Plasmon Coupling in Silver Nanosphere Pairs

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In this work we study the optical properties of silver metal nanosphere pairs by means of rigorous electrodynamics calculations based on the generalized multiparticle Mie theory. By correlating the dipole longitudinal plasmon wavelength with its corresponding value of the real part of the dielectric constant, and based on the dipole quasi-electrostatic approximation, we were able to derive a new plasmon ruler equation for the longitudinal dipole plasmon resonance of Ag dimers, suitable for a wide range of interparticle distances and radii. The new resonance condition equation, at variance with previous work on noble metal nanoparticle pairs, takes into account empirically retardation effects and multipole interactions, being a novel, accurate, and potentially useful tool for future applications in plasmonic nanometrology or sensor devices.

Introduction

Noble metal nanoparticles (NPs) are well-known to exhibit a strong interaction with light due to the excitation of localized surface plasmons, which are coherent oscillations of the metal electrons in resonance with an incident electromagnetic field of a given frequency.[1] On resonance, the plasmon oscillation gives rise to a strongly enhanced electric field at the NP surface[2] and to a strongly enhanced scattering pattern in the far-field;[3] furthermore, the plasmon resonance frequency is highly dependent on the shape, size, and dielectric environment of the NP.[4] These fascinating plasmon features have attracted great interest in recent years due to their potential application in several fields such as biochemical sensing,[5−7] medicine,[8−10] and nano-optical devices.[11−13]

For a system of two or more NPs close enough to each other, a new phenomenon arises as a result of plasmon coupling, which produces a significant change of the optical response. In this respect, a relevant parameter which controls the optical behavior is the interparticle distance. The effect of interparticle distance on plasmon coupling has been both theoretically and experimentally studied by several authors, using mainly Au NP pairs.[14−45] According to the illuminating direction with respect to the pair axis, a blue or red plasmon shift is observed on the extinction spectra when compared with isolated NPs, the magnitude of these plasmon shifts being more significant as the interparticle separation decreases.[15,16] This property of NP pairs has the potential to be a useful tool to measure nanoscale distances, for instance, in biological systems, as has been recently demonstrated by Soennichsen et al. and Reinhard et al., who were able to design a *plasmon ruler* on the basis of the spectral shift mentioned above.[17,18] This plasmon ruler has the advantages to measure, by optical means, distances in a much longer range and to have better photostability than fluorescence resonance energy transfer (FRET), a technique traditionally used in biological systems for distance measurements.[18] Although the distance dependence of FRET is well-known, there is a great interest nowadays to establish quantitatively the distance dependence of plasmon coupling due to the superior performance that these plasmonic devices will have with respect to FRET nanometrology measurements. In this respect, Jain et al. have reported a systematic series of experiments of the near-field coupling in Au nanodisk pairs and showed that the plasmon coupling strength for polarization along the interparticle axis decays nearly exponentially with almost the same decay length for different NP sizes, shapes, metal types, and medium dielectric constants. In addition, the authors quantitatively explained this behavior on the basis of a dipolar-coupling model using DDA simulations.[19] Most recently, this work has been extended to test the constancy of the exponential decay length value in the plasmonic ruler equation for other particle shapes and orientations. Their results indicate that the exponent is almost the same independent of size but is very sensitive to the shape.[15]

However, plasmon coupling on Ag NP pairs has been studied in less detail. The light scattering by individual Ag NPs and NP pairs of typical particle dimensions of some 100 nm and the polarizaration dependence have been studied spectroscopically by Tamaru et al., the experiments being in good agreement with numerical simulations performed using Mie scattering and the FDTD method.[20] Hao and Schatz have shown by means of classical electrodynamics calculations that the electric field enhancement around Ag spheres and triangular prism dimers is a strong function of the interparticle separation and that it scales with NP size, the magnitude of the enhancement being higher for dimers illuminated at the higher wavelength.[21] Systematic experiments on the optical properties of individual disk-shaped Ag pairs prepared by electron beam lithography have been performed by Gunnarson et al., determining that the dipole plasmon resonance red shifts dramatically as the interparticle distance is decreased for incident polarization parallel to the pair axis,[22] the magnitude of the shift being much larger than what was observed for Au pairs.[23,24] According to the above experimental and theoretical evidence, the optical response of Ag NP pairs is more sensitive to the change of the interparticle separation, in comparison with the Au NP pairs, improving, for instance, the sensitivity and range of the above-mentioned plasmon ruler properties.

