Eur. Phys. J. D **17**, 213–220 (2001)

THE EUROPEAN PHYSICAL JOURNAL D

EDP Sciences

Influence of lattice contraction on the optical properties and the electron dynamics in silver clusters

J. Lermé[1,a], M. Pellarin[1], E. Cottancin[1], M. Gaudry[1], M. Broyer[1], N. Del Fatti[2], F. Vallée[2], and C. Voisin[3]

[1] Laboratoire de Spectrométrie Ionique et Moléculaire, CNRS and Université de Lyon I, bâtiment A. Kastler, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France
[2] Centre de Physique Moléculaire Optique et Hertzienne, CNRS and Université de Bordeaux I, 351 cours de la Libération, 33405 Talence Cedex, France
[3] Laboratoire de Physique de la Matière Condensée, École Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex 05, France

Received 10 May 2001 and Received in final form 4 July 2001

Abstract. The effects of surface-induced lattice contraction on the size evolution of the surface plasmon resonance and of the electronic thermalization time in small silver clusters have been investigated in the framework of a mixed classical/quantum model. The increase of the conduction-electron density results in a blue-shift trend for decreasing cluster size. However this effect is counterbalanced by the increase of the dielectric function associated to the ionic-core background. Agreement with the blue-shift trend observed in experiment is recovered by introducing an inner surface skin of vanishing ionic-core polarizability having a thickness practically unchanged as compared to previous estimations. The influence of the lattice contraction on the electron dynamics is also discussed. It is shown that this influence is negligible as compared to the surface effects arising from the spillout and the inner skin of reduced ionic-core polarizability which are both responsible for a decrease of the electron thermalization time as the particle size decreases.

PACS. 36.40.-c Atomic and molecular clusters – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 71.45.Gm Exchange, correlation, dielectric and magnetic response functions, plasmons – 78.47.+p Time-resolved optical spectroscopies and other ultrafast optical measurements in condensed matter

1 Introduction

During the past decades a huge amount of experimental and theoretical works have been devoted to study the effects of the electronic and dielectric confinements on the optical properties of metal particles [1–8]. In the dipolar regime no size effect is predicted with respect to the light absorption within the classical Mie's theory [9], when a noticeable size-dependence – depending on the metal and the particle environment – is observed in this size range too [4–7]. It is now well established that the size-dependence is, to a large extent, rooted in finite-size quantum effects that are disregarded in the classical approach. Among them, the smooth decrease of the electron density at the particle surface is a systematic feature: the metal/vacuum or metal/matrix interface is not perfectly located, as it is assumed in classical electrodynamics where the Fermi wavelength λ_F is implicitly considered as negligible in comparison with all the other relevant length scales of the system. For instance in free sodium clusters the red-shift of the surface plasmon frequency as the particle radius decreases is directly correlated to the amount of electrons lying beyond the classical particle radius $R = r_s N^{1/3}$ (effect referred to as the spillout phenomenon; r_s is the Wigner-Seitz (WS) radius characterizing the bulk density and N the number of atoms in the cluster).

In the case of noble metal clusters the tiny size-dependence of the optical properties can be described – qualitatively – as the net result of the competition between opposite trends induced by two surface effects [10–17]. The competing red- and blue-shift trends stem from, in the one hand the spillout effect, and, on the other hand the surface skin of reduced ionic-core polarizability [18]. In phenomenological dielectric models (*i.e.* jellium-like) this ingredient is taken into account by assuming that the polarizable homogeneous medium describing the dielectric properties of the ionic cores (tightly-bound d electrons in the case of noble metals) extends only up to $R-d$, where d is the thickness of the skin of vanishing polarizability. This surface effect, introduced for the first time by Liebsch [10], was successfully applied to explain the size dependence of the surface plasmon

[a] e-mail: lerme@hplasim2.univ-lyon1.fr

frequency in noble metal clusters [10–16], especially the blue-shift trend (as the size decreases) observed for free Ag_N^+ clusters [11], and for matrix-embedded Ag_N [11–15], Au_N [15] and alloyed $(Au_xAg_{1-x})_N$ [16] clusters. Quantum calculations within the time-dependent local-density-approximation (TDLDA) formalism, carried out on small Ag_N^+ clusters in vacuum (thus free from matrix effects), lead to the estimate $d \approx 3-3.5$ a.u. [15]. This value is larger than the one deduced by Liebsch [10] from flat Ag-surface properties ($d \approx 1.5-2$ a.u.) or those assumed in previous investigations [19].

Besides the linear optical properties, the size-dependence of the thermalization dynamics of the conduction electrons in silver nanoparticles has been recently investigated by time-resolved femtosecond pump-probe experiments [20]. The results show a decrease of the electronic thermalization time as the size is reduced. Within a simple model where the electron-electron scattering rate induced by the screened Coulomb interaction is spatially averaged, the decrease of the thermalization time was found quite well estimated in taking into account the reduction of the screening at the cluster surface. The reduction of the local screening stems from, in the one hand the low-density electronic tail near the surface, and, on the other hand the surface skin of ineffective ionic-core polarizability. Let us remark that these two features lead here to similar size-trends, whereas they yield opposite effects with respect to the shift of the surface plasmon Mie's frequency.

