Eur. Phys. J. D **34**, 199–204 (2005)
DOI: 10.1140/epjd/e2005-00107-8

THE EUROPEAN PHYSICAL JOURNAL D

Effects of confinement on the electron and lattice dynamics in metal nanoparticles

J. Lermé[1,a], G. Celep[1], M. Broyer[1], E. Cottancin[1], M. Pellarin[1], A. Arbouet[2], D. Christofilos[2], C. Guillon[2], P. Langot[2], N. Del Fatti[2], and F. Vallée[2]

[1] Laboratoire de Spectrométrie Ionique et Moléculaire, CNRS and Université Lyon I, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne, France
[2] Centre de Physique Moléculaire Optique et Hertzienne, CNRS and Université Bordeaux I, 351 cours de la Libération, 33405 Talence, France

Received 6 September 2004

Abstract. Effects of confinement on the electron-electron (e-e) and electron-phonon (e-ph) thermalization dynamics in noble metal clusters are calculated using simple approaches. The model predictions are compared with femtosecond pump-probe measurements which display an acceleration of the e-e and e-ph relaxation dynamics. The size-effects on the e-e relaxation dynamics are consistent with a model involving the surface-induced reduction of the screening efficiency of the Coulomb e-e interaction. With regard to the e-ph relaxation dynamics, this model yields too large time constants, pointing out deficiencies of the standard modelling of the e-ph energy exchanges in bulk metals. Analysis of these deficiencies shows that the bare e-ion interaction has to be involved in the transition matrix element describing the non-adiabatic e-ph energy exchanges.

PACS. 36.40.-c Atomic and molecular clusters – 78.47.+p Time-resolved optical spectroscopies and other ultrafast optical measurements in condensed matter – 42.65.-k Nonlinear optics

1 Introduction

Effect of the confinement on the electron dynamics in nanometer-sized metal particles has been an intense field of research during the past decade [1–3]. Besides its importance from a fundamental point of view, a comprehensive understanding of the finite-size effects on the electron relaxation mechanisms is of primary interest due to the potential application of metal particles as building blocks for photonic or electronic integrated devices designed to process ultrafast signals. Time-resolved optical techniques have been recognized to be powerful tools for ensuring this challenge, but well-controlled experimental conditions are required to extract physically-meaningful results from very low intensity signals. Owing to insufficient resolution (too large light-pulse duration) very scarce reliable results on the internal electronic (e-e) relaxation are available [4] (time-scale on the order of one to a few hundreds fs), in contrast with the electron-phonon (e-ph) relaxation which takes place over a longer time scale (typically 1-2 ps). Regarding the measured e-ph thermalization time constants, one has however to mention that contradictory results about the size effects have been reported on [1–3, 5–7]. The discrepancies result very likely from the pump intensity-dependence of the measured kinetics which is rooted, to a large part, in the temperature-dependence of the electronic heat capacity.

These last years an experimental investigation on various metallic systems has been undertaken in the low perturbation regime, in using the same apparatus and — as far as possible — under similar experimental conditions, that depend on the kinetics to be measured [4, 7]. Usually, off-resonant probe excitation is selected for studying the e-ph kinetics (photon energy below both the interband-transition threshold ($\hbar\Omega_{ib}$) and the surface plasmon energy), whereas probe photon energy tuned near $\hbar\Omega_{ib}$ is required for e-e relaxation kinetics measurements. These studies are carried out over large size ranges and involve various embedding media. Let us summarize the major shared findings. Firstly, for large enough particles (typically above 10 nm in diameter), the thermalization time constants are found to converge towards the value measured on a 30 nm-thickness metal film, suggesting that the asymptotic large-diameter value reflects a bulk property. Secondly, for a given size, the time constants are found almost independent of the surrounding material, pointing out that the measured kinetics correspond to intrinsic dynamical processes inside the particles (very likely, the energy exchanges with the embedding material take place

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[a] e-mail: `lerme@lasim.univ-lyon1.fr`

at longer time scales). Thirdly, a systematic decrease of the e-e and e-ph relaxation time constants for decreasing particle sizes is observed, for each studied metallic system. Moreover the relative size evolutions are similar in all the systems, suggesting that common physical mechanisms underlie the confinement-induced changes of the e-e and e-ph thermalization kinetics.