For spherical NP pairs, there are several theoretical methodologies available to describe its interaction with electromagnetic

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radiation.[25−32] For instance, Nordlander has recently developed an original and valuable method which provides a simple and intuitive description of plasmon coupling in terms of bonding and antibonding combinations, the so-called plasmon hybridization model.[33,34]

A very simple conceptual framework to describe the interaction between two spherical NPs is given by the dipole quasi-electrostatic approach, which states the resonance condition as[35]

$$\varepsilon(\omega) = -\frac{8\sigma^3 + 1}{4\sigma^3 - 1}\varepsilon_m \quad (1)$$

$$\varepsilon(\omega) = -\frac{16\sigma^3 - 1}{8\sigma^3 + 1}\varepsilon_m \quad (2)$$

for the longitudinal (eq 1) and the transversal (eq 2) dipole mode, i.e., when the incident electric field is parallel and perpendicular to the dimer axis, respectively. In eq 1, ε_m stand for the dielectric constant of the surrounding media, and the resonances values of $\varepsilon(\omega)$, ε_{res}, depend on the relative separation parameter σ defined equal to S/D (D being the diameter of the spheres and S the center-to-center distance). This approximation indicates that the values of ε_{res} vary between -3 and -2 for $\sigma = 1$ and at infinite separation, respectively. In fact, the validity of equation eq 1 is the very basis of the universal scaling behavior reported by several authors as mentioned above.[19]

However, eq 1 only takes into account interactions between dipole excitations on each particle, whatever the sphere diameter, and, consequently, it does not provide an accurate description of the optical properties of NP pairs when higher order multipole interactions are significant and is limited to relatively large interparticle separations.[26] Including such multipole interactions does certainly improve the optical description, but, as we will see below, it is also necessary to solve the problem beyond the quasi-electrostatic approximation by taking into account retardation effects, due to the finite size of the nanospheres. The generalized multiparticle Mie theory (GMM) formulation developed by Xu is a suitable and rigorous formulation able to include exactly these electrodynamic effects and to solve this complex problem.[36] This methodology is an analytical far-field solution to electromagnetic scattering by an aggregate of spheres in a fixed orientation, which constitutes an extension of Mie theory to the multisphere case.

In a previous work we have developed a graphical method by means of which we were able to obtain, using the standing wave antenna model as a guide, a general resonance condition capable of predicting the plasmon peaks of finite length nanowires, of the form[3]

$$\mathrm{Re}(\varepsilon(\omega)_{res}) = f\varepsilon_m \quad (3)$$

where f is a function of nanowire length and diameter, dielectric environment, and multipole order of the plasmon resonance l.

In the present work, we will show that using the above-mentioned methodology to calculate accurately the values of $\mathrm{Re}(\varepsilon_{res})$ from GMM calculations and making simple modifications to the dipole plasmon coupling eq 1, we will be able to obtain a more general resonance condition for Ag nanosphere dimers, which can be applied to a wide range of Ag nanosphere radius (10−25 nm) and a long-range of NP separation, from nearly touching spheres to larger sphere -to-sphere separations. This paper is organized as follows: First, we will show that the plasmon shift of the dipole resonance mode in a given Ag NP pair is more significant than that for the Au one of the same dimensions and geometrical configuration. Second, we will analyze in a simple way the different contributions to the extinction spectra according to the incident polarization with respect to the dimer axis. Lastly, we will focus particularly on the Ag sphere NP pairs with the aim tof obtaining a more general plasmon ruler equation able to include retardation effects as well as multipole interactions, for various interparticle separations, sphere diameters, and different dielectric environments.