In a recent work by Cai *et al.* [21] a high-resolution-electron-microscopy analysis of the crystal lattice in supported and glass-embedded silver clusters (diameter-range 2–10 nm) show linear contraction of the lattice parameter with reciprocal particle size, giving evidence of an intrinsic surface-induced self-compression of the clusters. As a matter of fact such a change in the lattice parameter, either in small systems as metal clusters, or with respect to the outermost atomic layers of a flat surface, is a general physical effect [22–26]. Taking into account the lattice contraction these authors have successfully reproduced the available results on the optical properties of silver clusters, namely a blue-shift of the Mie's frequency as the size decreases, by simple classical Mie calculations, without involving the surface skin of ineffective polarizability. The size-dependent increase of the conduction-electron density induced by the lattice contraction is the only additional ingredient in the classical model. It results, more specifically, in changes of the bulk plasma frequency ω_p, the Fermi velocity v_F and the surface scattering-limited mean-free-path [27,28].

The purpose of this paper is to take into account the lattice contraction [21] in our theoretical interpretations related to both linear optical and dynamical properties in silver clusters. The following topics are addressed in this work: (1) in a first step the quantum results are compared with the classical calculations by Cai *et al.* when only the increase of the conduction-electron density is considered. (2) In a second step we include in the model the lattice contraction-induced change of the dielectric function $\varepsilon_c(\omega)$ corresponding to the ionic-core background. The size-dependence of the surface plasmon frequency is calculated in taking into account both effects. (3) The effective thickness d of the surface skin of vanishing ionic-core polarizability is evaluated in taking into account the lattice-contraction effects, by comparison with the available experimental results on Ag_N^+ clusters. (4) The influence of the lattice contraction on the electronic thermalization time in silver clusters is analyzed.

The theoretical framework and the results are presented in Sections 2 and 3, respectively. A brief conclusion is given in Section 4.

2 Theoretical background

Calculations based on the TDLDA formalism [29–31], including the absorption and screening properties of the ionic background, have been carried out within a mixed classical/quantal model. The ingredients of the model have been detailed in previous papers [15,32,33], and are outlined briefly. The ionic metal background is phenomenologically described by both: (i) a step-walled homogeneous spherical charge distribution (jellium) of radius $R = r_s N^{1/3}$, and, (ii) a homogeneous dielectric medium (core-electron dielectric function $\varepsilon_c(\omega)$, assumed to be bulk-like) extending up to $R_c = R - d$. $\varepsilon_c(\omega)$ has been extracted from the experimental macroscopical dielectric function of bulk silver [34] by a Kramers-Kronig analysis [15,32,35]. Let us emphasize that only the conduction electrons are quantum-mechanically described within the TDLDA formalism. The improved formalism developed in reference [33] is used throughout this work. The reader is referred to reference [15] for the predictions obtained for free Ag_N and Ag_N^+ clusters, when no lattice contraction is involved, and our previous estimation of the parameter d ($\approx$3–3.5 a.u.). Finally, let us point out that the classical Mie's frequency is recovered for large particle sizes.

Since the size effects in noble metal clusters are rather tiny, owing to competing effects, the numerical input parameters involved in the present calculations have to be specify in details. For the bulk WS radius and the electron mass we have taken $r_s(\infty) = 3.02$ a.u. [36] and $m^* = m_0$ (free electron mass). In the TDLDA formalism the evaluation of the Green functions $G(\mathbf{r}, \mathbf{r}', E) = \langle \mathbf{r}|[H - E - i\delta]^{-1}|\mathbf{r}'\rangle$, that are involved for calculating the independent-electron density-density correlation function $\chi_0(\mathbf{r}, \mathbf{r}', E)$, requires the use of a finite value (that acts as a numerical smoothing parameter) for the infinitesimal δ-parameter [29–31]. This amounts – in a rough picture – to attributing an intrinsic width 2δ to each bound–bound particle–hole excitation line. The values $\delta = 100$ meV has been selected in order to keep the computational time reasonable. Let us stress that by no means δ has to be considered as related to the bulk relaxation time τ_b entering the classical model. In most calculations the δ-value is large enough to smooth out the fragmented band pattern

due to the coupling with individual particle-hole excitations (Landau damping [37,38]). Except for some small sizes exhibiting a more pronounced fragmented pattern (multi-peak structure or a main peak with shoulders) in comparison with neighbouring studied sizes, the frequency corresponding to the maximum of the spectrum, defined as the surface plasmon frequency (ω_{M}), does not depend noticeably on the selected δ-value.

The effect of the bulk relaxation time deserves to be commented. In a classical approach $\Gamma_{\mathrm{b}} = \hbar\tau_{\mathrm{b}}^{-1}$ is the Mie-band width in the asymptotic limit (large cluster radius). This parameter reflects the electron scattering processes in the bulk material, due to collisions with phonons (main factor), lattice defects, impurities... The value used in reference [21] ($\tau_{\mathrm{b}}^{-1} = 2.70 \times 10^{13}$ s^{-1} for silver), close to the value 2.50×10^{13} s^{-1} deduced from the silver dc-resistivity at room temperature [39], leads to a band-width equal to $\Gamma_{\mathrm{b}} = 17$ meV. Except for very large cluster sizes, this value is considerably lower than the surface scattering-induced contribution in the damping parameter $\Gamma(R) = \Gamma_{\mathrm{b}} + \hbar A v_{\mathrm{F}}(R)/R$, which is involved in the classical model. Consequently the classical Mie's frequency, given approximately by the equation (Eq. (5) in Ref. [21])

