Nonequilibrium electron energy-loss kinetics in metal clusters

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Abstract. Ultrafast energy exchanges of a non-Fermi electron gas with the lattice are investigated in silver clusters with sizes ranging from 4 to 26 nm using a femtosecond pump–probe technique. The results yield evidence for a cluster-size-dependent slowing down of the short-time energy losses of the electron gas when it is strongly athermal. A constant rate is eventually reached after a few hundred femtoseconds, consistent with the electron gas internal thermalization kinetics, this behaviour reflecting evolution from an individual to a collective electron–lattice type of coupling. The timescale of this transient regime is reduced in small nanoparticles, in agreement with speeding up of the electron–electron interactions with size reduction. The experimental results are in quantitative agreement with numerical simulations of the electron kinetics.

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1. Introduction

Controlling and understanding the properties of nanomaterials has been an intense field of research during the last few decades. It has been motivated by both fundamental interests and the very broad technological applications of nanostructured systems in many different fields. The interaction processes of elementary excitations inside a cluster (electronic and vibrational interactions, spin dynamics, ...) and their coupling with the environment (surrounding matrix, adsorbed molecules, other nanoparticles, ...) play key roles here. With the advance of femtosecond lasers they can now be selectively investigated using time-resolved optical techniques that permit us to directly monitor energy and charge exchange kinetics at a nanometric scale.

In the case of metallic materials, time-resolved studies are based on selective optical excitation of the electrons on a timescale shorter than that of the electron relaxation processes. The different steps of nonequilibrium electron relaxation are subsequently followed with a time-delayed probe pulse. This monitors the time evolution of an optical property of the material that depends on the electron distribution or lattice temperature, i.e., that is modified by electron excitation. This approach, first used in bulk metal [1]–[6], has been recently extended to clusters embedded in a matrix, deposited on a substrate or in a gas jet. Information has for instance been obtained on ultrafast electron interactions (electron–electron (e–e) and electron–lattice energy exchanges), acoustic vibrations and energy exchanges with the matrix [7]–[9].

In particular, it has been recently shown that, after optical excitation by a femtosecond pulse, establishment of an electron temperature by e–e scattering takes place on a few hundred femtosecond timescale in both bulk and nanostructured noble metal materials [4]–[6, 10]. This slow kinetics is a consequence of the reduction of the e–e scattering probability by screening of the Coulomb interaction and Pauli exclusion principle effect [1, 4]–[6, 8]. In noble metal clusters, the electron thermalization has been shown to be accelerated by screening reduction due to surface effects for sizes smaller than about 10 nm, the characteristic thermalization time \( \tau_{th} \) decreasing from \( \approx 350 \) fs in bulk silver and large silver nanoparticles to \( \approx 200 \) fs in 4 nm Ag clusters [8]–[10]. In bulk noble metals, the electron–lattice energy exchanges, via electron–phonon (e–ph) scattering, take place on a longer but comparable timescale (typically 1 ps). In nanoparticles, measurements performed in Ag-doped glass samples have shown an increase of the electron cooling rate in small clusters, with a size dependence similar to that of the electron internal thermalization rate [8, 9]. These results, obtained in the weak-excitation regime (maximum electron temperature rise smaller than typically 200 K), are in contrast to those reported in the strong-excitation regime, mostly for colloidal solutions [7, 8, 11]. As discussed in [7] and [8], this discrepancy could be due to the excitation dependence of the electron kinetics in the strong-excitation regime.