Methodology

The GMM method has been described in detail in several places, so we will only give a brief summary here.[46,47] In the GMM method, scattered fields from each of the L individual spheres are solved in respective sphere-centered reference systems. In an arbitrarily chosen primary j_0th coordinate system, the Cartesian coordinates of the origins of these L displaced coordinate systems (i.e., the sphere centers) are (X^j, Y^j, Z^j), $j = 1, 2, ..., L$. To solve multisphere-scattering through the Mie-type multipole superposition approach, the incident plane wave is expanded in terms of vector spherical wave functions in each of the L sphere-centered coordinate systems. Then, the total electromagnetic field incident upon each sphere in the aggregate is obtained, which consists of two parts: (1) the initial incident plane wave and (2) scattered waves from all other spheres in the aggregate. The next step, of vital importance to achieve a complete multisphere light-scattering solution, is to construct a single field representation for the total scattering field from the aggregate as a whole, by expanding it in vector spherical wave functions. Finally, with the total scattered field at hand and based on the analytical expressions for amplitude scattering matrix of an aggregate of spheres, it is possible to derive rigorous formulas for other fundamental scattering properties as extinction cross section.[46,47] The calculations presented in this work correspond to noble metal nanosphere pairs of the same diameter D, where the direction of the incident wave vector $\mathbf{k}$ is perpendicular to the dimer axis. In all the simulations we have used the dielectric function tabulated by Palik for Ag and Au.[48] For each dimer analyzed, the separation between the nanospheres ($\sigma \geq 1.05$) is large enough that nonlocal effects on the dielectric constant can be neglected.[49]

Results and Discussion

As it has been reported in previous experimental and theoretical studies, when two Au NPs approach each other, a red shift of the extinction peak associated with the longitudinal resonance mode is observed due to the increase of the magnitude of plasmon coupling as the distance between them decreases.[19] For Ag NPs, as it is expected, the same phenomena occurs as is shown in Figure 1a for Ag nanospheres pairs ($D = 20$ nm) in vacuum for several σ values given unpolarized incident light.

For $\sigma = 3$, the extinction spectrum is practically indistinguishable from that of an isolated Ag nanosphere ($\sigma \rightarrow \infty$) of the same D, showing a sharpened peak located at around $\lambda = 360$ nm. For $\sigma = 1.5$, a slight red shift of the extinction peak is observed; however, if the nanospheres are getting closer up to $\sigma = 1.1$, the extinction spectrum changes dramatically. The peak splits into two well-defined and spectrally separated extinction peaks, one at $\lambda \sim 360$ nm and the other one notably red-shifted with respect to the former, at $\lambda \sim 400$ nm. The most significant separation between the peaks (almost 100 nm) is observed for $\sigma = 1.05$, i.e., when the spheres are very close to each other. This phenomenon is the result of strong plasmon coupling and

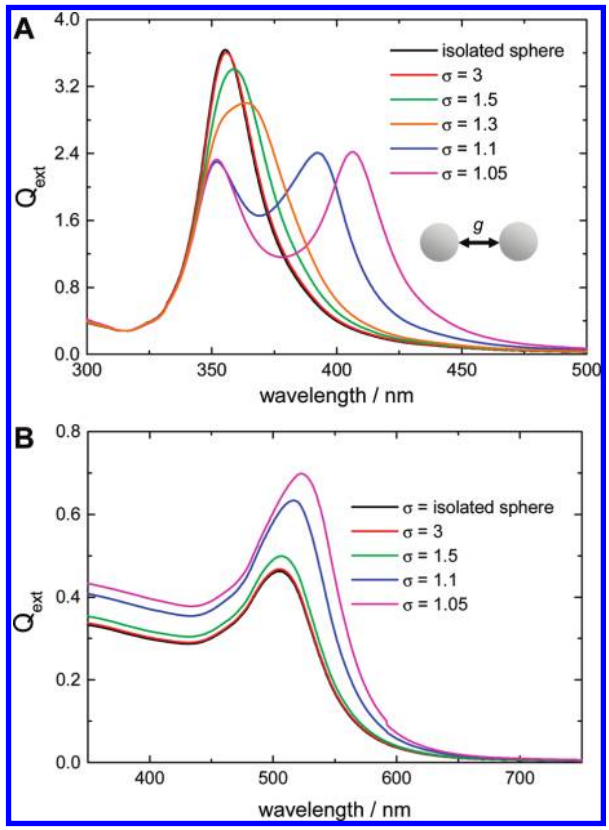

Figure 1. Extinction spectrum for (a) Ag and (b) Au dimers, both with $r = 10$ nm, in vacuum, for several values of the relative separation parameter σ. Note that, as $\sigma \rightarrow 1$, the dipolar plasmon peak is red-shifted, the magnitude of this shift being more significant for the Ag dimer than for the corresponding Au dimer.

