# Electronic temperature effects on the optical response of silver nanoparticles

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**Abstract.** The electronic temperature dependence of the optical absorption of silver nanoparticles is investigated in the framework of the time-dependent local-density approximation at finite temperature. Below the spectral region of interband transitions, we have found that the electronic temperature leads to a broadening and spectral shift of the surface plasmon resonance. The calculated differential transmission is in good agreement with recent experimental measurements obtained with time resolved pump-probe techniques.

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## 1 Introduction

Ultrafast spectroscopy using femtosecond laser pulses is a well suited technique to study the electronic energy relaxation mechanisms in metallic nanoparticles [1,2]. The experiments have been carried out with nanoparticles of noble metals containing several thousands of atoms and embedded in a transparent matrix. By using a time resolved pump-probe configuration it is possible to have access to the spectral and temporal dependence of the differential transmission, $\frac{\Delta \bar{T}}{T}(t,\omega)$, defined as the normalized difference between the probe pulse with and without the pump pulse. This quantity contains the information concerning the electron dynamics which is measured as a function, of the pump-probe time delay $t$ and of the laser frequency $\omega$.

For pump-probe delays longer than a few hundreds of femtoseconds the thermalization of the electrons is achieved leading to an increase of the electronic temperature of several hundreds of degrees. However, *the electronic distribution is not in thermal equilibrium with the lattice*, the thermal relaxation to the lattice being achieved in a few picoseconds *via* the electron-phonon scattering. The energy exchange between the electrons and the lattice can be described by the two temperature model leading to a time-dependent electronic temperature $T_e(t)$. Providing that the relative changes of the dielectric function with respect to a non-perturbed system are weak (linear regime) and that it is only due to a modification of the electronic

temperature of the confined quantum electron distribution, one may identify the spectral dependence of the differential transmission measured for a given time delay as the difference of the linear absorption cross-sections evaluated at different electronic temperatures.

In order to model and interpret the experimental results, the optical absorption cross-sections of silver nanoparticles encapsulated in an alumina matrix are evaluated in the framework of the time-dependent local-density approximation (TDLDA) at finite-temperature within the spherical jellium model. In this model only the $5s$ valence electrons are fully treated quantum-mechanically whereas the screening effects associated with the polarization of the localized $4d$ electrons are included by means of a background which is taken into account *via* the experimental dielectric function of the bulk metal, $\epsilon_d(\omega)$ [3–5]. This approach is made in the spirit of evaluating the importance of the conduction electrons in the dynamical behavior of the surface plasmon resonance, which so far as not been attempted. Let us emphasize that the contribution of the core electrons is also important to consider as was shown in previous works [1,2]. In these papers the corresponding interband contribution to the dielectric function was modelled with a temperature-dependent RPA bulk-like dielectric function, the temperature being itself time-dependent *via* a two temperature model. Strictly speaking, one should take into account finite-size effects on the electronic distribution, an effect which becomes important only for small size aggregates. In this work we will not incorporate the core electrons. The screening coming from the surrounding

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matrix is taken into account through a constant dielectric function, $\epsilon_m$ [6]. Finally, thermal effects are included using the Fermi-Dirac statistics within the grand-canonical ensemble. We show that our theoretical model is able to reproduce the main trends of the experimental results. In particular, the broadening and spectral shift of the surface plasmon are well reproduced. In the following, atomic units are used unless otherwise specified and $k_B$ is the Boltzmann's constant.

## 2 Theoretical method

### 2.1 Ground-state

The metallic nanoparticles are described in the spherical background jellium model, which is known to be a very good approximation for closed-shell clusters. This model consists in replacing the real ionic core potential by the potential of a constant positive background corresponding to a uniformly distributed charge density $\varrho_I$ [7]. For a nanoparticle of radius $R = r_s N^{1/3}$ having $A$ singly-charged ionic cores and $N$ valence electrons, this potential is given by

$$V_{\mathrm{jel}}(\boldsymbol{r}) = -\int V_{\mathrm{C}}(\boldsymbol{r}, \boldsymbol{r}') \, \varrho_I(\boldsymbol{r}') \, \mathrm{d}\boldsymbol{r}' \qquad (1)$$

with

$$\varrho_I(\boldsymbol{r}') = \begin{cases} \left(\frac{A}{V}\right) = \frac{3}{4\pi r_s^3} & \text{for} & r' \leq R \\ 0 & \text{for} & r' > R \end{cases}. \qquad (2)$$