The electron thermalization times are much larger than the duration of the now available femtosecond optical pulses offering the unique possibility of analysing the properties of an athermal quasi-free electron gas. This has been exploited in bulk noble metal to demonstrate that, in this nonequilibrium situation, the energy loss rate to the lattice is reduced as compared to the one for a thermal system [5, 6, 12]. A similar effect is expected in clusters, but on a shorter timescale and with a smaller amplitude due to the faster electron gas internal thermalization. This interplay between electron–lattice coupling and e–e scattering has not yet been reported in these systems, probably because its observation requires high-sensitivity short-timescale measurements in the weak-perturbation regime. In this paper, we are experimentally and theoretically investigating...
Figure 1. Computed electron distribution change in silver induced by intraband absorption of a 30 fs pulse for time delay of 0 fs (full curve) and 500 fs (dotted curve) for a maximum equivalent excitation temperature of 370 K. $\hbar \Omega_{ib}$ is the interband transition threshold between the top of the d-bands and the Fermi surface ($\hbar \Omega_{ib} \approx 3.9$ eV in silver). The arrows indicate intraband electron excitation at $\hbar \omega_{pp} \approx 3$ eV and off resonant probing at $\hbar \omega_{pr} \approx 1.5$ eV. $E_B$ indicates where the position of the conduction band bottom would be if one could assume a perfectly parabolic isotropic band shape.

these first steps of nonequilibrium electron relaxation in silver clusters, focusing on the short-timescale evolution of the electron–lattice energy exchange and its correlation with electron internal thermalization.

2. Nonequilibrium electron excitation

In noble metals, optical absorption is associated with intra-conduction-band transitions (quasi-free electron absorption) and, above a threshold $\Omega_{ib}$, with interband transitions from the full d-bands to empty states above the Fermi energy $E_F$. In our experiments, an athermal nonequilibrium electron distribution is selectively created using a femtosecond pump pulse of frequency $\omega_{pp}$ below the interband transition threshold ($\omega_{pp} < \Omega_{ib}$) (figure 1). Only intraband absorption takes place, modifying the conduction electron distribution [4, 13]. Electrons with an energy $E$ between $E_F - \hbar \omega_{pp}$ and $E_F$ are excited above the Fermi energy with a final energy between $E_F$ and $E_F + \hbar \omega_{pp}$ (figure 1). Describing the conduction electrons by a one-particle distribution function $f$ and assuming an isotropic parabolic conduction band, the distribution change created by the pump pulse at time $t$ is given by [4]:

$$\frac{df_{exc}}{dt}(E, t) = B I_p(t) \left\{ \sqrt{E - \hbar \omega_{pp}} f(\sqrt{E - \hbar \omega_{pp}}, t)[1 - f(E, t)] - \sqrt{E + \hbar \omega_{pp}} f(\sqrt{E + \hbar \omega_{pp}}, t)[1 - f(E + \hbar \omega_{pp}, t)] \right\},$$

(1)
where $E$ is the electron energy, $I_p$ the pump pulse intensity and $B$ a parameter describing the electron–photon coupling efficiency. Neglecting electron energy relaxation during the excitation process, a steplike shape nonequilibrium electron distribution is created.

Even for very short pump pulses, the above picture is modified when taking into account the finite pulse duration. During the excitation process, the injected energy is redistributed among the electrons by e–e scattering and, to a lesser extent, transferred to the lattice by e–ph interaction. The kinetics of the excitation and energy redistribution processes have been shown to be well described by the electron Boltzmann equation [4, 6]:

$$\frac{df(E,t)}{dt} = \frac{df(E,t)}{dt} \bigg|_{e-e} + \frac{df(E,t)}{dt} \bigg|_{e-ph} + \frac{df_{exc}}{dt}(E,t). \quad (2)$$

The first and second terms on the right-hand side are the e–e and e–ph scattering rates, respectively. Their expressions are given in [6] for a bulk metal, assuming a screened Coulomb potential for e–e scattering and deformation potential e–ph coupling. Though this is a rough approximation in metal, it has been shown that the exact nature of the e–ph coupling does not influence the computed electron dynamics. This is a consequence of the fact that, the lattice temperature $T_L$ being larger than the Debye temperature $\Theta_D$, electron distribution changes on the energy scale of a phonon have a minor influence on the overall dynamics.