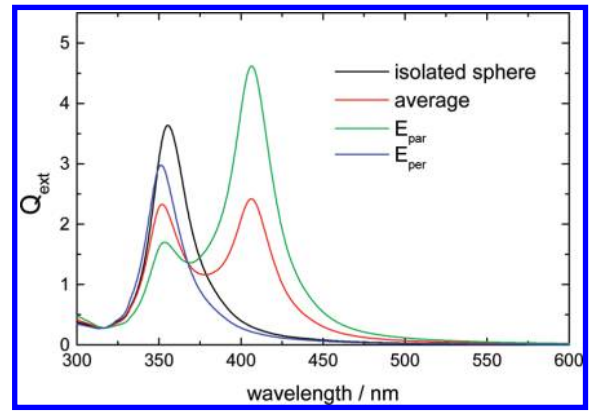

Figure 2. Extinction spectra for longitudinal and perpendicular incident polarization with respect to the dimer axis on the extinction spectrum of a Ag dimer, $r = 15$ nm, in vacuum. The average extinction spectrum for both polarizations is also shown.

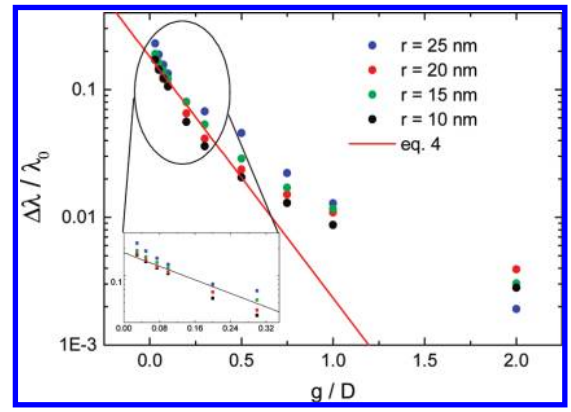

Figure 3. Fractional plasmon shift vs the ratio of interparticle gap to sphere diameter for Ag dimers of different sizes in vacuum (dots); the data do not lie on the curve described by eq 4 (solid red line). The inset is added to better illustrate the deviation of the behavior of Ag particles from eq 4 for small (g/D) values. Note that the y axis scale is logarithmic.

indicates that the electromagnetic interaction between the nanospheres is much more significant for interparticle separation lower than $\sigma = 1.5$, which agrees with previous studies on NP dimer arrays.[21,25]

In general, most of the investigations related to plasmon coupling between NPs are concerned with gold nanosphere and nanodisc pairs. In those cases, the magnitude of the plasmon shift is considerably smaller in comparison to the Ag system; thus, spliting of the extinction spectrum into two well-defined and spectrally separated peaks is more difficult to be observed. In some cases, the appearance of a shoulder in the spectra is observed (see Figure 1b); this fact can be accounted for taking into account that the electromagnetic fields are, in general, stronger for Ag NP pairs.[19,50] As it has been previously proposed based on this internanoparticle distance dependent extinction spectra, practical and accurate optical devices able to determine lengths on the nanometric scale could be designed. Thus, the results shown above suggest that Ag NP pairs are a potentially more appropriate device for nanometrology applications.

According to the state of the incident light, the spectral features described above can be interpreted as the result of two different incident polarizations; the effects of each one on the extinction spectrum for $\sigma = 1.05$ are displayed in Figure 2. When the incident polarization is parallel to the dimer axis, two peaks are clearly observed; the peak at the higher wavelength is associated with a longitudinal plasmon resonance of dipole character, whereas the peak at $\lambda \sim 360$ nm is associated with the spectral superposition of higher order longitudinal resonance modes, whose main contribution arises from the quadrupole one. On the other hand, when the incident polarization is perpendicular to the dimer axis, only one peak is observed (which presents a weak blue shift as $\sigma \rightarrow 1$) associated with a dipole transversal plasmon resonance.