For Ag we have used $r_s = 3.02$ a.u. The potential, $V_{\mathrm{C}}(\boldsymbol{r}, \boldsymbol{r}')$, which appears in (1) corresponds to the Coulomb interaction between two charges situated at $\boldsymbol{r}$ and $\boldsymbol{r}'$ in a medium constituted by a sphere, of radius $R$ and static dielectric function $\epsilon_d(0)$, and embedded in a transparent matrix with a constant dielectric function $\epsilon_m$ [8,9]. In the present work we have assumed that $\epsilon_d(0)$ is temperature independent. The electronic system is assumed to be at a thermal equilibrium with a temperature, $T_e$. In the Kohn-Sham formulation of the density functional theory at finite-temperature within the grand-canonical ensemble [10–14], the ground-state electronic density $\rho$ of an $N$-electron system is written, in terms of single-particle orbitals and energies $\varphi_i$ and $\varepsilon_i$, as

$$\rho(\boldsymbol{r}) = \sum_{k=1}^{N} f_k \, \rho_k(\boldsymbol{r}) = \sum_{k=1}^{N} f_k \, |\varphi_k(\boldsymbol{r})|^2 \qquad (3)$$

where $f_k = [1 + \exp\{(\varepsilon_k - \mu)/k_B T_e\}]^{-1}$ are the Fermi occupation numbers and $\mu$ the chemical potential. These orbitals and energies obey the Schrödinger equation

$$\left[ -\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\boldsymbol{r}) \right] \varphi_i(\boldsymbol{r}) = \varepsilon_i \varphi_i(\boldsymbol{r}) \,, \qquad (4)$$

where $V_{\mathrm{KS}}(\boldsymbol{r})$ is an effective single-particle potential given by

$$V_{\mathrm{KS}}(\boldsymbol{r}) = V_{\mathrm{jel}}(\boldsymbol{r}) + V_{\mathrm{H}}[\rho(\boldsymbol{r})] + V_{\mathrm{xc}}[\rho(\boldsymbol{r})] \,, \qquad (5)$$

where $V_{\mathrm{H}}[\rho(\boldsymbol{r})]$ is the Hartree potential and $V_{\mathrm{xc}}[\rho(\boldsymbol{r})]$ the exchange-correlation potential defined by

$$V_{\mathrm{xc}}[\rho(\boldsymbol{r})] = \frac{\delta F_{\mathrm{xc}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} \qquad (6)$$

where $F_{\mathrm{xc}}[\rho(\boldsymbol{r})]$ is the exchange-correlation free energy. The temperature appears in the self-consistent procedure only through the occupation numbers and the exchange-correlation free energy. For low temperature (i.e. $T_e \ll T_F[\rho(\boldsymbol{r})]$ where $T_F[\rho(\boldsymbol{r})] = \frac{1}{2k_B}\left(3\pi^2\rho(\boldsymbol{r})\right)^{2/3}$ is the local Fermi temperature), $F_{\mathrm{xc}}[\rho(\boldsymbol{r})]$ may be safely replaced by it's value at $T_e = 0$, that is by $E_{\mathrm{xc}}[\rho(\boldsymbol{r})]$. This approximation is particularly valid inside the particle where the local density is almost constant and close to the bulk one. The bulk Fermi temperature of noble metals being usually very high ($T_F \sim 6.4 \times 10^4$ K for Ag) the above approximation is fully justified. However, near the surface the local density decreases by two to three orders of magnitude leading to a much smaller local Fermi temperature. Therefore, close to the surface the temperature variation of $F_{\mathrm{xc}}[\rho(\boldsymbol{r})]$ is important and must be taken into account. In the present study we have assumed that $F_{\mathrm{xc}}[\rho(\boldsymbol{r})] = E_{\mathrm{xc}}[\rho(\boldsymbol{r})]$. Since the functional form of $E_{\mathrm{xc}}$ is generally not known, several approximations have been proposed. In the local-density approximation (LDA), the electronic density of the inhomogeneous system is considered to be locally uniform. Thus, the results of the homogeneous interacting electron gas may be used as an input data to investigate inhomogeneous electronic systems as metallic nanoparticles. In this work, we have used the form obtained by Gunnarsson and Lundqvist [15] for a uniform electron gas in the framework of the LDA. The chemical potential is determined self-consistently by requiring the conservation of the total number of electrons from equation (3).