$$\omega_{\mathrm{M}}^2(R) = \left[\omega_{\mathrm{p}}^2(R)/B\right] - \left[\Gamma(R)/\hbar\right]^2 \qquad (1)$$

is poorly affected (negligible overestimation) if τ_{b}^{-1} is set equal to zero in this equation ($B = 2\varepsilon_{\mathrm{m}} + \mathrm{Re}[\varepsilon_{\mathrm{c}}(\omega = \omega_{\mathrm{M}})]$ where ε_{m} is the matrix dielectric function; see the note [40]). Nevertheless the results reported in reference [21], as well as the classical ones reported in this work, include the bulk contribution in the relaxation time. In the present quantum calculations the bulk contribution in the relaxation time is not included in the model since the coupling with the vibrations of the background are disregarded. Only the surface scattering-limited mean-free-path contribution is implicitly taken into account through the Landau damping [37,38,41]. Therefore the width of the Mie band decreases towards zero for increasing cluster radii in quantum calculations involving an homogeneous inert background and an infinitesimal δ-value [41]. In the present calculations the asymptotic value (very large radii R) of the full width at half maximum is actually 2δ, as it was checked by inspecting the calculated absorption spectra. These remarks suggest that the calculated Mie frequencies are probably very slightly overestimated as compared to those that would be obtained within a quantum model including the coupling with the vibrations.

3 Results and discussion

For a cluster containing N atoms, the lattice contraction is calculated by solving the following equation (Eq. (10) in Ref. [21])

$$\frac{r_{\mathrm{s}}(N) - r_{\mathrm{s}}(\infty)}{r_{\mathrm{s}}(\infty)} = -\frac{2}{3}\frac{Kf}{r_{\mathrm{s}}(N)N^{1/3}} \qquad (2)$$

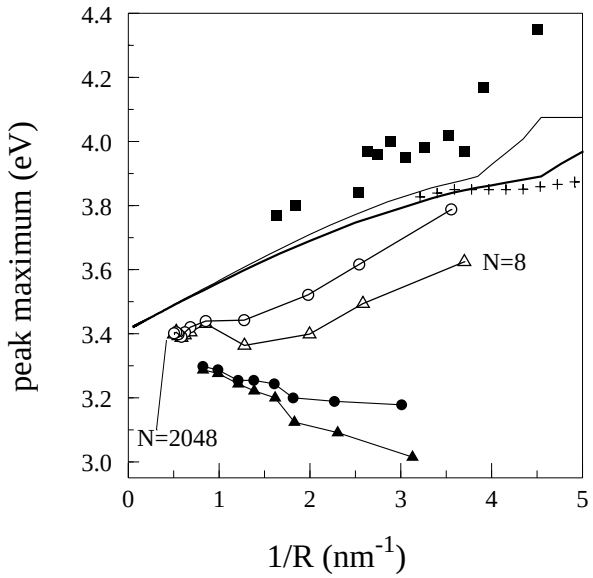

Fig. 1. The size-evolution of the maximum of the Mie band in the absorption spectra of free silver clusters, when only the increase of the conduction-electron density is taken into account in the model. Black squares: experimental data on Ag_N^+ clusters [11]. Thick full line curve: theoretical predictions within the Mie theory including the surface scattering-limited mean-free-path effect ($A = 0.25$). Crosses: maximum of the Mie band for $A = 0.25$ (see text). Thin full line curve: results when only the size dependence of the plasma frequency ω_{p} is considered ($A = 0$). Triangles: results of the quantum calculations for Ag_N clusters with (empty symbols) and without (black symbols) lattice contraction. Circles: results of the quantum calculations for Ag_N^+ clusters with (empty symbols) and without (black symbols) lattice contraction.

where K is the compressibility and f the surface stress. In the classical model used in reference [21] the size-dependent lattice contraction acts through the changes of: (i) the plasma frequency ($\omega_{\mathrm{p}}(N) = \omega_{\mathrm{p}}(\infty)[r_{\mathrm{s}}(\infty)/r_{\mathrm{s}}(N)]^{3/2}$); (ii) the surface-induced contribution in the relaxation-time ($\hbar A v_{\mathrm{F}}(N)/[r_{\mathrm{s}}(N)N^{1/3}]$, with $A = 0.25$ [27] and the Fermi velocity $v_{\mathrm{F}}(N) = v_{\mathrm{F}}(\infty)r_{\mathrm{s}}(\infty)/r_{\mathrm{s}}(N)$). In the quantum model all these effects are implicitly taken into account through the increase of the jellium density, namely through the N-dependence of the jellium radius $R = r_{\mathrm{s}}(N)N^{1/3}$. Results obtained within the classical model (frequency minimizing the expression $|\omega_{\mathrm{M}}^2(R) - \omega^2|$, where $\omega_{\mathrm{M}}^2(R)$ is the right side of Eq. (1)), for free Ag_N clusters, are shown in Figure 1 (thick full line curve), and compared to the available experimental data (black squares) on free hot Ag_N^+ clusters [11]. The results obtained with $A = 0$ are also displayed (thin full line curve).

In this crude classical model the change of the bulk plasma frequency ω_{p} is the major effect ruling the size dependence of the surface plasmon frequency ω_{M}. The "irregularities" in the size evolution, observed for very

small particle radii, result from the overlap of the Mie band with the interband transitions (interband threshold $\omega_{\rm IB} \approx 3.85$ eV). When the Mie's frequency is close or above $\omega_{\rm IB}$ (the real and imaginary components of $\varepsilon_{\rm c}(\omega)$ vary strongly), the value deduced from the minimization of the above analytical expression is too crude, and the peak maximum has to be obtained by plotting the absorption spectrum. The crosses are the results obtained by this latter method, for $A = 0.25$.