In the following we will focus on the longitudinal dipole resonance mode, as it gives rise to the most significant shifts. In this respect, Jain et al. have recently derived a universal plasmon scaling behavior, supported by a dipole−dipole interactions model, a so-called plasmon ruler equation which can be used to estimate the interparticle separation from an experimentally observed plasmon shift

$$\frac{\Delta\lambda}{\lambda_0} \approx 0.18 \exp\left(\frac{-(g/D)}{\tau}\right) \qquad (4)$$

where $\Delta\lambda/\lambda_0$ is the fractional plasmon shift ($\Delta\lambda = \lambda_{res} - \lambda_0$, λ_{res} and λ_0 being the resonance values for the longitudinal dipole plasmon mode and for the isolated sphere, respectively), and g is the interparticle edge-to-edge separation. According to these authors, the universality of the scaling behavior lies in the fact that the decay constant $\tau = 0.23$ in eq 4 for the plasmon coupling is similar, independent of the nanoparticle size, metal type, or medium dielectric since these parameters only govern the magnitude of the fractional shift.

However, we have obtained a very different behavior of the longitudinal plasmon shift $\Delta\lambda/\lambda_0$ for Ag nanosphere pairs. The above-mentioned scaling behavior is not observed any longer

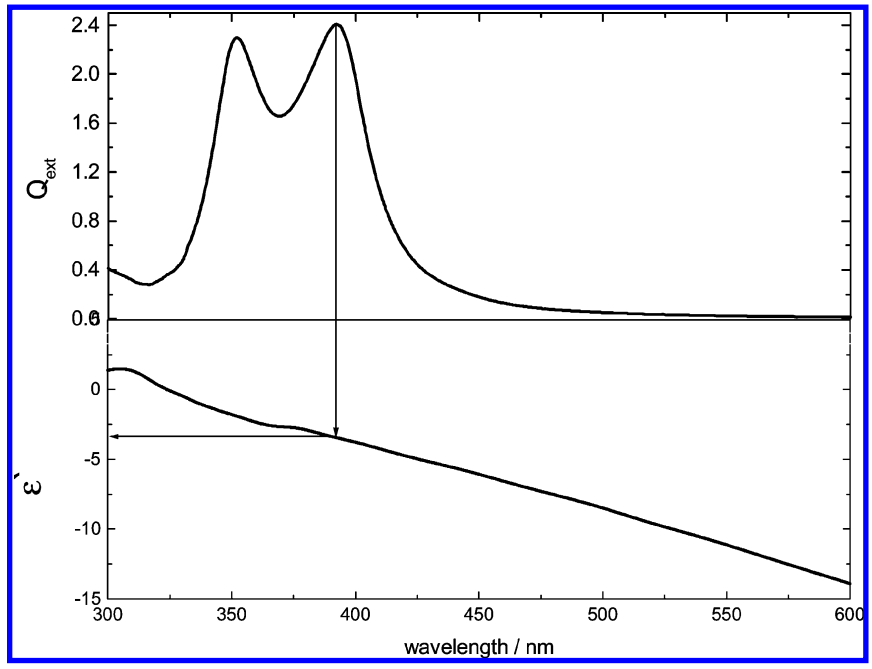

Figure 4. Graphical representation of the method used to correlate λ_{res} and the real part of the dielectric constant for the dipole longitudinal plasmon resonance mode, $\varepsilon`_{res}$, for a typical Ag NP pair.

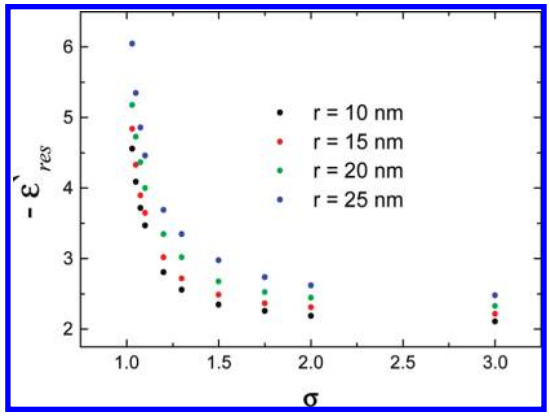

Figure 5. $\varepsilon`_{res}$ values determined using the graphical method depicted in Figure 4, from the extinction spectra calculated using GMM theory, for the longitudinal plasmon mode vs σ for Ag dimers of different sizes, in vacuum.

since both the magnitude of the fractional shift and the decay constant depend on the diameter of the nanoparticle pair (see Figure 3). Therefore, for the size range and interparticle separation studied here, this topic deserves further analysis. As this "universal" plasmon ruler equation has been obtained based on a dipole−dipole model, it should be desirable to obtain a scaling law or resonance condition which surpasses the limitations given by eq 4.