### 2.2 Excited states

#### 2.2.1 Zero temperature: $T_e = 0$

The optical response of the valence electrons ($s$ electrons) is treated quantum-mechanically whereas the classical Mie theory is used to describe the light absorption by the $d$ electrons. In the usual first-order TDLDA at $T_e = 0$, the induced electronic density $\delta\rho(\boldsymbol{r}; \omega)$ is related to $V_{\mathrm{ext}}(\boldsymbol{r}'; \omega)$, the Fourier transform (with respect to time) of the external potential associated to the electric field of the laser, by [16–18]

$$\delta\rho(\boldsymbol{r}; \omega) = \int \chi(\boldsymbol{r}, \boldsymbol{r}'; \omega) \, V_{\mathrm{ext}}(\boldsymbol{r}'; \omega) \, \mathrm{d}\boldsymbol{r}' \qquad (7)$$

where $\chi(\boldsymbol{r}, \boldsymbol{r}'; \omega)$ is the retarded density correlation function. In the dipole approximation ($R \ll \lambda$ where $\lambda$ is the wave-length of the incident radiation) the external potential is given by

$$V_{\mathrm{ext}}(\boldsymbol{r}'; \omega) = -E_0 \, z'$$
$$\times \begin{cases} \frac{3\epsilon_m}{\epsilon_d(\omega)+2\epsilon_m} & \text{for} \quad r' \leq R \\ 1 - \frac{(\epsilon_d(\omega)-\epsilon_m)}{\epsilon_d(\omega)+2\epsilon_m}\left(\frac{R}{r'}\right)^3 & \text{for} \quad r' > R \end{cases}. \qquad (8)$$

It is possible to rewrite the induced density as

$$\delta\rho(\boldsymbol{r};\omega) = \int \chi^0(\boldsymbol{r},\boldsymbol{r}';\omega)\, V_{\text{tot}}(\boldsymbol{r}';\omega)\,\mathrm{d}\boldsymbol{r}' \qquad (9)$$

with

$$V_{\text{tot}}(\boldsymbol{r};\omega) = V_{\text{ext}}(\boldsymbol{r};\omega) + \int \frac{\delta\rho(\boldsymbol{r}';\omega)}{|\boldsymbol{r}-\boldsymbol{r}'|}\,\mathrm{d}\boldsymbol{r}'$$
$$+ \int f_{\text{xc}}[\rho](\boldsymbol{r},\boldsymbol{r}';\omega)\delta\rho(\boldsymbol{r}';\omega)\,\mathrm{d}\boldsymbol{r}' \quad (10)$$

where the function $f_{\text{xc}}[\rho](\boldsymbol{r},\boldsymbol{r}';\omega)$ is the Fourier transform of the time-dependent kernel defined by $f_{\text{xc}}[\rho](\boldsymbol{r},t;\boldsymbol{r}',t') \equiv \delta V_{\text{xc}}[\rho](\boldsymbol{r},t)/\delta\rho(\boldsymbol{r}',t')$ and $\chi^0(\boldsymbol{r},\boldsymbol{r}';\omega)$ is the non-interacting retarded density correlation function. From equations (7, 9, 10) we see that $\chi^0$ and $\chi$ are related by an integral equation (Dyson-type equation)

$$\chi(\boldsymbol{r},\boldsymbol{r}';\omega) = \chi^0(\boldsymbol{r},\boldsymbol{r}';\omega) + \iint \chi^0(\boldsymbol{r},\boldsymbol{r}'';\omega)$$
$$\times K(\boldsymbol{r}'',\boldsymbol{r}''';\omega)\,\chi(\boldsymbol{r}''',\boldsymbol{r}';\omega)\,\mathrm{d}\boldsymbol{r}''\mathrm{d}\boldsymbol{r}''', \quad (11)$$

with the residual interaction defined by

$$K(\boldsymbol{r},\boldsymbol{r}';\omega) = V_{\text{C}}(\boldsymbol{r},\boldsymbol{r}';\omega) + f_{\text{xc}}[\rho](\boldsymbol{r},\boldsymbol{r}';\omega). \quad (12)$$