The time-dependent electron distribution functions computed using (1) and (2) are shown in figure 1 for a 30 fs pump pulse with $\hbar \omega_{pp} \approx 3$ eV. With the e–e scattering efficiency scaling as $(E - E_F)^2$, electron states away from $E_F$ relax on a few-femtosecond scale (the lifetime of electron states 1 eV above $E_F$ is about 20 fs). This leads to a fast build-up of the induced distribution change amplitude $\Delta f(E,t) = f(E,t) - f_0(E)$ around $E_F$ ($f_0$ is the equilibrium electron distribution function at the initial temperature $T_0$) that takes place concurrently with excitation by the pump pulse. This fast energy redistribution is at the origin of the $\Delta f(E)$ shape distortion as compared to instantaneous excitation (figure 1). However, e–e scattering being strongly reduced close to $E_F$, the electron distribution stays athermal for few hundred femtoseconds. Establishment of a hot Fermi distribution with temperature $T_e$ takes place with a characteristic time $\tau_{th} \approx 350$ fs in bulk silver [6].

The above electron dynamics modelling has been developed for bulk metals. As a first approximation, it can be used for interpreting the ultrafast response of not too small particles (at least for $D \geq 3$ nm) where the main band structure features of the bulk material are retained [14]. Enhancement of the e–e and e–ph scattering efficiencies by surface effects has to be taken into account in confined systems. As a rough approximation, it can be done by phenomenologically increasing the amplitude of the corresponding scattering rate in (2).

During and after their internal thermalization, the electron gas loses its energy to the lattice by e–ph scattering. Electron–lattice thermalization is eventually reached in a few picoseconds; the characteristic electron–lattice thermalization time is $\sim 1$ ps, only about three times slower than that for internal electron thermalization. Energy losses to the lattice on the timescale of the electron gas thermalization are thus non-negligible and can be monitored by a second femtosecond probe pulse in time-resolved experiments.

3. Experimental set-up

Experiments were performed exciting and probing the electrons of silver nanoparticles using the fundamental and second harmonic frequencies of a Ti:sapphire laser. Our experimental system
Figure 2. Time dependence of the normalized transmission change $\Delta T/T$ measured off resonance at $\hbar \omega_{pr} \approx 1.5$ eV for resonant excitation of the surface plasmon resonance $\hbar \omega_{pp} \approx \hbar \Omega_R \approx 3$ eV in spherical Ag nanoparticles in glass of average diameter $D = 24$ nm.

is based on a home-made femtosecond Ti:sapphire oscillator generating 25 fs frequency tunable near-infrared pulses with an average power of 1 W at 80 MHz. Part of the pulse train is used as the probe beam ($\hbar \omega_{pr} \approx 1.5$ eV). The pump beam is created by frequency doubling the remaining part in a 100 $\mu$m thick BBO crystal. After recompression in a fused silica prism pair the blue pulse duration, measured by cross-correlation with the infrared pulse, is about 30 fs. A standard pump–probe set-up has been used with mechanical chopping of the pump beam at 1.5 kHz and lock-in and differential detection of the probe beam transmission change. The pump and probe beams were independently focused into the sample using fused silica lenses over 30 $\mu$m focal spots.

Measurements were performed in samples formed by spherical silver nanoparticles embedded in a 50BaO–50P$_2$O$_5$ glass matrix. They were prepared by a fusion and heat treatment technique [15]. The metal volume fraction, $p$, is in the range (1–5) $\times$ 10$^{-4}$. Different samples with particle mean diameter $D$ ranging from 4 to 26 nm with a standard size deviation smaller than 10% were used. For comparison, measurements were also performed in optically thin ($L = 23$ nm) polycrystalline silver films.