As far as we know, a rigorous resonance condition able to predict quantitatively the values of λ_{res}, or in the more general case, the values of the real part of the dielectric constant valuated at the resonance wavelength, $\varepsilon`_{res}$, for the longitudinal dipole mode of a pair of Ag nanospheres, has not been given yet, for any sphere radius, separation, and surrounding media. By means of the correlation depicted in Figure 4 we have determined the relation between $\varepsilon`_{res}$ for the longitudinal dipole mode and a given value of σ for several spherical radii, as shown in Figure 5 determined from rigorous GMM calculations. The absolute $\varepsilon`_{res}$ values depend on the nanosphere radius and decrease nearly exponentially with $\sigma$. Note that, for the NP of smallest diameter, as $\sigma$ increases, $\varepsilon`_{res}$ approximates the asymptotic value of -2 which corresponds to the $\varepsilon`_{res}$ value of an isolated sphere in the quasi-electrostatic limit, indicating that our results are consistent with those expected at infinite separation.

It should be instructive to compare the data depicted in Figure 5 with the values predicted according to the dipole quasi-electrostatic approximation for two spherical particles (see eq 1). Note that in this approximation the $\varepsilon`_{res}$ values depend only on the parameter $\sigma$, and the limiting values are $\varepsilon`_{res} = -3$ for $\sigma = 1$ and $\varepsilon`_{res} = -2$ for $\sigma \sim \infty$, whatever the sphere diameter. The curves depicted in Figure 5 do not follow this behavior since they reach a diameter dependent limiting value for $\sigma = 1$ and ∞. This indicates that the dipole approximation is not able to describe accurately the plasmon shift of Ag nanosphere dimers in the all size regime as $\Delta\lambda$ depends on σ and D. Therefore, an accurate description of the plasmon shift requires that retardation effects as well as multipole interactions should be considered explicitly.

Although the dipole approximation is only a qualitative description for NPs interactions, it can be used as an appropriate starting point. Previous work performed with more accurate multipole solutions in the quasi-static limit indicates that the dipole approximation is not accurate for $\sigma < 1.5$,[25] which means that the contribution of higher order multipoles to the longitudinal dipole resonance is negligible for $\sigma > 1.5$. Taking this into account, it seems reasonable to use eq 1 to fit the curves in Figure 5 for $\sigma > 1.5$, but including corrections to consider retardation effects. It is possible to empirically introduce these effects into the dipole approximation, for $\sigma > 1.5$, by multiplying the σ^3 term in the numerator and denominator of eq 1 by functions of the sphere radius $f(r)$ and $g(r)$. These functions must satisfy the condition that $f(r) \rightarrow 8$ and $g(r) \rightarrow 4$, as $r \rightarrow 0$, i.e., when retardation effects become negligible. By means of a careful examination, we found that the functions $f(r) = 8/(1 + (r/30)^3)$ and $g(r) = 4/(1 + (r/26)^3)$ fulfill this requirement and satisfactorily fit the data. Even though the respective exponent that affects the variable r in $f(r)$ and $g(r)$ arises from the fitting procedure, it is possible to conjecture that its value may be related to

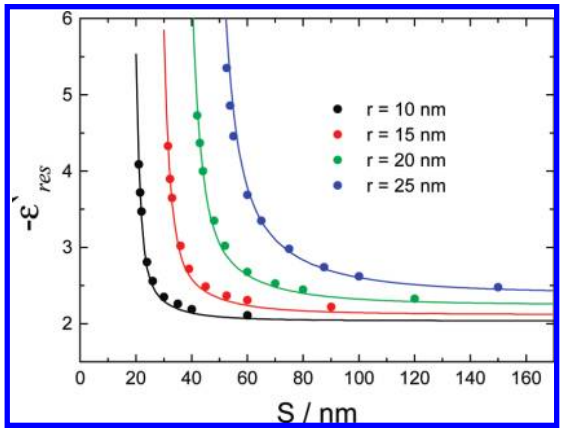

Figure 6. Comparison between $\varepsilon`_{res}$ values vs the separation S for a Ag dimer, of different sizes, in vacuum, calculated from the spectra using GMM theory (solid points) with eq 6 (solid curves). Note the excellent quality of eq 6 to fit the exact calculations.