In the adiabatic local-density approximation (ALDA) the exchange-correlation kernel is frequency-independent and local and reduces to [16,18]

$$f_{\text{xc}}[\rho](\boldsymbol{r},\boldsymbol{r}') = \left[\frac{\partial V_{\text{xc}}}{\partial\rho}\right]_{\rho=\rho(\boldsymbol{r})}. \qquad (13)$$

It should be mentioned that the functional, $V_{\text{xc}}[\rho]$ in the above equation is the same as the one used in the calculation of the ground-state (see (6)). Notice also that, the Coulomb interaction, $V_{\text{C}}$, appearing in (12) is frequency dependent *via* the dynamical dielectric function associated to the $d$ electrons [9]. For closed-shell clusters (spin-saturated electronic systems), we have

$$\chi^0(\boldsymbol{r},\boldsymbol{r}';\omega) = 2\sum_{jk}\left[f_j^0 - f_k^0\right]\frac{\varphi_j^*(\boldsymbol{r})\varphi_k(\boldsymbol{r})\varphi_k^*(\boldsymbol{r}')\varphi_j(\boldsymbol{r}')}{\omega - (\varepsilon_k - \varepsilon_j) + \mathrm{i}\delta}$$
$$= \sum_k^{occ} \varphi_k^*(\boldsymbol{r})\varphi_k(\boldsymbol{r}')G^+(\boldsymbol{r},\boldsymbol{r}';\varepsilon_k + \omega)$$
$$+ \sum_k^{occ} \varphi_k(\boldsymbol{r})\varphi_k^*(\boldsymbol{r}')G^{+*}(\boldsymbol{r},\boldsymbol{r}';\varepsilon_k - \omega) \quad (14)$$

where $\varphi_k(\boldsymbol{r})$ and $\varepsilon_k$ are the one-electron Kohn-Sham wave functions and energies, respectively. $G^+$ is the one-particle retarded Green's function and $f_k^0$ are the Fermi occupation numbers at $T_e = 0$ K (0 or 1). All the above quantities are obtained with the procedure described in the preceding section with $f_k = f_k^0$ in equation (3). In order to produce numerically tractable results we have added a small imaginary part to the probe frequency so $\omega \to \omega + \mathrm{i}\delta$. The numerical value of $\delta$ has been estimated from the experimental optical density [1].

## 2.2.2 Finite temperature: $T_e \neq 0$

At finite electronic temperature, the grand-canonical non-interacting retarded density correlation function reads [19]

$$\chi^0(\boldsymbol{r},\boldsymbol{r}';\omega;T_e) = \frac{1}{Z_G}\sum_{n,N}\exp\left\{-\frac{1}{k_BT_e}\left[E_n(N) - N\mu\right]\right\}$$
$$\times \chi^0_{n,N}(\boldsymbol{r},\boldsymbol{r}';\omega;T_e) \qquad (15)$$

where $Z_G$ is the grand-canonical partition function

$$Z_G = \sum_{n,N}\exp\left\{-\frac{1}{k_BT_e}\left[E_n(N) - N\mu\right]\right\} \qquad (16)$$

with $E_n(N)$ the energy of the state $|nN\rangle$ having $N$ electrons, $\mu$ the chemical potential and

$$\chi^0_{n,N}(\boldsymbol{r},\boldsymbol{r}';\omega;T_e) = \sum_m \frac{\langle nN|\hat{n}(\boldsymbol{r})|mN\rangle\,\langle mN|\hat{n}(\boldsymbol{r}')|nN\rangle}{\omega - (E_m(N) - E_n(N)) + \mathrm{i}\delta}$$
$$- \frac{\langle nN|\hat{n}(\boldsymbol{r}')|mN\rangle\,\langle mN|\hat{n}(\boldsymbol{r})|nN\rangle}{\omega + (E_m(N) - E_n(N)) + \mathrm{i}\delta}.$$