In order to explain, at least partly, the acceleration of the relaxation processes in small noble metal particles, the reduction of the screening efficiency close to the surface has been tentatively brought forwards, within a model approach involving the same ingredients as those responsible for the finite-size effects on the linear optical properties [8]. Briefly, this model takes into account the specific electronic and dielectric properties at the surface, that are related to, on the one hand the spillout of the electron-density tail beyond the classical particle radius, and, on the other hand the surface skin of ineffective d-electron polarisability. Let us emphasize that, with respect to the e-ph relaxation, other alternative mechanisms, involving for instance the vibrational surface modes, may contribute to the size effects [5,6]. In bulk metals the screening of the Coulomb interaction is of central importance for describing dynamical processes involving energy or momentum exchanges between the metal constituents (electrons and ions). These processes are, at the microscopic level, described in terms of two-body e-e and e-ph scattering events. Since the corresponding transition matrix elements involve the Coulomb interaction operator, it is clear that the electronic screening, which describes the self-consistent correlated response of the many-interacting electron system, plays a central role in modifying noticeably the effective two-body interaction forces. In the bulk the two main factors ruling the screening strength are: (i) the background core electron-related dielectric function ϵ_b (for noble metals, this contribution corresponds to the real and virtual transitions between occupied *d*-bands and the *s*-*p* conduction-band), (ii) the average conduction-electron density n_0 [9]. As emphasized above, close to the particle surface, both screening sources are reduced, leading to a size-dependent relative decrease of the mean screening efficiency, i.e. to an increase of the net effective mean scattering rate.

In Section 2 the experimental and model results are presented and briefly discussed in order to introduce the physical context of this work. At the end of this section it will be emphasized that, in addition to the overestimation of the relative size-trend for Au, the theoretical model — although grounded on a widespread Condensed-Matter (CM) description — suffers from serious deficiencies. In Section 3 the major results we obtained in analyzing these deficiencies for the bulk are given. This exploratory work indicates that the standard CM modelling of the non-adiabatic electron-lattice energy exchanges, which involves screened e-ph interactions, is actually incorrect. Finally, with regard to the finite size-effects on the e-ph thermalization, some hints on possible additional effects are presented (Sect. 4).

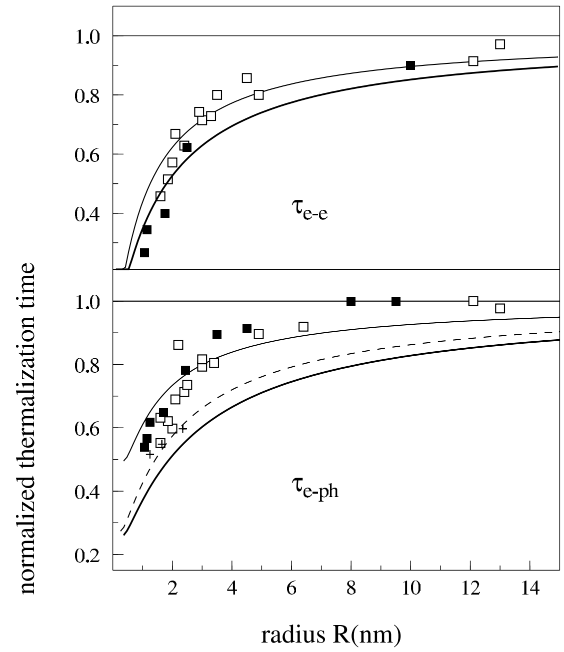

Fig. 1. Size dependence of the e-e (upper figure) and e-ph (lower figure) thermalization time constants. The experimental results [black squares (Au), empty squares (Ag), crosses (Cu)] have been normalized relative to the bulk time constant deduced from measurements on the metal films. The model predictions [thick line (Au), thin line (Ag), dashed line (Cu)] have been normalized relative to the asymptotic (large R) theoretical value.