4. Nonequilibrium electron energy relaxation

A signature of the creation of an athermal distribution is the transient reduction of the occupation of electron states well below $E_F$ (i.e. for $E_F - E \gg k_B T_e$), that are fully occupied in thermal equilibrium (figure 1). This occupation change can be detected by monitoring the induced interband absorption of the probe pulse that excites d-band electrons to these free conduction band states. Its frequency $\omega_{pr}$ must satisfy

$$\hbar \omega_{pp} > \hbar \Omega_{ib} - \hbar \omega_{pr} \gg k_B T_e. \tag{3}$$

In the case of silver $\hbar \Omega_{ib} \approx 4$ eV and, for instance, these conditions are verified for a blue pump $\hbar \omega_{pp} \approx 3$ eV and an infrared probe $\hbar \omega_{pr} \approx 1.5$ eV pulses (or the reverse, infrared pump and
blue probe). The probe transmission change measured in these conditions in a $D = 24$ nm silver nanoparticle sample is shown in figure 2 as a function of the delay $t_D$ between the pump and probe pulses. The short-timescale transient peak reflects the transient population of the monitored short-living electronic states about 2.5 eV below $E_F$, confirming the broad electron distribution perturbation induced by the pump pulse. As in silver films [12], the long delay signal ($t_D > 50$ fs) is dominated by the intraband contribution to $\Delta T/T$ and will not be discussed here.

Relaxation of the nonequilibrium electrons is probed by monitoring the time-dependent sample transmission change $\Delta T/T$ of a femtosecond probe pulse in off-resonant conditions (i.e. for a probe photon energy $\hbar \omega_{pr}$ well below the interband transition threshold $\hbar \Omega_{ib}$). In these conditions and for a not strongly out of equilibrium situation (i.e., for $\Delta f$ extending over an energy range much smaller than $\hbar (\Omega_{ib} - \omega_{pr})$ below $E_F$), $\Delta T/T$ is almost insensitive to the details of the electron distribution and proportional to the electron gas excess energy density $\Delta u_e$ [5, 6]:

$$\Delta T/T(t_D) \propto \Delta u_e(t_D) \propto \int E \Delta f(E, t_D) \, dE.$$  \hspace{1cm} (4)

For a blue probe pulse, these conditions are realized after a few tens of femtoseconds, permitting us to directly monitor electron energy losses to the lattice.

This is confirmed by computing the time evolution of $\Delta T/T$ for $\hbar \omega_{pr} = 3$ eV from the calculated electron distribution change as described in [8]. It is very similar to that computed for $\Delta u_e$, with only a slight deviation for short time delays when the distribution is strongly athermal, i.e., occupation of electron states far below $E_F$ are modified.

**Figure 3.** Time behaviour of the normalized transmission change $\Delta T/T$ measured off resonance with the interband transitions ($\hbar \omega_{pp} \approx 3$ eV) for $\hbar \omega_{pr} \approx 1.5$ eV in $D = 26$ nm (full curve) and $D = 6$ nm (dotted curve) Ag nanoparticles in glass. The inset shows the same data on the logarithmic scale after subtraction of the long delay residual signal $(\Delta T/T)_b$ for the $D = 26$, 6 and 4 nm samples (from top to bottom; the curves are vertically shifted for clarity). The dashed curves correspond to an exponential decay with $\tau_{e-ph} = 820, 680$ and 600 fs, respectively, with a better than 5% precision.
Figure 4. (a) Measured and (b) calculated temporal evolution of the transmission change $\Delta T/T - \Delta(T/T)_b$ in Ag nanoparticles with average diameter $D = 26$ nm (top), 6 nm (middle) and 4 nm (bottom) on the short-time logarithmic scale. The dashed lines correspond to an exponential decay with $\tau_{e-ph} = 820, 680$ and 600 fs, respectively.

The transmission changes $\Delta T/T$ measured in $D = 4, 6$ and 26 nm samples are shown in figure 3. The $\Delta T/T$ amplitude has been checked to scale linearly with the pump fluence, confirming that multiphoton excitation plays a minor role here [16]. On a long timescale, $t_D \geq 1$ ps, they decay exponentially in all samples as shown by plotting them on a logarithmic scale after subtraction of their small residual background (for $t_D > 10$ ps). This regime corresponds to a constant e–ph energy transfer rate and is in agreement with the theoretical results for a thermalized electron gas in the weak-perturbation regime (two-temperature model). The extracted decay time yields an effective e–ph coupling time close to the one measured in bulk materials for the $D = 26$ nm sample. As reported before, it decreases for smaller sizes, reflecting the increase of the electron–lattice coupling in small clusters [8, 9].