The empty triangles in Figure 1 are the predictions of the quantum calculations, carried out in the size range $N = 8-2048$ (magic sizes), in the absence of the surface skin of vanishing polarizability ($d = 0$). Let us emphasize that both models have an identical asymptotic Mie-frequency for very large radii ($\omega_{\rm M}(\infty) \approx 3.41$ eV). This is less apparent in the "quantum curve" because of quantum finite-size effects, but the four largest investigated sizes ($N = 1314$, 1556, 1778, 2048; $1/R \approx 0.5$ nm^{-1}) converge clearly towards this value. Except in the small size range ($N < 100$) the size evolution is almost quenched in the quantum model, whereas a steady strong blue-shift trend is observed in the "classical" size-evolution over the entire size domain. The discrepancies between the quantum and classical predictions are very large in the small size range. Obviously the Mie's frequencies obtained in quantum calculations are lower because the spillout effect is disregarded in the classical approach. This stresses that this quantum effect is of main importance, and has to be appropriately modelled when using a classical model, first for a fine quantitative comparison with experimental data, and, second, to infer more reliably the physics underlying the net size effects observed in experiment. It is clear that applying the raw classical model to sodium clusters (lattice contraction is also theoretically predicted for alkali metals [24,25]) would lead to a blue-shift trend instead of the red-shift trend that is experimentally observed [4–6]. As rightly emphasized by Cai *et al.* and many other authors, other eventual size-dependent factors neglected so far, for instance related to the electronic band structure or the effective electron mass, could be responsible for part of the observed finite-size effects.

In the absence of the surface skin of ineffective screening, the theory/experiment (data on Ag_N^+ clusters) discrepancy is reduced by the charge effect (calculations performed on the magic – electronic – sizes $N' = N+1$; empty circles in Fig. 1). The charge effect is strong for small clusters and negligible for clusters containing more than a few hundred atoms. The charge effect is manifestly insufficient to bring the theory in accordance with experiment.

Finally let us stress that the lattice contraction affects quite strongly the quantum predictions, as in the classical approach, since the size evolution previously calculated [15] in the absence of lattice contraction exhibits a slight red-shift trend as the size decreases, for both neutral and charged clusters (black triangles and squares for Ag_N and Ag_N^+ in Fig. 1).

The influence of the effective electron mass m^* deserves to be discussed and numerically estimated, due to the tiny finite-size effects. In a first approximation the effect can be anticipated to act as a simple scaling factor $\omega_{\rm M} \propto m^{*-1/2}$ through the plasma frequency $\omega_{\rm p}$, resulting roughly in a global shift of the size-evolution curves, especially a blue-shift for $m^* < m_0$. The present calculations involve the value $m^* = m_0$. In reference [35] the values $m^*/m_0 = 0.96$ and 1.09 are obtained by matching the experimental dielectric function of bulk silver at $\hbar\omega = 0.62$ eV and 2.5 eV, respectively, in assuming a Drude dielectric function for the conduction electrons. The spectral-dependence of m^* is the reason why the simple prescription $m^* = m_0$ is used throughout this work. Moreover the linear extrapolation of the experimental data on Ag_N^+ clusters is consistent with the corresponding asymptotic value 3.41 eV, as it can be seen in Figure 1. Let us emphasize that the suitability of such an extrapolation procedure has however to be called into question owing to, in the one hand the finite-size effects, and, on the other hand the spectral dependence of $\varepsilon_{\rm c}(\omega)$ and – possibly – of the other parameters. In reference [21] the effective mass $m^* = 0.96m_0$, deduced by Johnson and Christie [42] in the infrared spectral range has been used (the asymptotic value is $\omega_{\rm M}(\infty) \approx 3.47$ eV in this case). The linear fit of the experimental data, including those obtained on large Ag_N clusters in solid argon after introducing a corrective factor to take into account the dielectric constant of the matrix, converges towards the asymptotic value 3.5 eV [11,21]. Most of the data related to the Ar-embedded Ag_N clusters are however noticeably above the linear fit. Involving larger sizes leads obviously to a more reliable determination of the asymptotic value $\omega_{\rm M}(\infty)$. However, using experimental data on large matrix-embedded clusters requires to estimate with a very high accuracy the corrective factor. As pointed out in reference [15] the frequency-shift induced by the local porosity at the metal/matrix interface is of crucial importance for analyzing the results. Moreover the cluster temperature in reference [11] (free sputtered Ag_N^+ clusters) is estimated to be larger than 10^3 K, when the measurements on neutral Ag_N clusters embedded in solid argon [12,17] are performed at very low temperature. Therefore the asymptotic value $\omega_{\rm M}(\infty)$ (and thus m^*) cannot be reliably determined – with a high accuracy – from the available experimental results. Debating on the best effective mass to be selected in silver clusters is out of the scope of this paper, and is not elucidated so far. Quantum calculations, using the value $m^* = 0.96m_0$, have been carried out for Ag_N and Ag_N^+ clusters and have shown that a possible lowering of the effective electron mass relative to m_0, of the order of a few percents, is quite insufficient to bring theory in accordance with experiment.