2 Experimental and model results

The time-resolved spectroscopy experiments have been performed using a high-sensitivity femtosecond pump-probe setup. Details of the apparatus can be found elsewhere [1,4,7]. From the recorded transient differential transmission and reflection changes $\Delta T(\tau)/T$ and $\Delta R(\tau)/R$ (τ is the delay between the probe and pump pulses) the transient linear changes of the effective complex dielectric function of the samples can be deduced, from which the real- and imaginary-component changes $\Delta\epsilon_1(\tau)$ and $\Delta\epsilon_2(\tau)$, corresponding to the metal particles, can be obtained. In relating both dielectric-function components to the electron population modifications $\Delta n(\mathbf{k},\tau)$ through Lindhard-type expressions of the metal dielectric function, the e-e relaxation kinetics may be extracted ($\mathbf{k}$ is the electron wave-vector).

The experimental time-constants characterizing the internal e-e thermalization are shown in Figure 1, for Ag and Au. In order to plot all the results on the same figure the values are normalized relative to the bulk value of the corresponding metal [τ_{e-e}(bulk) $\approx$ 350 fs and 450 fs for Ag and Au, respectively]. No analytical formula can be given for expressing the e-e thermalization time. Let us stress that this time constant characterizes a global stochastic process of the electron gas, and has not to be confused with the Fermi-liquid-theory electron life-times [9], which depend strongly on the energy relative to the Fermi energy (E_F) and the temperature. The expression of the electron life-times indicates only that an approximate scaling law of the form $\tau_{e-e} \backsim \epsilon_b^{1/2} n_0^{5/6}$ is expected. Simulation of the e-e relaxation dynamics for the bulk (≈ film), calculated in solving the Boltzmann kinetic-equations in the framework of the Fermi liquid theory (involving a screened e-e Coulomb interaction), allows to reproduce quite well the short-time experimental signals. For the metal particles such a model approach is not technically feasible, because of the loss of the translational symmetry (wavefunctions appropriate to the spherical symmetry are required, and the position-dependent non-local susceptibility has to be introduced for describing properly the screening in such finite systems). As briefly mentioned in Section 1, the relative size effects have been roughly estimated in spatially averaging the local bulklike scattering rate inside the particle volume, through the position-dependent electron density $n(r)$ and background dielectric constant $\epsilon_b(r)$ [4]. The good agreement between theory and experiment suggests that the observed decrease of the time constant $\tau_{e-e}(R)$ with decreasing size results from the local reduction of the screening strength close to the surface.

When the probe photon energy is well below $\hbar\Omega_{ib}$, the experimental signal following the pump-pulse duration can be shown to be proportional to the electron-gas energy excess $\Delta E_e(\tau)$ relative to the equilibrium thermalized state. Assuming that the electron and phonon gases are independently thermalized [temperatures $T_e(\tau)$ and $T_{ph}(\tau) \approx T_0$ (room temperature), respectively], the electron cooling dynamics is well described by the well-known "two-temperature model". In the low perturbation regime, the electronic heat capacity $C_e(T_e)$ can be identified with $C_e(T_0)$, and an exponential decay of both $T_e(\tau)$ and $\Delta E_e(\tau)$ is predicted. The time constant is given by $\tau_{e-ph} = C_e(T_0)/G$, where G is the so-called electron-phonon coupling constant. Under standard approximations, and using the Boltzmann kinetic-equations, an analytical formula for the e-ph thermalization time can be derived

$$\frac{1}{\tau_{\text{e-ph}}} = \frac{A}{MT_0 n_0^{1/3}} \int_0^{q_d} q^3 \frac{|W(q)|^2}{|\epsilon(q)|^2} dq \qquad (1)$$

