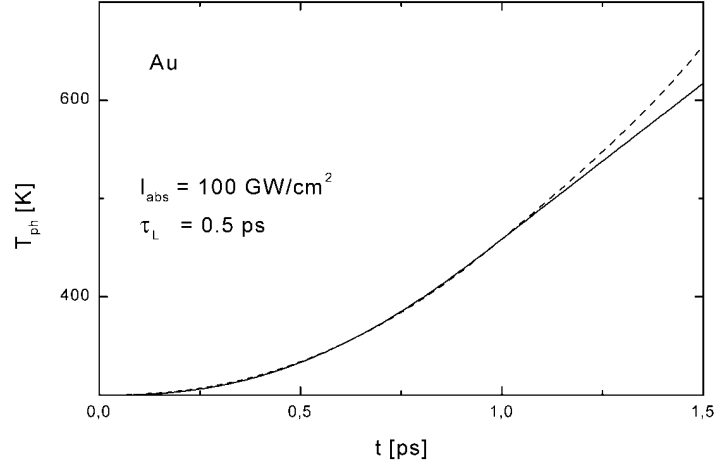


Figure 7. Temperature of the phonons at the surface calculated by means of the ETTM: with the main part of equation (31) (solid curve) (see text) and with λ given by equation (39) (dashed curve).

equation (29). From this it follows directly for the frequency dependent conductivity

$$\sigma(\omega, T_e, T_{ph}, t) = e^2 e^{-(t^2/2\tau_L^2)} \sum_k \frac{\vec{v}^2 \tau}{(1 - i\omega\tau)} \left(-\frac{\partial f_0}{\partial E} \right) \quad (42)$$

where we have omitted the thermoelectric part by using the same points as discussed in the thermal case in the context of equation (26). It can be shown that the correction due to the temperature dependence of the chemical potential is smaller for the electrical conductivity compared to the thermal one. For this reason, we approximate in what follows the Fermi energy by its value μ_0 at zero temperature. Thus, in the free electron case we find after integration over the angles and altering the variables from k to E :

$$\sigma(\omega, T_e, T_{ph}, t) = \frac{\sigma_D}{\sqrt{\mu_0} \tau_D} e^{-(t^2/2\tau_L^2)} \int dE \sqrt{E} \frac{\tau(E, T_e, T_{ph})}{[1 - i\omega\tau(E, T_e, T_{ph})]} \left(-\frac{\partial f_0}{\partial E} \right) \quad (43)$$

where σ_D is the Drude conductivity, that is $\sigma_D = ne^2\tau_D/m$, and τ_D is the related scattering time. To evaluate the integral we apply the Sommerfeld expansion and obtain for the complex electrical conductivity

$$\begin{aligned} \sigma(\omega, T_e, T_{ph}, t) = \sigma_D \Gamma e^{-(t^2/2\tau_L^2)} & \left\{ \left[(1+z) - \frac{z}{12} - \frac{\pi^2 k_B^2 T_e^2}{24\mu_0^2} (1+z) + \frac{z\Gamma\omega^2\tau_D^2}{6} \right] \right. \\ & \left. + i\omega\tau_D \left[1 - \frac{z}{6(1+z)} - \frac{\pi^2 k_B^2 T_e^2}{24\mu_0^2} + \frac{z\Gamma\omega^2\tau_D^2}{6(1+z)} \right] \right\} \quad (44) \end{aligned}$$

with the new abbreviation

$$\Gamma = \Gamma(\omega, T_e, T_{ph}) = \frac{1}{(1 + z(T_e, T_{ph}))^2 + \omega^2\tau_D^2}. \quad (45)$$

It is easy to verify that equation (44) turns into the familiar Drude expression for a stationary electric field in the case of local thermal equilibrium and for not too high temperatures, that is for $z \ll 1$. Although the correction terms to the standard expression of the electrical conductivity are of similar structure to those of the thermal one their quantitative contribution is smaller. The reason for this behaviour can be found in the product $\omega\tau_D$ that is much larger than unity

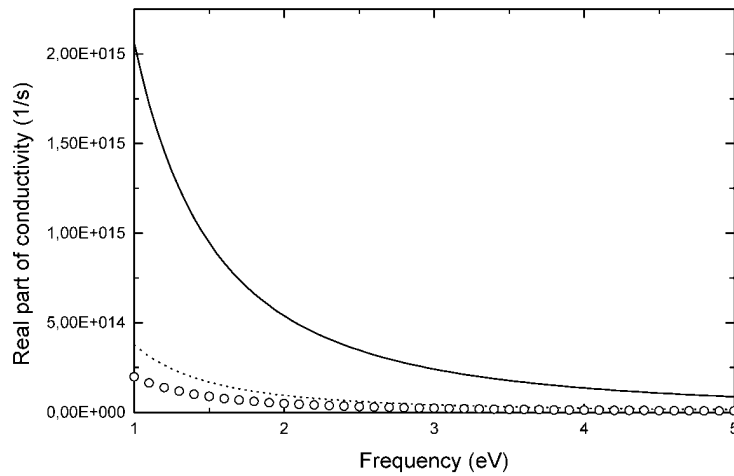


Figure 8. Real part of the conductivity (s^{-1}) of gold as a function of the frequency (eV) calculated at $t = 0$; dotted and solid line equation (44) for $T_{ph} = 300$ K and $T_e = 10\,000$ K and 3000 K, respectively, (O) Drude's theory.