We now tackle the second topic listed at the end of the Introduction. Actually, when the lattice parameter is lower, the ionic-core – as well as the conduction-electron – density increases. From this effect results a size-dependent increase of the ionic-core dielectric function $\varepsilon_{\rm c}(\omega)$, and a competing red-shift trend is thus anticipated (see for instance the classical expression Eq. (1)). As it is well-known, a mere scaling law $\chi_{\rm c}(\omega, N) = \chi_{\rm c}(\omega, \infty)[r_{\rm s}(\infty)/r_{\rm s}(N)]^3$, where $\chi_{\rm c}$ is the ionic-core

background susceptibility, is not suitable for dense materials because of strong local-field effects. A simple Clausius-Mossoti formula, namely $\chi_c(\omega) = [n_c\alpha_c(\omega)/\varepsilon_0]/[1 - n_c\alpha_c(\omega)/3\varepsilon_0]$, where $\alpha_c(\omega)$ is the core polarizability and n_c the ion density, constitutes a reasonable numerical approximation for estimating the size-dependence of $\varepsilon_c(\omega) = 1 + \chi_c(\omega)$. This statement is supported by the work of Sturm *et al.* [43] who have investigated the effects of the core polarization on the dielectric properties of simple metals within the random-phase approximation. These authors have shown that, in the case of metals with cubic symmetry, and provided that the conduction-electron charge fluctuations induced by the short-wavelength local fields of the core dipoles can be neglected, $\varepsilon_c(\omega)$ expresses as a pure Clausius-Mossoti formula. The neglected charge fluctuations would lead merely to a change of the factor 1/3 in the second term of the denominator in the Clausius Mossoti formula. Let us remark that $\alpha_c(\omega)$, which depends on atomic localized orbitals, can be assumed to be unsignificantly modified by the lattice contraction. The size-dependence of n_c leads to the following change in the ionic-core dielectric function

$$\varepsilon_c(\omega, r_s(N)) = \frac{\varepsilon_c(\omega) + 2 + 2\nu[\varepsilon_c(\omega) - 1]}{\varepsilon_c(\omega) + 2 - \nu[\varepsilon_c(\omega) - 1]} \qquad (3)$$

where $\nu = [r_s(\infty)/r_s(N)]^3$ is the density ratio, and $\varepsilon_c(\omega)$ in the right side is the dielectric function for $r_s(\infty)$.

The model predictions with this additional effect, in the absence of the surface skin of ineffective ionic-core polarizability ($d = 0$), are shown in Figure 2, for neutral and charged clusters (empty triangles and circles connected with continuous lines, respectively). The thick full-line curve is the result obtained within the classical approach. Unlike alkali clusters, where the influence of the ionic-core polarization is minor, a red-shift of the Mie's frequency is actually induced by lattice contraction in silver particles. The red-shift trend for decreasing particle radius is scarcely stronger than the one reported in reference [15] for $d = 0$ in the absence of lattice contraction (see Fig. 1). This indicates that the blue- and red-shift trends induced by the lattice contraction (trends corresponding respectively to the increase of the conduction-electron and ionic-core densities) balance almost perfectly in quantum calculations. The quantum results include the spillout effect and are thus lower than the classical ones, except for the smallest investigated sizes. The discrepancies are however very tiny, and this is at first sight astonishing, in view of the much larger differences between classical and quantum results that are observed in Figure 1. This seemingly inconsistent feature is actually a direct illustration of the interdependence of the surface effects [18], emphasizing the non-additivity of the various finite-size effects: because of the spillout effect less electrons are inside the cluster, namely less electrons are sensitive to the size-evolution of $\varepsilon_c(\omega)$. Therefore, for a given increase of ε_c, the red-shift of the surface plasmon frequency is lower than the one that would be obtained in involving a hard-walled electronic density. In other words the red-shift induced by the increase of $\varepsilon_c(\omega)$ is lower in the quantum model than in the classical one. These remarks point out again that, depending of the sophistication of the cluster model, specifically-parametrized quantum effects have to be included for studying small particles within a simple classical approach.

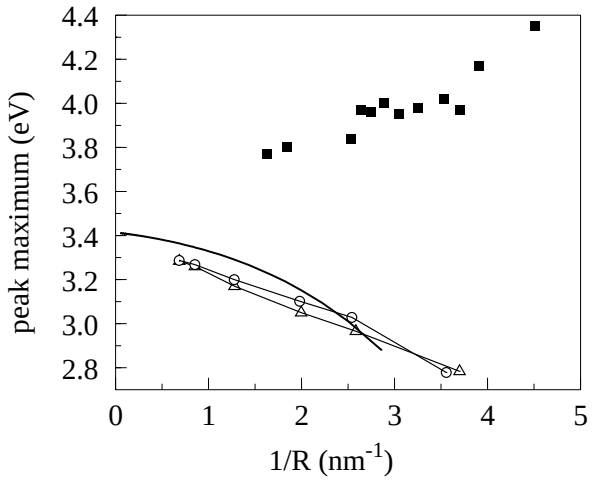

Fig. 2. The size-evolution of the maximum of the Mie band in the absorption spectra of free silver clusters, in taking into account the size-dependence of the ionic-core dielectric function ε_c (Eq. (3)). Black squares: experimental data on Ag_N^+ clusters [11]. Triangles and circles: results of the quantum calculations for Ag_N and Ag_N^+ clusters, in the absence of the surface skin of reduced ionic-core polarizity ($d = 0$). The thick full line curve is the classical prediction ($d = 0$).