The situation is very different on a short timescale, as shown in figure 4. For large nanoparticles and films, the short-timescale $\Delta T/T$ decay clearly shows that the electron gas energy loss rate to the lattice is initially slow and increases over a timescale of a few hundred femtoseconds to reach its long delay value. This behaviour is a direct consequence of the
existence of a long-living athermal electron gas. During the excitation process, a very small number of electrons gains a large excess energy as compared to $k_B T_0$. As a crude approximation, separating the electron gas into unperturbed and nonequilibrium electrons, only the latter ones can lose energy by phonon emission. Their number increases with time as e–e scattering redistributes energy among the carriers: this leads to an overall increase of the energy loss rate to the lattice during the early stages of the internal electron gas thermalization [5, 12]. As internal thermalization is approached, the above separation is no longer valid and a constant energy loss rate is eventually reached, corresponding to collective electron gas–lattice interaction as described by the two-temperature model. This evolution from a quasi-individual to a collective electron behaviour is responsible for the observed short-time non-exponential decay of the excess energy.

In small metal nanoparticles, e–e scattering is enhanced by surface effects making the electron gas internal thermalization faster ($\tau_{th} \approx 250$ and 200 fs for $D = 6$ and 4 nm silver nanoparticles, respectively) [10]. The transient nonequilibrium regime for e–ph energy exchanges is thus expected to be observed only on a shorter timescale, i.e., an exponential behaviour should be reached on a smaller timescale. This is in agreement with the experimental results in $D = 6$ and 4 nm samples, the transient regime being barely observable for the smallest nanoparticles (figure 4(a)).

The above description of the interplay between electron thermalization and energy losses can be made more quantitative by computing the electron gas relaxation dynamics using the electron Boltzmann equation. The time evolution of $\Delta u_e$ calculated for the bulk silver conditions is shown in figure 4(b) and exhibits the same behaviour as the experimental ones for the film or large-nanoparticle cases. Similar calculations performed assuming instantaneous internal thermalization of the electron gas only show an exponential decay of $\Delta u_e$ in agreement with the two-temperature model.

For the nanoparticles, as a first approximation, the simulations were repeated modifying the e–e and e–ph scattering rate to match their increase with cluster size reduction. The results are in very good agreement with the experimental ones showing the same transient evolution of the signal decay to an exponential behaviour on a reduced timescale with size reduction. This confirms the strong interplay between e–e and e–ph scattering observed in bulk metals and yields further evidence of the acceleration of the electron energy exchanges in small clusters.

5. Conclusion

Using a two-colour femtosecond pump–probe technique, we have investigated the ultrafast energy exchanges of a nonequilibrium electron gas with the lattice in silver nanoparticles. Experiments performed in the weak-perturbation regime in off resonant conditions permit us to monitor the evolution of the energy losses during the early stages of the electron gas kinetics as it evolves from an athermal to a thermal distribution.

The results demonstrate that, as in bulk metals, the electron gas energy losses to the lattice are slowed down for a non-Fermi distribution. Electron energy subsequently decays exponentially in agreement with the two-temperature model for a Fermi electron distribution. This thermalized regime is reached faster in small nanoparticles, confirming the recently demonstrated increase of the e–e interactions with size reduction. The experimental results are in quantitative agreement with numerical simulations of the electron kinetics phenomenologically introducing an increase of the efficiency of the electron interactions. These investigations open up many perspectives...
for the experimental analysis of the properties of strongly out of equilibrium electrons. Their interpretation however requires theoretical developments going beyond usual approximations in metals, in particular to properly describe many-body effects in this transient nonequilibrium regime.

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