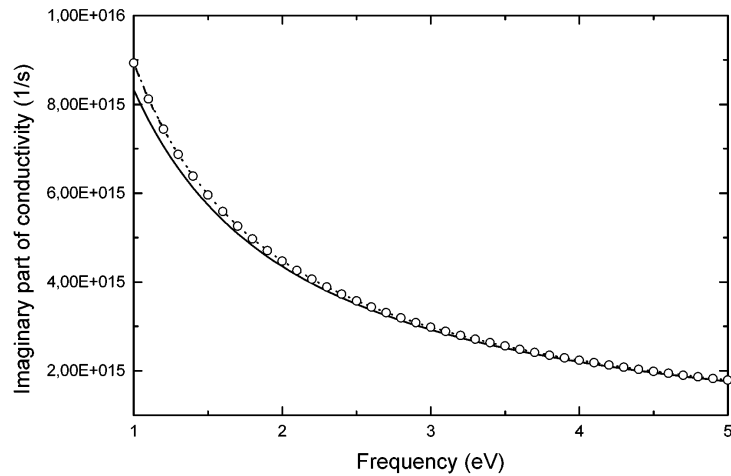


Figure 9. Imaginary part of the conductivity (s^{-1}) of gold as a function of the frequency (eV) calculated at $t = 0$; dotted and solid line equation (44) for $T_{ph} = 300$ K and $T_e = 10\,000$ K and 3000 K, respectively, (O) Drude's theory.

for laser frequencies in the visible range and above. On the other hand, even small changes of the complex conductivity can lead to significant corrections to the optical properties due to the interlocked structures of the real and imaginary part that are involved. In figures 8 and 9, a comparison between Drude's conductivity and the first order modifications are plotted.

It is remarkable that the corrections to the real part are much larger than to the imaginary one. This outcome agrees well with the experiment reported by Elsayed-Ali *et al* (1991). The authors found for gold films that in response to a fs laser pulse the imaginary part of the dielectric function undergoes a significantly higher perturbation than the real one.

Taking into account the second order of the expansion, equation (23.2), one obtains considerably stronger changes of the real and imaginary part. In this respect, the resulting

expressions again depend explicitly on time and on the laser power through the expansion parameter p_0 . The equations belonging to them are rather long and will, therefore, be presented in a separate paper together with the conclusions for the optical properties.

In conclusion of this section, we discuss the relationship between the electrical and thermal conductivity known as the Wiedemann–Franz law

$$\lambda = \sigma T L_0 \quad (46)$$

where L_0 is the Lorenz number, $L_0 = 3(\pi k_B/3e)^2$.

Regarding only the lowest order terms, equations (31) and (44), it becomes immediately clear that they do not carry out such a simple relation because the electrical conductivity is time dependent but the thermal one is not. This is not surprising since both currents are driven by different forces. The electric field vanishes when the laser pulse is over; the thermal gradient, of course, remains. In the static case, however, where the electron and phonon temperature coincide we obtain

$$\frac{\lambda}{\sigma T} \approx \frac{\lambda_{LTE}}{(1+z(T))} \frac{(1+z(T))}{\sigma_D T} = L_0 \quad (47)$$

if only the leading terms were taken into account. That is the Wiedemann–Franz law keeps its validity also at higher temperatures due to the mutual canceling of the correction term $(1+z)$. This is confirmed by accurate measurements of the Lorenz ratio of liquid metals (Ida and Guthrie 1993).

5. Summary

In this paper we have investigated the nonequilibrium electron distribution in metals in the transient regime by means of a second order expansion of the Boltzmann equation. By definition the transition range is located between the time necessary for the establishment of the electron temperature and the time where a description by the standard steady state equations is justified. The lower time limit is estimated to be about 100 fs while the upper one depends on the regarded physical property and therefore it can span a long time interval.

For the description of the electrical and thermal currents in the transition range we have derived relaxation functions and calculated the relaxation times related to them. It was shown that for the electrical transport the relaxation time corresponds to Drude’s momentum scattering time. It is, for this reason, usually smaller than the lower time boundary of the model. Consequently, the steady state equation (Ohm’s law) is sufficient for the calculation of the electrical conductivity and of related properties. Nevertheless, also Ohm’s law becomes modified due to the local nonequilibrium between the electrons and phonons.

For the heat flow, however, the situation is completely different because it is governed by the temperature relaxation time. This quantity is given by the ratio of the electronic specific heat over the coefficient of energy exchange between the electron and phonon subsystems. For metals with a strong electron–phonon coupling and a high Debye temperature this coefficient is large and, consequently, the relaxation time is small. In the case of noble metals, for example, the situation is opposite and the relaxation time can take on values as long as picoseconds. If this happens the calculation of the electron temperature distribution must be based on the hyperbolic differential equation and no longer on the parabolic one. As a consequence, the spreading of the temperature loses its normal diffusive character and shows wavelike behaviour damped by phonon emission. Furthermore, new effects can appear in thin films like spatial and temporal modulations caused by the backscattering from the rear side. For applications it may be important that higher temperatures near the surface result from the delay of the heat transport in comparison with the diffusive description. This phenomenon is additionally amplified by

the nonlinear temperature dependence of the electronic thermal conductivity that was at first derived by Hüttner (1998) and extended here to the second order corrections. Moreover, the nonequilibrium energy distribution of the electrons in gold was evaluated during and after the interaction with an fs laser pulse. The comparison with the experiment offers a good agreement.

In conclusion, a closed theory is proposed for the treatment of the local thermal nonequilibrium between the electron and phonon subsystems and for the transient behaviour of electronic properties. This approach was successfully used for the calculation of the electrical and thermal conductivity that now depend explicitly on the time and the laser frequency and for the determination of the time evolution of the electron energy distribution.

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