In the above expression $\hat{n}(\boldsymbol{r})$ is the particle density operator defined from the wave field operators by

$$\hat{n}(\boldsymbol{r}) = \hat{\psi}^+(\boldsymbol{r})\hat{\psi}(\boldsymbol{r}) \qquad (17)$$

with $\hat{\psi}^+(\boldsymbol{r}) = \sum_k \hat{a}_k^+\,\varphi_k^*(\boldsymbol{r})$ and $\hat{\psi}(\boldsymbol{r}) = \sum_k \hat{a}_k\,\varphi_k(\boldsymbol{r})$. By using standard field theory techniques it is possible to show that

$$\chi^0(\boldsymbol{r},\boldsymbol{r}';\omega;T_e) = \sum_k f_k\varphi_k^*(\boldsymbol{r})\varphi_k(\boldsymbol{r}')G^+(\boldsymbol{r},\boldsymbol{r}';\varepsilon_k + \omega;T_e)$$
$$+ \sum_k f_k\varphi_k(\boldsymbol{r})\varphi_k^*(\boldsymbol{r}')G^{+*}(\boldsymbol{r},\boldsymbol{r}';\varepsilon_k - \omega;T_e) \quad (18)$$

where $f_k = [1 + \exp\{(\varepsilon_k - \mu)/k_BT_e\}]^{-1}$. In this work, we have assumed that the residual interaction, (12), is temperature independent. This assumption is consistent with the use of $F_{\text{xc}}[\rho(\boldsymbol{r})] = E_{\text{xc}}[\rho(\boldsymbol{r})]$ in the calculation of the ground-state properties. Therefore, as for $T_e = 0$, the response function is solution of the Dyson equation (11) with $\chi^0$ given by (18). For spherically symmetric systems the response function may be written as

$$\chi(\boldsymbol{r},\boldsymbol{r}';\omega;T_e) = \sum_{lm}\frac{\tilde{\chi}_l(r,r';\omega;T_e)}{[rr']^2}\,Y_{lm}(\hat{r})Y_{lm}^*(\hat{r}'). \quad (19)$$

From the frequency-dependent dipole polarizability defined by

$$\alpha_s(\omega;T_e) = \frac{4\pi}{3}\int_0^\infty\int_0^\infty \tilde{\chi}_1(r,r';\omega;T_e)[rr']^3\mathrm{d}r\mathrm{d}r' \quad (20)$$

one obtains the dipolar absorption cross-section

$$\sigma(\omega;T_e) = \frac{4\pi\omega}{c\sqrt{\epsilon_m}}\operatorname{Im}\left[\alpha_s(\omega;T_e) + \alpha_d(\omega)\right] \qquad (21)$$
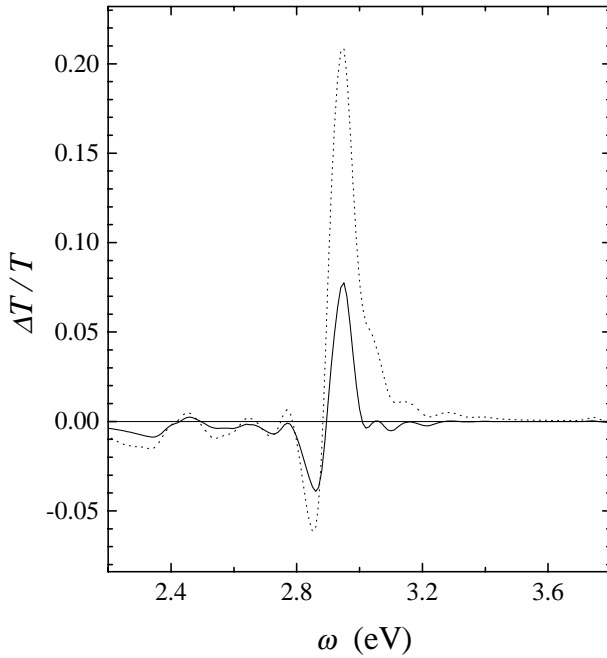
**Fig. 1.** Theoretical differential transmission for Ag$_{2998}$ as a function of the photon energy of the probe and for two different values of $T_e$; full line: $T_e = 600$ K; dotted line: $T_e = 1200$ K.
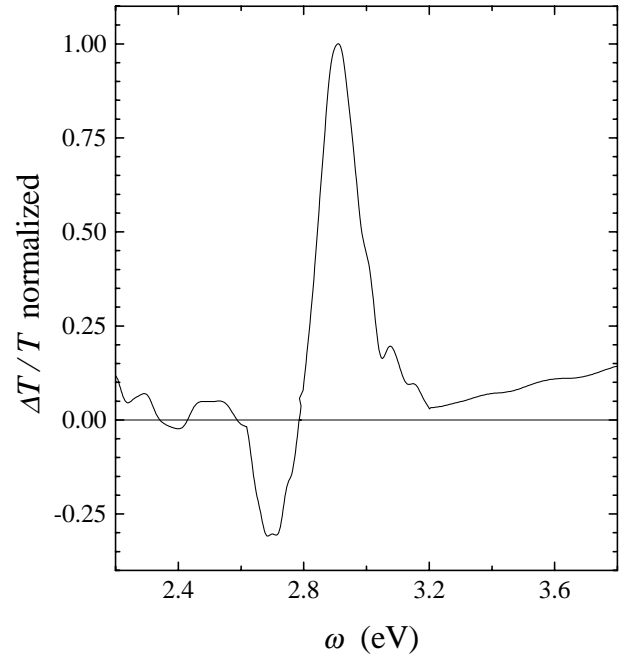