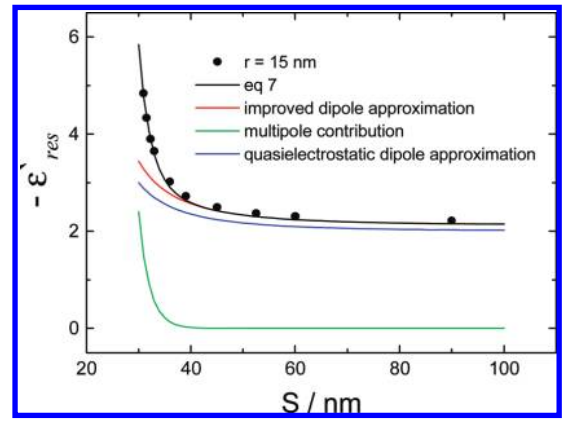

Figure 7. Comparison between $\varepsilon`_{res}$ for different interparticle separations S for a Ag dimer, with $r = 15$ nm, in vacuum, calculated using GMM (solid points), with eq 6 (black curve). Contribution of each term to eq 6: improved dipole quasi-electrostatic approximation (red curve), higher order modes contribution (green curve). The dipole quasi-electrostatic approximation given by eq 1 (blue curve) it is also plotted for comparison.

the fact that the intraparticle restoring potential is inversely proportional to the volume or r^3. In this way eq 1 becomes

$$-\varepsilon`_{res} = \frac{f(r)\sigma^3 + 1}{g(r)\sigma^3 - 1}\varepsilon_m \tag{5}$$

For $\sigma < 1.5$, it should be necessary to consider not only retardation effects but also the contribution of higher order multipoles. Quantitatively, the magnitude of these effects is given by the difference between the value of $\varepsilon`_{res}$ obtained from the GMM simulation and the value determined using eq 5. In addition, we found that this difference decays as an exponential function. After many trials, we determined that by adding to eq 5 the exponential term given by

$$j(\mathrm{r}) = 2.4\exp[-2r(\sigma - 1)/h(r)] \tag{6}$$

with $h(r) = 0.2 + 0.125r$, retardation effects and the contribution of higher order multipoles, at short NP separations, could be incorporated in a simultaneous way.

Therefore, for the longitudinal dipole mode, the resonance condition can be written more accurately as follows:

$$-\varepsilon`_{res} = \frac{f(r)\sigma^3 + 1}{g(r)\sigma^3 - 1} + 2.4\exp[-2r(\sigma - 1)/h(r)] \tag{7}$$

The excellent agreement between the values of $\varepsilon`_{res}$ obtained using eq 7 and the exact values calculated from GMM is shown in Figure 6 for different sphere sizes and separations $S$. Probably, the functional form of eq 7 could remain valid to describe the dependence of $\varepsilon`_{res}$ on σ beyond the size range presented here. It should be noted that the parameters 30 and 26 introduced in functions $f(r)$ and $g(r)$, respectively, were obtained empirically by means of an optimization procedure performed for the specific size range, so it is not expected that they will be able to accurately describe the dependence of $\varepsilon`_{res}$ on σ out of the size range studied.

In relation to the practical applications of nanosphere pairs as a plasmon ruler, the size range analyzed comprises a kind of optimal r values. For $r \leq 10$ mn, the magnitude of the plasmon shift, even though it is appreciable, it is not as pronounced as desirable. Moreover, the distance range capable to be measured by a plasmon ruler decreased with its size. Therefore, for small distance measurements (1−10 nm), the FRET technique should be more suitable. On the other hand, for $r \geq 25$ nm, the structural perturbations that introduce the nanospheres that perform the measurement into the system could be substantial, especially for biological systems. Besides, the sensitivity of the plasmon decreases with r, as has been demonstrated experimentally for Au nanoparticle pairs.[18a] From all the reasons mentioned above, Tabor et al.[15] have recently concluded that for general applications the ideal nanoparticle shape and size selection should be a small nanosphere ($r < 25$ nm).

The relative contributions of each term to eq 7 are illustrated separately in Figure 7 along with the exact results for a particular Ag dimer with $r = 15$ nm. The first term on the right side of eq 7 accounts only for dipole−dipole-like interactions between the nanospheres including retardation effects through the functions $f(r)$ and $g(r)$ and gives the principal contribution for $\sigma > 1.5$. Note that this term is not able to describe quantitatively the shifts of $\varepsilon`_{res}$ as the spheres are closer than $\sigma < 1.5$. The second term accounts for the contribution of multipole interactions as well as retardation effects, being almost zero for large interparticle separations and giving significant contribution for small σ values (σ around 1.5−1.4 depending on the sphere radius).