The remaining discrepancies between quantum theory and experiment gives evidence of the relevance of the inner surface skin of vanishing ionic-core polarizability, and we have re-estimated the d-value in taking into account the lattice contraction. In the model involving only the increase of the jellium density, values of the order of 1.5–2 a.u. have been found consistent with the experimental data on Ag_N^+ in the medium size range. As compared to our previous work [15] the estimated d-values are obviously lower since the lattice contraction contributes also to a blue-shift of the Mie's frequency. When the size dependence of $\varepsilon_c(\omega)$ is taken into account in the model, d-values of the order of 3 a.u. (see Fig. 3), similar to those obtained in our previous work [15], are consistent with the experimental data in the medium-size range. Obviously this estimation is very rough since only two experimental data lie in this size range. The large discrepancies observed for the smallest investigated sizes (sizes $N' = 9$ and 21) are probably due to fact that the present model (homogeneous jellium and dielectric medium, Clausius-Mossoti formula), which disregards completely the discrete ionic structure and suitable only for large enough particles, is too crude for describing the optical properties in the very small-size range. However let us point out that non-negligible expansion of the lattice by thermal effects, resulting – possibly – in a decrease of the Mie's resonance, is not ruled out for very small clusters. In reference [11] the authors

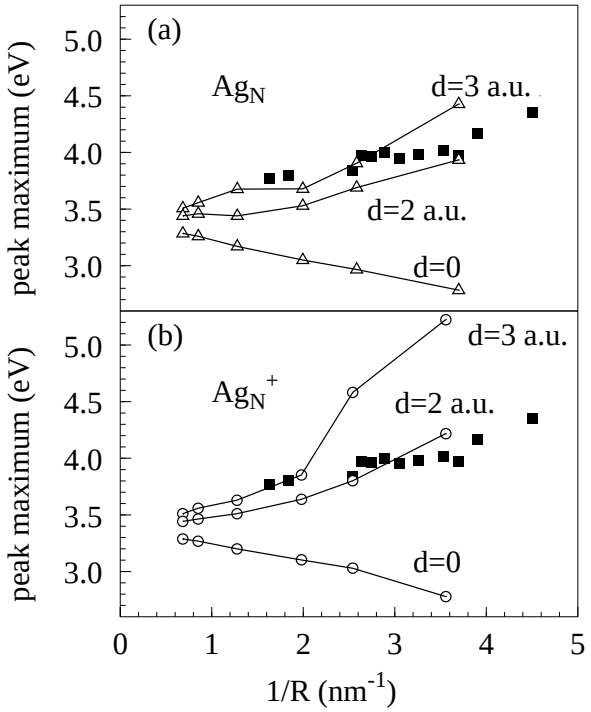

Fig. 3. The size-evolution of the maximum of the Mie band in the absorption spectra of free silver clusters, in taking into account the size-dependence of the ionic-core dielectric function ε_c (Eq. (3)), for various thicknesses of the inner surface skin of vanishing ionic-core polarizability. Black squares: experimental data on Ag_N^+ clusters [11]. (a) Results of the quantum calculations for Ag_N clusters. (b) Results of the quantum calculations for Ag_N^+ clusters.

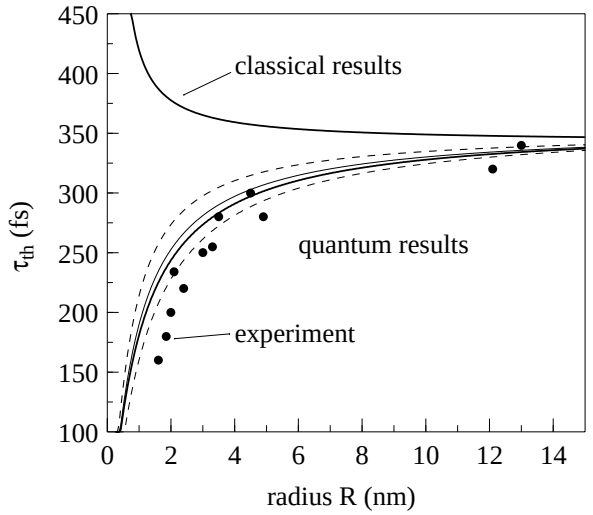

Fig. 4. The size-evolution of the electron thermalization time $\tau_{\rm th}(R)$ in silver clusters, in taking into account the effects of lattice contraction, except for the lower dashed line curve ($d =$ 3 a.u., no lattice shrinkage), within the two-region dielectric model. Black circles: experimental data [20]. Lower thick full line curve: thickness of the surface skin of vanishing ionic-core polarizability $d = 3$ a.u. Thin full line curve: $d = 2$ a.u. Upper dashed line curve: $d = 0$ (no skin of reduced polarizability). The upper full line curve shows the result of the classical model (step-walled electron density and $d = 0$).

estimate the temperature of the Ag_N^+ clusters produced by their sputtering source to be of the order of 2 000–3 000 K. Thus thermal effects could explain the discrepancies between the experimental data on very small Ag_N^+ clusters, obtained by photodepletion spectroscopy, and the present model calculations. At this stage such an explanation is only speculative.