**Fig. 2.** Normalized experimental spectrum of $\Delta\bar{T}/\bar{T}$ of silver nanoparticles encapsulated in an alumina matrix for a pump-probe delay of 2 ps [1].

with the classical dipole polarizability of the $d$ electrons given by

$$\alpha_d(\omega) = \epsilon_m \left[ \frac{\epsilon_d(\omega) - \epsilon_m}{\epsilon_d(\omega) + 2\epsilon_m} \right] R^3. \qquad (22)$$

In order to compare with the experimental measurements, one defines the differential transmission as

$$\frac{\Delta\bar{T}}{\bar{T}} = \frac{\bar{T}(T_e, \omega) - \bar{T}(T_0, \omega)}{\bar{T}(T_0, \omega)} = -\Delta\tilde{\alpha}(\omega)\, l \qquad (23)$$

$$= \frac{3}{2\pi R^2} \left[ \sigma(\omega; T_0) - \sigma(\omega; T_e) \right] \qquad (24)$$

where $l = 2R$ is the sample thickness (here, the diameter of the particle), $\bar{T}(T_e, \omega)$ and $\bar{T}(T_0, \omega)$ are the probe transmission in the presence and absence of the pump and $\Delta\tilde{\alpha}(\omega)$ is the pump-induced absorption change, respectively. Obviously $\bar{T}(T_0, \omega)$ corresponds to an absorption at room temperature $T_0 = 300$ K for the conditions where the pump-probe experiments have been performed.

## 3 Results

In Figure 1, the predictions of the differential transmission obtained from equation (23) for the closed-shell nanoparticle Ag$_{2998}$ as a function of the photon energy of the probe are presented. The diameter of the nanoparticle is 4.6 nm and the calculations have been carried out with $\delta = 0.1$ eV and $\epsilon_m = 1.5$. At $T_e = 0$ K, 97 orbitals are occupied ($occ = 97$ in equation (14)) while at $T_e = 1200$ K, 158 orbitals have to be included in the calculation (see Eq. (18)).

The comparison is made for two electronic temperatures $T_e = 600$ K and $T_e = 1200$ K. The photon energy ranges from 2.2 eV to the interband threshold energy at 3.8 eV *i.e.* in the spectral region associated to the surface plasmon of Ag nanoparticles. All these values correspond to typical experimental conditions [1]. The asymmetric shape of $\Delta\bar{T}/\bar{T}$ around the resonance energy is related to a combination of a redshift and a broadening of the surface plasmon resonance.

Figure 2 shows the experimental spectrum of $\Delta\bar{T}/\bar{T}$ obtained for a pump-probe delay of $t = 2$ ps. The pump pulse is set at 400 nm (second harmonic of a titanium sapphire laser amplified at 5 kHz) and the probe comes from a continuum generated in a sapphire crystal with the fundamental of the amplified laser [1]. The asymmetric spectral shape of the differential transmission spectrum in Figure 2 which is related to the shift and broadening of the plasmon may have several origins. As pointed out in references [1,2], the interband transition induces a modification of the real part of the dielectric function in this spectral region, the resonance being far enough from the interband threshold to induce significant changes of the corresponding imaginary part. As stressed in reference [2], this is a strong indication that intraband processes also play an important role. Indeed, as clearly seen in Figure 1, the conduction electrons contribution leads both to a shift and to a broadening. We can therefore conclude that one has to consider equally the interband and intraband part on the same footing. While it was previously taken into account in a phenomenological way *via* a shifted and broadened Lorentzian shape, here it is derived directly from a quantum many-body model within the TDLDA approach.