where A is a constant, M the ion mass, q_D the Debye wave-vector, $\mathbf{q}$ the wave-vector of the annihilated or created phonon, $W(q)$ and $\epsilon(q)$ are the corresponding Fourier components of the bare e-ion interaction and of the static dielectric function, respectively [$\epsilon(q) \approx \epsilon_b + (q_{TF}(n_0)/q)^2$ where $q_{TF}(n_0)$ is the Thomas-Fermi wave-vector]. In this approach, widespread in the Solid-State literature, the e-ph scattering matrix element involves basically the *screened* e-ion interaction. Historically the "prescription" concerning the screening of the e-ion interaction can be traced back to the early work by Bardeen in the context of the Bloch theory of conductivity [10]. As for the e-e thermalization the relative size-effects have been roughly estimated in spatially averaging the local scattering rate, through the position-dependent parameters governing the screening efficiency in $\epsilon(q)$. The theoretical results are presented in Figure 1 [empty-core Ashcroft parametrization of the bare e-ion interaction; the ionic radii tabulated in Ref. [12] have been taken for the radius of the empty-core radius] and compared with the normalized experimental measurements. The calculated normalized relative size-effects are found in rather good agreement with the experiments, except for a noticeable overestimation for Au, over the entire size range. Besides the differences in the ion mass, and slightly different mean electron densities n_0, the three noble metals differ essentially in the value of their static interband dielectric constant ($\epsilon_b \approx 5.9$, 3.7 and 6.7, for Cu, Ag and Au, respectively). We have thus suspected this model to overestimate the ϵ_b-dependence of the e-ph coupling constant G [11]. Moreover, the model leads to wrong predictions with regard to the absolute magnitude, as well as to the bulk metal-to-metal e-ph time constant ratios. From the experiments on the 30 nm-thickness films, the following approximate values are extracted: $\tau_{e-ph}(\text{Cu}) \approx 620$ fs, $\tau_{e-ph}(\text{Ag}) \approx 870$ fs, $\tau_{e-ph}(\text{Au}) \approx 1150$ fs. The model predictions for the bulk are: $\tau_{e-ph}(\text{Cu}) \approx 1.9$ ps, $\tau_{e-ph}(\text{Ag}) \approx 2.3$ ps, $\tau_{e-ph}(\text{Au}) \approx 9.5$ ps. These large values, that are inconsistent with the experiment, have forced us to call into question the reliability of the standard CM approach. These discrepancies pose the question of the relevance of the screening in the non-adiabatic electron-lattice energy exchanges.

3 Electron-lattice energy exchanges: the role of the screening

In this section we point out the inconsistencies of the standard CM description, and argue that the transition matrix element ruling the non-adiabatic energy exchanges between the electrons and the lattice involve the *bare* e-ion interaction. The simple arguments given in the beginning will be rigorously grounded at the end of this section. Basically, the physical picture on which is founded the standard CM approach consists of delocalized electrons in a periodic potential, described by Bloch-states, exchanging energy and momentum with a set of independent oscillators (harmonic approximation) via creation or annihilation of phonons, through a screened e-ion interaction. The standard formulation rests physically on a *model Hamiltonian* of the following type

$$H_B = \sum_i \left[-\frac{\hbar^2}{2m} + W(\mathbf{r}_i) \right] + V_{ee} + H_{e-ph}(...\mathbf{r}_i..., ...\mathrm{Q}_{j,\boldsymbol{q}}...) + \frac{1}{2} \sum_{j,\boldsymbol{q}} \left[\mathrm{P}^*_{j,\boldsymbol{q}} \mathrm{P}_{j,\boldsymbol{q}} + \omega_j(\boldsymbol{q})^2 \mathrm{Q}^*_{j,\boldsymbol{q}} \mathrm{Q}_{j,\boldsymbol{q}} \right] \qquad (2)$$

$W(\mathbf{r}_i)$ is the periodic potential experienced by the electrons, the $Q_{j,\mathbf{q}}$'s are the normal phonon modes (j stands for the acoustic branch, $\mathbf{q}$ for the phonon wave-vector), V_{ee} is the e-e Coulomb interaction, and H_{e-ph} is the bare e-ph interaction [departure of the overall e-ion interaction V_{en} from its value at the equilibrium lattice geometry (V^0_{en}), restricted ordinarily to the first order with respect to the ion displacements $R_{nu} - R^0_{nu} = s_{nu}$, with $u = x$,

y or z. $H_{e-ph} \approx \sum_{i,j\mathbf{q}} Q_{j,\mathbf{q}} V_{j,\mathbf{q}}(\mathbf{r}_i)$]. Since the only effect of V_{ee} that is retained in the CM approach, at least in the present context, consists in the e-ion interaction screening, $H_{e-ph} + V_{ee}$ could be directly replaced by the screened e-ph Hamiltonian.

