Calculation and measurement of radiation corrections for plasmon resonances in nanoparticles

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The problem of plasmon resonances in metallic nanoparticles can be formulated as an eigenvalue problem under the condition that the wavelengths of the incident radiation are much larger than the particle dimensions. As the nanoparticle size increases, the quasistatic condition is no longer valid. For this reason, the accuracy of the electrostatic approximation may be compromised and appropriate radiation corrections for the calculation of resonance permittivities and resonance wavelengths are needed. In this paper, we present the radiation corrections in the framework of the eigenvalue method for plasmon mode analysis and demonstrate that the computational results accurately match analytical solutions (for nanospheres) and experimental data (for nanorings and nanocubes). We also demonstrate that the optical spectra of silver nanocube suspensions can be fully assigned to dipole-type resonance modes when radiation corrections are introduced. Finally, our method is used to predict the resonance wavelengths for face-to-face silver nanocube dimers on glass substrates. These results may be useful for the indirect measurements of the gaps in the dimers from extinction cross-section observations.

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I. INTRODUCTION

Plasmon resonances in metallic nanoparticles occur under two conditions: (1) the wavelengths of the incident radiation are appreciably larger than the geometric dimensions of the metallic nanoparticles and (2) the dielectric permittivity of nanoparticles is negative at these wavelengths. The first condition suggests that plasmon resonances are, by and large, electrostatic in nature, while the second condition implies that the uniqueness of electrostatic solutions may be broken and nonzero source-free solutions of electrostatics may exist. These source-free solutions are plasmon modes and they occur for special negative values of the nanoparticle permittivity (i.e., resonance permittivities). Integral techniques¹⁻⁶ have been suggested for the analysis of plasmon resonances. In particular, the problem of computing the negative resonance values of the permittivity has been framed as an eigenvalue problem for specific boundary integral equations.^{3–6} This eigenvalue approach reveals that within the electrostatic approximation the resonance values of the nanoparticle permittivity (and, consequently, the resonance wavelengths) depend only on the shape of the nanoparticles but not their dimensions.

When the incident wavelengths are much larger than the nanoparticle dimensions, time harmonic electromagnetic fields within the nanoparticles and around them vary with almost the same phase. As a result, at any instant of time these fields resemble electrostatic fields. As the dimensions of nanoparticle are increased, the quasistatic condition is not strictly valid, and retardation (wave) effects manifest themselves.^{7–10} In this situation, the accuracy of the electrostatic approximation may be compromised and appropriate radiation corrections for the calculation of resonance permittivities are needed. By using the perturbation technique, such radiation corrections have been derived.⁶ In this paper, these radiation corrections are tested through their comparison with experimental data. This comparison reveals that these radiation corrections may be quite accurate. This suggests that the radiation corrections can be used to gauge the size of plasmonic nanoparticles based on spectroscopy data, for example, during the optimization of a synthetic protocol. Furthermore, these radiation corrections may be valuable in the analysis of plasmon resonances in nanoparticle clusters which are typically employed in various applications, for instance, in surface enhanced Raman spectroscopy (SERS).^{11–20} For this reason, the computational results for radiation corrections are presented here for face-to-face nanocube dimers for various "gap-to-cube edge length" ratios. These computational data may be useful for the deduction of gap distances between nanoparticles from extinction cross-section measurements.

In the paper, an extensive study of radiation corrections for cubic nanoparticles and their comparison with measured extinction spectra of nanocube ensembles is presented. This study is of physical significance for the following reasons. First, the use of cubic nanoparticles is very promising for SERS research because high electric fields can be achieved near corners and edges of nanocubes. Second, the dipole plasmon spectrum of nanocubes is quite rich. Namely, nanocubes (unlike nanospheres) have many dipole modes with different resonance wavelengths. At small nanocube dimensions, these wavelengths are bunched together and the linewidth of the extinction peak of the first (highest resonance wavelength) dipole mode conceals the extinction peaks due to other dipole modes. As the dimensions of the nanocubes are gradually increased, the resonance wavelengths of the dipole modes become more separated and the extinction peaks of other dipole modes are gradually revealed. It is demonstrated in the paper that the radiation corrections accurately describe this physical phenomenon and predict that the second dipole mode becomes dominant in the extinction spectra of nanocube ensembles as nanocube dimensions are increased. The radiation corrections also reveal the sensitivity of different dipole modes to the rounding of corners and edges and to the variation of the dimensions of the nanocubes. Associated with these sensitivities is the inhomogeneous broadening of the extinction spectra, which may be critical in the design of reliable plasmonic structures for electric-field enhancement. Finally, all physical features of the extinction spectra have been explained by using dipole modes and radiation effects, i.e., without invoking higher order multipole "dark" modes.