We tackle now the fourth point listed in the Introduction. The almost perfect balancing of the two effects induced by the lattice contraction on the Mie's frequency is not expected with respect to the electron dynamics, since the increase of the conduction-electron and ionic-core densities results *in both cases* in an enlargement of the screening of the Coulomb interaction, and thus of the thermalization time. Within the model described in reference [20] the size-dependence of the electronic thermalization time $\tau_{\rm th}(R)$ has been calculated in taking into account the lattice contraction, namely the changes of the electron density and of the ionic-core dielectric function. The numerical density surface profile obtained from self-consistent TDLDA ground-state calculations has been used throughout this study. For each model calculation, the absolute values of the calculated $\tau_{\rm th}(R)$ have been set in order to reproduce the experimental measurement on a silver film [44]. The results are displayed in Figure 4, for $d = 0$ (no skin of vanishing ionic-core polarizability; upper dashed curve), $d = 2$ a.u. (thin full line curve) and $d = 3$ a.u. (thick full line curve), and compared with the results obtained for $d = 3$ a.u. when no lattice contraction is involved (lower dashed curve). We can see that the lattice shrinkage, which is in fact noticeable only for small particle radii, has a poor influence on the electron dynamics over the entire size range. These results confirm that, in small silver particles, the enlargement of the spatially-averaged scattering rate stems from the smooth decrease of the electron density at the surface and the skin of reduced ionic-core polarizability. The upper full line curve in Figure 4 shows the results of the classical model (step-walled electron density) in taking into account the lattice contraction, for $d = 0$. Obviously the classical model predicts an increase of the thermalization time as the particle radius is reduced.

4 Conclusion

Quantum TDLDA calculations have been carried out to study the influence of lattice contraction on the optical properties and the electron dynamics in silver clusters.

The increase of the conduction-electron and ionic-core densities leads to opposite size trends with regard to the

size-evolution of the surface plasmon frequency. The size-dependent enlargement of the dielectric function $\varepsilon_c(\omega)$ corresponding to the ionic cores results in a red-shift trend which balances almost perfectly the blue-shift trend resulting from the increase of the conduction-electron density. The calculations lead to a slight red-shift trend for decreasing cluster size, attributable mainly to the spillout effect. Agreement with the blue-shift trend observed in experiment can be only achieved by introducing the inner surface skin of reduced polarizability, as it was assumed in previous works. The skin-thickness parameter d, estimated in taking into account the lattice contraction to be of the order of 3 a.u., is scarcely modified relative to the previous estimation [15].

With regard to the electron dynamics, a more efficient screening of the Coulomb interaction results from the increase of both the conduction-electron and ionic-core densities. However the induced decrease of the electron-electron scattering rate is relatively small and does not correspond to the observed increase of this rate. In fact the effect of the lattice contraction in small particles does not affect strongly the electronic thermalization time, the size dependence of which is determined by both the smooth decrease of the electron density at the surface and the skin of vanishing ionic-core polarizability.