As a matter of fact, although of widespread use in the literature, the model Hamiltonian H_B is not consistent with the basic metal Hamiltonian

$$H = T_e + V_{ee} + V_{en}(...\mathbf{r}_i..., ...\mathbf{R}_n...) + V_{nn} + T_n \qquad (3)$$

where standard notations have been used. Since V_{en} is the only term coupling the positively-charged ionic system and the negatively-charged electronic system, it is clear that the separate treatment of the electronic and ionic problems is strictly impossible. The standard procedure consists in adding to the electronic part $T_e + V_{ee}$ the e-ion interaction taken at the equilibrium lattice configuration (i.e. V^0_{en}), allowing to generate electronic states including, from the outset, physical properties that are rooted in the periodicity of the lattice (band structure). But this first step clearly prevents definitely the ionic system from being neutralized, necessary prerequisite for defining an equilibrium lattice geometry. Artificial ansatz met sometimes in the literature, consisting for instance in introducing homogeneous — negative and positive — charge distributions for handling independently the electronic and ionic Hamiltonians are indeed incorrect, and actually amounts to counting two times the e-ion interaction V_{en} [13]. More precisely, such a procedure has only to be considered as an approximation, suitable in specific contexts, for solving roughly, either the electronic problem, or the ionic problem. However, care has to be taken for treating physical processes involving the full Hamiltonian, as the e-ph coupling problem, in order to avoid double-counting of physical ingredients that contribute both in the electronic and lattice properties. In comparing H_B and H it is clear that the normal modes in H_B have to be derived from the bare ion-ion interaction V_{nn} solely. Since all the ions are positively charged, the definition of a "bare phonon spectrum" in unclear, and has to be rigorously defined, whatever the metal sample size is. This "bare spectrum" rests necessarily on an artificial procedure (introduction of a fictitious neutralizing homogeneous negatively-charged background for instance). However the spurious additional contributions introduced through the ad-hoc procedure have to be subtracted from the full Hamiltonian.

In fact, in the model Hamiltonian H_B, the electronic screening is already implicitly taken into account in two terms. First, the screening is essential for defining a periodic (or flat) potential over the entire volume. For example, the self-consistent effective electronic potential arising from DFT calculations on spherical jellium-clusters is completely different from the bare ionic potential which is quadratic inside the particle volume. Second, the observable strongly-dispersed phonon spectrum, having the correct long-wavelength behaviour $\omega(q \to 0) = v_s q$ (v_s is the sound velocity) entering the Hamiltonian H_B is the "dressed phonon spectrum", i.e. the ionic vibrational spectrum derived from the effective short-range ion-ion interaction (screened ion-ion interaction). Starting from a model Hamiltonian expressing as H_B, in which the phonon Hamiltonian is assumed built from a "bare phonon spectrum" $\Omega(q)$ [the $\Omega(q)$'s are on the order of the ionic plasma frequency], Bardeen and Pines have shown in applying a canonical transformation that the e-ph interaction H_{e-ph}, in presence of the V_{ee} term (inducing thus many-body effects, i.e. screening effects), yields renormalized (or "dressed") phonon frequencies scaling as $\omega^2(q) = \Omega^2(q)/\epsilon(q)$ [14]. It is thus clear that in applying the canonical transformation on H_B (which involves the low-frequency renormalized spectrum) a spurious additional renormalization of the spectrum would result. This indicates that V_{ee} has necessarily to be eliminated from the Hamiltonian H_B in order to avoid double-renormalization of the phonon spectrum. If V_{ee} is eliminated, it is therefore clear that screening the e-ion interaction in H_{e-ph} for describing the energy exchanges between the electrons and the phonons is an incorrect prescription. This arguing indicates that the screening effects, in the present context, are fully taken into account in the renormalized phonon spectrum. Moreover, in a recent paper published during this work, and based on elaborate first-principles Green-function methods, the inconsistency of Hamiltonians of type H_B [referred to as "Fröhlich-type Hamiltonians" by Leeuwen] has been also pointed out [15].