As mentioned above, it would be desirable that a complete resonance condition can be able to predict accurately the change in $\varepsilon`_{res}$ not only with r and σ but also with the dielectric environment. In order to analyze this issue, we have, on the one hand, calculated the extinction spectra for Ag NP pairs with different D and S values placed in media with different dielectric constant, ε_m, and determined the $\varepsilon`_{res}$ values as described in Figure 4, using the exact GMM theory. On the other hand, we have computed the $\varepsilon`_{res}$ values using eq 6 and assuming a linear dependence between $\varepsilon`_{res}$ and ε_m according to the following equation:

$$-\varepsilon`_{res} = \left(\frac{f(\mathrm{r})\sigma^3 + 1}{g(\mathrm{r})\sigma^3 - 1} + 2.4\exp[-2\mathrm{r}(\sigma - 1)/h(\mathrm{r})]\right)\varepsilon_m \tag{8}$$

The exact $\varepsilon`_{res}$ values vs the $\varepsilon`_{res}$ values computed by means of eq 8 give a linear dependence with slope unit (see Figure 8),

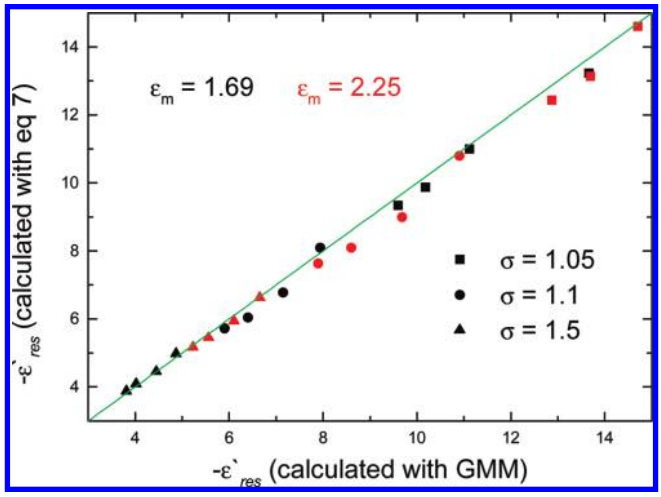

Figure 8. $\varepsilon`_{res}$ values for Ag NP pairs for the four different diameters studied and different $\sigma$ values, in media with different dielectric constants ($\varepsilon_m$), calculated using eq 7 as a function of the corresponding $\varepsilon`_{res}$ values obtained from the extinction spectra using GMM theory according to the procedure described in Figure 4. The green curve corresponds to the curve of unit slope.

a result that implies that the $\varepsilon`_{res}$ values calculated according to eq 8 are accurate.

Therefore, it can be stated that eq 8 constitutes a general resonance condition valid for any Ag nanosphere pair of equal diameter in the size regime studied here, for a wide range of interparticle separations (from nearly touching spheres to infinite separation) and for any surrounding dielectric environment.

Conclusions

In summary, we have performed a systematic study on the plasmon coupling in Ag nanosphere pairs using exact GMM electrodynamics calculations. In particular, we have analyzed the effect of nanospheres radius, separation, and dielectric media on the longitudinal plasmon resonance. Based on the quasi-electrostatic approximation, we derived a complete resonance condition able to predict the $\varepsilon`_{res}$ values for the longitudinal dipole resonance mode given the nanosphere radius, separation, and dielectric environment, which is consistent with previous theoretical and experimental work. This expression provides meaningful physical insight and allowed us to interpret quantitatively the plasmon shift according to two principal contributions: retardation effects as well as multipole interactions. For $\sigma > 1.5$, the plasmon shift is mainly due to dipole−dipole-like interactions. Higher order multipole contributions are in general important for $\sigma < 1.5$ and become more significant as $\sigma \sim 1$. In addition, we determined that retardation effects cannot be ignored for all the range of nanosphere radius analyzed. The resonance condition derived in this work constitutes an accurate plasmon ruler equation for Ag NP pairs and could be very useful for guiding future experiments and/or the developing and fabrication of plasmonic devices.

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