## 4 Conclusions and perspectives

The present work is part of a theoretical study aiming at understanding the role of the electronic temperature on the optical response of metallic nanoparticles. So far, we have only treated the temperature effects at a self-consistent-field level. Even if this theoretical model is able to reproduce the main trends of the experimental results, more studies are necessary. In particular, an explicit temperature dependence of the exchange-correlation free energy, $F_{xc}[\rho(\mathbf{r})]$, should be included in the model. The finite-temperature field formalism seems to be well adapted to undertake this task [12,20]. Also, even if the surface plasmon resonance is situated below the region of interband transitions, the temperature dependence of the screening (real part of $\epsilon_d(\omega)$) coming from the $d$ electrons must be investigated (*e.g.* within the RPA and the band model of Rosei [21]). Finally, we have assumed that the constant, $\delta$ describing the damping due to the electron-electron collisions (beyond the mean-field approximation) does not depend on the temperature. By using the self-consistent-field dielectric function of a homogeneous electron gas at finite temperature [22] and a statistical approximation [23,24], one may calculate $\delta$ for any temperature. We are presently working on these improvements. Another problem, which deserves to be mentioned in connection with the finite size of the system is the equivalence between different statistical ensembles. In the thermodynamic limit, the grand-canonical, canonical, and microcanonical ensemble are expected to provide the same results. However, their equivalence is no longer ensured when the number of electrons is finite. For the size considered in this work, $N \sim 3000$, the differences between the predictions of the above statistical ensembles are expected to play a minor role. For smaller clusters however the question of the appropriate thermodynamics is interesting to investigate.

## References

1. J.-Y. Bigot *et al.*, Chem. Phys. **251**, 181 (2000)
2. C. Voisin, N. Del Fatti, D. Christofilos, F. Vallée, J. Phys. Chem. B **105**, 2264 (2001), and references therein
3. A. Liebsch, Phys. Rev. Lett. **71**, 145 (1993)
4. H. Ehrenreich, H.R. Philipp, Phys. Rev. **128**, 1622 (1962)
5. J. Lermé, Eur. Phys. J. D **10**, 265 (2000)
6. A. Rubio, Ll. Serra, Phys. Rev. B **48**, 18222 (1993)
7. W. Ekardt, Phys. Rev. B **29**, 1558 (1984)
8. Ll. Serra, A. Rubio, Z. Phys. D **40**, 262 (1997)
9. J. Lermé *et al.*, Eur. Phys. J. D **4**, 95 (1998)
10. N.D. Mermin, Phys. Rev. **137**, A1441 (1965)
11. W. Kohn, L.J. Sham, Phys. Rev. **140**, A1133 (1965)
12. U. Gupta, A.K. Rajagopal, Phys. Rep. **87**, 259 (1982)
13. W. Yang, Phys. Rev. A **38**, 5504 (1988)
14. M. Brack, O. Genzken, K. Hansen, Z. Phys. D **21**, 65 (1991)
15. O. Gunnarsson, B.I. Lundqvist, Phys. Rev. B **13**, 4274 (1976)
16. A. Zangwill, P. Soven, Phys. Rev. A **21**, 1561 (1980)
17. W. Ekardt, Phys. Rev. B **31**, 6360 (1985)
18. M. Petersilka *et al.*, Phys. Rev. Lett. **76**, 1212 (1996)
19. W. Yang, Phys. Rev. A **38**, 5512 (1988)
20. A.L. Fetter, J.D. Walecka, *Quantum Theory of Many-Body Systems* (Mc Graw-Hill, New-York, 1971)
21. R. Rosei, Phys. Rev. B **10**, 474 (1974)
22. P.-A. Hervieux, J.-Y. Bigot, to be submitted
23. P.M. Echenique *et al.*, Chem. Phys. **251**, 1 (2000)
24. D. Penn, Phys. Rev. B **35**, 482 (1987)