The above arguments, and the difficulty in splitting strictly the metal Hamiltonian (Eq. (3)) into an electronic part, a phonon part (each subsystem having to be charge neutralized) and a — small — residual term, strongly suggests that the e-ph coupling problem is incorrectly described by the *model Hamiltonian* H_B. Indeed, the e-ph coupling problem must be tackled in using a strategy where the renormalized phonon spectrum is properly defined, without resorting to the spurious introduction of neutralizing backgrounds. To our opinion the only correct method is actually the Born-Oppenheimer (BO) approach, which is known to give accurate vibrational frequencies, not only for small molecules, but also for large crystals [16]. In addition, contrary to the standard CM formulation (Eq. (2)), the BO approach allows to separate from the outset the adiabatic reversible e-ph scattering events [17] from the stochastic events corresponding to the irreversible (i.e. non-adiabatic) energy exchanges between the electrons and the ions. This aspect is of crucial importance if e-ph dynamical processes are investigated through Boltzmann-like rate-equations, that are suitable only if incoherent scattering events occur. In the BO approach the first step consists in solving the electronic eigen-value problem with $H_e = H - T_n$, where the electronic quantities depend parametrically on the ion positions $\{\mathbf{R}_n\}$ [$H_e|\psi^e\rangle = E|\psi^e\rangle$]. This leads to the well-known result stating that the electronic energy $E(...\mathbf{R}_n...)$ plays the role of a potential energy for the ionic motions [18]. Second, the transition matrix elements, the so-called non-adiabatic terms of the Molecular Physics, are ensured by the ion kinetic energy operator T_n and involve the first (major term) and second derivatives of the electronic BO wavefunction with respect to the ionic coordinates. The transition matrix element between two different BO electron-phonon factorized states [labels i (electronic energy E_i) and f (E_f)] reads as (major term)

$$-\hbar^2 \sum_{j,\boldsymbol{q}} \left\langle \Phi_f^{\rm ph} \right| \langle \psi_f^{\rm e} | \left[\frac{\partial}{\partial Q_{j\boldsymbol{q}}} |\psi_i^{\rm e}\rangle \right] \left[\frac{\partial}{\partial Q_{j\boldsymbol{q}}} \left| \Phi_i^{\rm ph} \right\rangle \right] \qquad (4)$$

where the electronic and phonon states are labelled by the superscripts "e" and "ph", respectively (the ion mass factor M is included in the normal vibrational coordinates).

Actually, it can be easily proved that the electronic matrix element is proportional to a matrix element of the *bare* operator $\partial V_{en}/\partial Q_{j\mathbf{q}}$. Since $|\psi_f^e\rangle$ and $|\psi_i^e\rangle$ are distinct BO-electronic states one has $\langle \psi_f^e|\psi_i^e\rangle = 0$ and $\langle \psi_f^e|H_e|\psi_i^e\rangle = 0$, for any ionic configuration $\{\mathbf{R}_n\}$. Differentiating both equations with respect to $Q_{j\mathbf{q}}$ leads to the exact relation

$$\langle \psi_f^{\rm e} | \left[\frac{\partial}{\partial Q_{j\mathbf{q}}} |\psi_i^{\rm e}\rangle \right] = \frac{1}{E_i - E_f} \langle \psi_f^{\rm e} | \frac{\partial V_{en}}{\partial Q_{j\mathbf{q}}} |\psi_i^{\rm e}\rangle \qquad (5)$$