References

1. J.A.A.J. Perenboom, P. Wyder, Phys. Rep. **78**, 173 (1981).
2. D.M. Wood, N.W. Ashcroft, Phys. Rev. B **25**, 6255 (1982).
3. W.P. Halperin, Rev. Mod. Phys. **58**, 533 (1986).
4. V.V. Kresin, Phys. Rep. **220**, 1 (1992).
5. M. Brack, Rev. Mod. Phys. **65**, 677 (1993); W.A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).
6. *Comments on Atomic and Molecular Physics*, edited by C. Bréchignac, Ph. Cahuzac, Vol. 31, pp. 135-478 (1995).
7. U. Kreibig, M. Vollmer, *Optical Properties of Metal Clusters* (Springer, New York, 1995).
8. C.F. Bohren, D.R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley Publish., New-York, 1998).
9. G. Mie, Ann. Phys. (Leipzig) **25**, 377 (1908).
10. A. Liebsch, Phys. Rev. Lett. **71**, 145 (1993); Phys. Rev. B **48**, 11317 (1993).
11. J. Tiggesbäumker, L. Köller, K.H. Meiwes-Broer, A. Liebsch, Phys. Rev. B **48**, R1749 (1993).
12. S. Fedrigo, W. Harbich, J. Buttet, Phys. Rev. B **47**, 10706 (1993).
13. V.V. Kresin, Phys. Rev. B **51**, 1844 (1995).
14. (a) Ll. Serra, A. Rubio, Z. Phys. D **40**, 262 (1997); (b) Phys. Rev. Lett. **78**, 1428 (1997).
15. J. Lermé, B. Palpant, B. Prével, M. Pellarin, M. Treilleux, J.L. Vialle, A. Perez, M. Broyer, Phys. Rev. Lett. **80**, 5105 (1998).
16. E. Cottancin, J. Lermé, M. Gaudry, M. Pellarin, J.L. Vialle, M. Broyer, B. Prével, M. Treilleux, P. Mélinon, Phys. Rev. B **62**, 5179 (2000).
17. K.P. Charlé, W. Schulze, B. Winter, Z. Phys. D **12**, 471 (1989).
18. Let us remark that the respective magnitude of these two effects cannot be extracted from numerical quantum calculations in a simple way: all the surface effects are interdependent because the Fermi wavelength, of the order of the spatial radial extent of the low-density electronic surface tail, is much larger than the thickness d of the skin of reduced polarizability.
19. d-values equal to 1.9 a.u., 2 a.u. and 3.5 a.u. have been assumed in reference [13] (approximate analytical model involving Thomas-Fermi ground-state electron densities), reference [14a] (standard TDLDA formalism involving dielectric media) and references [15,16] (TDLDA), respectively. As emphasized by Kresin, the value $d = 1.9$ a.u. is too low to explain the experimental blue shift. This author suspects an overestimation of the spillout within the Thomas-Fermi approximation. In reference [12] (classical multi-shell dielectric model applied to silver clusters embedded in solid argon) a Drude dielectric function $\varepsilon_s(\omega)$ is used over the radial range $[R-d, R+t]$, where $d = 5.3$ a.u. and $t = 0.85$ a.u. is a spillout parameter. In fact mimicking the spillout electronic tail by a Drude dielectric function has to be called into question since $\varepsilon_s(\omega)$ is the dielectric function of an electron gas *neutralized by a positive jellium*. A simple argument allows to be convinced that this ansatz is not correct. Classically the surface plasmon frequency in a homogeneous small particle of radius R is given by $\omega_M = \omega_p/[2\varepsilon_m + \mathrm{Re}(\varepsilon_c)]^{1/2}$. If the above ansatz for describing the dielectric properties of the spillout region is used, the absorption spectrum corresponds to the one of a slightly larger cluster ($R' = R + t$) with an inner skin of vanishing ionic-core polarizability of thickness t, and a blue-shift is obtained instead of the expected red-shift. As a matter of fact the model calculations of Fedrigo *et al.* correspond to those of larger clusters (radius $R' = R + t$) involving a skin of reduced polarizability of thickness $d' = d + t = 6.15$ a.u. Such a very large value, that is required to fit the experimental data, is due to the fact that the local porosity at the metal/matrix interface is partly responsible for the observed net blue-shift [15] and was not taken into account in reference [12]. This points out that the estimation of the effective thickness d should involve free clusters.
20. C. Voisin, D. Christofilis, N. Del Fatti, F. Vallée, B. Prével, E. Cottancin, J. Lermé, M. Pellarin, M. Broyer, Phys. Rev. Lett. **85**, 2200 (2000).
21. W. Cai, H. Hofmeister, M. Dubiel, Eur. Phys. J. D **13**, 245 (2001).
22. G. Apai, J.F. Hamilton, J. Stohr, A. Thompson, Phys. Rev. Lett. **43**, 165 (1979).
23. M. Copel, T. Gustafsson, W.R. Graham, S.M. Yalisove, Phys. Rev. B **33**, 8110 (1986).
24. B. Montag, P.G. Reinhard, J. Meyer, Z. Phys. D **32**, 125 (1994).
25. J.P. Perdew, M. Brajczewska, C. Fiolhais, Solid State Commun. **88**, 795 (1993).
26. A. Vieira, C. Fiolhais, M. Brajczewska, J.P. Perdew, Int. J. Quant. Chem.: Quant. Chem. Symp. **30**, 325 (1996).
27. H. Hövel, S. Fritz, A. Hilger, U. Kreibig, Phys. Rev. B **48**, 18178 (1993).
28. With regard to embedded clusters, the introduction of an outer vacuum rind for mimicking the local porosity at the metal/matrix interface [15,16] was however required

to bring the model calculations in agreement with experiment.
29. M.J. Stott, E. Zaremba, Phys. Rev. A **21**, 12 (1980).
30. A. Zangwill, P. Soven, Phys. Rev. A **21**, 1561 (1980).
31. W. Ekardt, Phys. Rev. B **31**, 6360 (1985).
32. J. Lermé, B. Palpant, B. Prével, E. Cottancin, M. Pellarin, M. Treilleux, J.L. Vialle, A. Perez, M. Broyer, Eur. Phys. J. D **4**, 95 (1998).
33. J. Lermé, Eur. Phys. J. D **10**, 265 (2000).
34. E.D. Palik, *Handbook of optical constants of solids* (Academic Press Inc., New York, 1995/1991), Vol. I and II.
35. H. Ehrenreich, H.R. Philipp, Phys. Rev. **128**, 1622 (1962).
36. C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons Inc, New York, 1983).
37. C. Yannouleas, R.A. Broglia, Ann. Phys. (NY) **217**, 105 (1992).
38. C. Yannouleas, E. Vigezzi, R.A. Broglia, Phys. Rev. B **47**, 9849 (1993).
39. N.W. Ashcroft, N.D. Mermin, *Solid State Physics* (Saunders College Publishing, Philadelphia, 1988).
40. In reference [21] the core electron "dielectric function" $\varepsilon_{\rm b}(\omega)$ (b stands for "bulk") is actually the dielectric susceptibility related to the core-electron polarizability, namely $\varepsilon_{\rm b}(\omega) = \varepsilon_{\rm c}(\omega) - 1$ (see Eq. (3) in Ref. [21]). The spectral dependence of the real part of $\varepsilon_{\rm c}(\omega)$ is then obtained by adding 1 to the curve plotted in the Figure 1 of reference [21].
41. C. Yannouleas, Phys. Rev. B **58**, 6748 (1998).
42. P.B. Johnson, R.W. Christy, Phys. Rev. B **6**, 4370 (1972).
43. K. Sturm, E. Zaremba, K. Nuroh, Phys. Rev. B **42**, 6973 (1990).
44. N. Del Fatti, C. Voisin, M. Achermann, S. Tzortzakis, D. Christofilos, F. Vallée, Phys. Rev. B **61**, 16956 (2000).