in noting that the term involving $\partial V_{nn}/\partial Q_{j\mathbf{q}}$ vanishes since V_{nn} does not depend on the electronic coordinates (moreover, for degenerate states, the matrix element of $\partial V_{en}/\partial Q_{j\mathbf{q}}$ vanishes). In the above equation all the quantities depend on the $Q_{j\mathbf{q}}$'s. Since for a large system (bulk) the phonon spectrum is independent of the BO-electronic state $E_i - E_f$ is equal to its "equilibrium-value" $[E_i - E_f](\{\mathbf{R}_n^0\}) = E_i^0 - E_f^0$, and is then independent of the vibrational normal coordinates. To the lowest order $\partial V_{en}/\partial Q_{j\mathbf{q}}$, ψ_f^e and ψ_i^e have to be taken at the equilibrium geometry. As it will be seen below, this amounts to disregarding direct multi-quanta/phonon processes, as assumed in the standard approach (H_{e-ph} restricted to the first order expansion of V_{en} relative to the equilibrium geometry). Under this approximation the non-adiabatic transition matrix element, expressed in terms of the $Q_{j\mathbf{q}}$'s, can be factorized and reads as

$$-\frac{\hbar^2}{(E_i^0 - E_f^0)} \sum_{j,\boldsymbol{q}} \langle \psi_f^{\rm e} | \frac{\partial V_{en}}{\partial Q_{j\boldsymbol{q}}} |\psi_i^{\rm e}\rangle \left\langle \Phi_f^{\rm ph} \right| \frac{\partial}{\partial Q_{j\boldsymbol{q}}} \left| \Phi_i^{\rm ph} \right\rangle. \qquad (6)$$

From this expression it can be inferred that the transition matrix element is non-vanishing provided that the two phonon states $\Phi_f^{\rm ph}$ and $\Phi_i^{\rm ph}$ differ only in a single quantum [the sum over $(j, \mathbf{q})$ reduces actually to a single term since, in the harmonic approximation, the phonon states are products of one-dimensional vibrational states]. Noting that $P_{j\mathbf{q}} = (\hbar/i)(\partial/\partial Q_{j\mathbf{q}}))$ the ph-matrix element can be related to the matrix element of the operator $Q_{j\mathbf{q}}$, leading to the expression

$$\frac{(E_f^{\rm ph} - E_i^{\rm ph})}{(E_i^0 - E_f^0)} \sum_{j,\boldsymbol{q}} \langle \psi_f^{\rm e} | \frac{\partial V_{en}}{\partial Q_{j\boldsymbol{q}}} |\psi_i^{\rm e}\rangle \left\langle \Phi_f^{\rm ph} \right| Q_{j\boldsymbol{q}} \left| \Phi_i^{\rm ph} \right\rangle. \qquad (7)$$

For initial and final electron-phonon states having the same total energy, the energy ratio in the above equation is equal to unity (the denominator and numerator are both equal to the quantum $\hbar\omega$ of the phonon mode involved in the process). Assuming the independent electron approximation in the final expression only (Eq. (7)), the standard CM matrix element of the operator H_{e-ph} with the *bare* (i.e. *unscreened*) e-ph interaction is recovered. This result supports the previous discussion about the double-counting of the screening effects in the Fröhlich-Bloch-type Hamiltonian. The non-adiabatic transions, corresponding to irreversible energy exchanges between the electrons and the phonons, are therefore ruled — to the lowest order with respect to the $Q_{j\mathbf{q}}$ — by the bare e-ion interaction.

4 Surface effects

With regard to the electron-lattice energy transfer in nanoparticles, the above discussion does not exclude screening reduction as a possible mechanism contributing to the size effect. However, inclusion of the screening reduction close to the nanoparticle surface is a difficult task since, in the context of the above discussion, screening is included in the dressed phonon frequencies. Conversely to electron-electron scattering, it cannot be introduced only in a space dependent renormalization of the interaction potential, but requires renormalization of the vibrational modes close to the surface. This can be done only in a more general approach describing confined vibrational and electronic modes interacting via a realistic coupling potential. In this context of alteration of both the involved states and coupling potential, let us emphazise that additional effects can also contribute. In particular, energy exchanges in the bulk material occur to a large extent through the coupling of the electrons with the longitudinal modes (strain modes; a single bulk acoustic branch contributes noticeably to the e-ph relaxation). This mode selection can be relax in nanoparticules, increasing the number of modes contributing to the interaction, and, consequently the electron-lattice energy exchanges as compared to the bulk metal case.

Actually, this effect has been suggested and previously introduced by describing electron-lattice energy exchanges in the context of electron interaction with the capillary surface modes (shape deformations, no strain) and acoustic surface modes (density changes) of the particle [19]. The former effect could be roughly considered as an effective surface-induced coupling with transverse surface modes and the latter that, in this model, yields a minor contribution, to interaction with longitudinal-like modes. The difficulty here is in correctly normalizing the interactions, in particular, the maximum capillary-mode frequency, and to connect the predicted confined and bulk material e-lattice coupling. This has led to different conclusions drawn by different authors. In reference [5] (gold particles; 1.3 nm $< R <$ 4.2 nm) the e-ph coupling constant $G(R)$ has been estimated in adding the capillary and acoustic surface mode contributions, $G_{cap}(R)$ and $G_A(R)$, to the bulk film-value: $G(R) = G_b + G_{cap}(R) + G_A(R)$, where $G_b = C_e(T_0)/\tau_{e-ph}$. Note that redundant mode counting results from such an approach. The authors conclude that the coupling with the surface modes do not alter significantly the effective e-ph coupling constant for particles of diameter exceeding 2 nm, in accordance with their experimental results. As mentioned in Section 1, the effect of the temperature [enlargement of $C_e(T)$ for small particles] probably blurs the size dependence of G. In reference [6] (gallium particles; 5 nm $< R <$ 9 nm) a simple expression $G(R) = G_{cap}(R)$ has been assumed, and, using a reasonable capillary-mode frequency cutoff, very good agreement with their experimental data was obtained, with a decreasing τ_{e-ph} time constants with size.

Though introduction of capillary modes is a first approach to include a possible contribution of transverse-like modes in confined metals, a more refined modelling is clearly necessary to connect the bulk and nanoparticle data. Note, in particular, that if $G(R)$ is identified with $G_{cap}(R)+G_A(R)$ [19] a larger energy transfer time in clusters than in the bulk is obtained, in spark contrast with the experimental results in noble metals. The definite interpretation and quantitative modelling of the finite-size effects in τ_{e-ph}, to which several mechanisms could contribute, remains an open question.

5 Conclusion

In this paper the e-e and e-ph thermalization kinetics in small noble metal nanoparticles have been investigated in the framework of simple approaches built from the Fermi-liquid theory and Condensed-Matter Physics ingredients, with surface-induced corrections. With regard to the e-e relaxation, the experimental data are found consistent with a model taking into account the modification of the screening of the bare e-e Coulomb interaction close to the surface. Concerning the e-ph relaxation, the standard CM modelling leads to too slow kinetics, pointing out that the finite-size effects on the e-ph relaxation kinetics are very likely rooted in a (or several) distinct mechanism. With respect to the bulk material, inconsistencies of the standard CM description of the non-adiabatic electron-lattice energy exchanges have been pointed out. Additional experimental data on various systems, and above all more elaborated models (and "first-principles" Molecular-Dynamics simulations for very small clusters) including appropriate electron-states and phonon-spectra, are required to analyze and disentangle the respective part of the various mechanisms likely contributing to the finite size-induced increase of the effective e-ph coupling constant relative to the bulk.

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18. In a forthcoming paper we will show that the normalized phonon frequencies $\omega(\mathbf{q})$ obtained in the BO approach can be expressed in terms of the $\mathbf{q}$-Fourier components of the two-body e-ion and ion-ion interactions and $\epsilon(\mathbf{q})$, exhibiting — for pure Coulomb interactions — the correct long-wavelength behaviour $\omega(\mathbf{q}) = \Omega/\epsilon(\mathbf{q})^{1/2}$, where Ω is the bare ionic plasma frequency. All the aspects of the screening effects, in relation with the e-ph coupling problem, investigated through the BO approach, will be reported and discussed in a detailed forthcoming paper
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