II. THEORETICAL METHOD

A. Plasmon resonances as an eigenvalue problem

To start this discussion, we first describe how plasmon resonances can be mathematically treated as an eigenvalue problem for specific boundary integral equations. Consider a metallic nanoparticle of arbitrary shape (see Fig. 1). The resonance values of the dielectric permittivity $\varepsilon_k^{(0)}$ can be computed in the electrostatic approximation by solving the eigenvalue problem for the following integral equation:^{3–6}

$$\sigma_k^{(0)}(Q) = \frac{\lambda_k}{2\pi} \oint_S \sigma_k^{(0)}(M) \frac{\vec{r}_{MQ} \cdot \vec{n}_Q}{r_{MQ}^3} dS_M.$$
(1)



FIG. 1. The metallic nanoparticle bounded by surface S.

The eigenvalues λ_k are related to the resonance permittivities by

$$\lambda_k = \frac{\varepsilon_k^{(0)} - \varepsilon_0}{\varepsilon_k^{(0)} + \varepsilon_0},\tag{2}$$

where ε_0 is the dielectric constant of free space. The eigenfunctions $\sigma_k^{(0)}(M)$ correspond to surface electric charge density distribution functions over surface *S*, *M* and *Q* are points on surface *S*, \vec{r}_{MQ} is the vector from *M* to *Q*, and \vec{n}_Q is the outward-pointing unit normal to *S* at *Q*. The superscript "(0)" indicates that $\varepsilon_k^{(0)}$ and $\sigma_k^{(0)}$ are computed in the electrostatic approximation. When the metallic nanoparticle is embedded in a homogeneous medium of dielectric constant $\varepsilon = \varepsilon_r \varepsilon_0$ (e.g., water), ε_0 is replaced by ε .

By solving the eigenvalue problem (1), the resonance permittivities for various plasmon modes can be found from formula (2). In order to determine the plasmon resonance frequencies, the dispersion relation of the metal $\varepsilon(\omega) =$ $\varepsilon'(\omega) + i\varepsilon''(\omega)$ is employed. In the electrostatic limit, radiation losses and "ohmic" losses [due to the imaginary part $\varepsilon''(\omega)$ of the dielectric permittivity] are neglected. The resonance frequencies $\omega_k^{(0)}$ are identified by the condition

$$\varepsilon'(\omega_k^{(0)}) = \varepsilon_k^{(0)}.$$
 (3)

There exists a complementary approach^{5,6} to the calculation of $\varepsilon_k^{(0)}$. In this approach, a double layer of electric charges (dipoles) of density $\tau_k^{(0)}(M)$ on *S* is used instead of the single layer charge density $\sigma_k^{(0)}(M)$. This leads to the eigenvalue problem for the following integral equation adjoint to (1):

$$\tau_k^{(0)}(Q) = \frac{\lambda_k}{2\pi} \oint_S \tau_k^{(0)}(M) \frac{\vec{r}_{QM} \cdot \vec{n}_M}{r_{MQ}^3} dS_M,$$
(4)

and the same formulas (2) and (3) can be used to compute the resonance permittivities $\varepsilon_k^{(0)}$ and resonance frequencies $\omega_k^{(0)}$, respectively.

We point out that the structure of integral equations (1) and (4) implies that the eigenvalues λ_k , and, consequently, the resonance permittivities $\varepsilon_k^{(0)}$ depend on the shape of nanoparticles but not on their dimensions.⁶ It is also apparent that the computed values of $\varepsilon_k^{(0)}$ do not depend on nanoparticle material and can be used in formula (3) for any form of the dispersion relation of the metal to determine the corresponding resonance frequencies. In this way, the properties of plasmon resonances which depend on nanoparticle shape are fully separated from the properties which depend on nanoparticle material.

In the described eigenvalue approach to the calculation of plasmon modes and their resonance wavelengths the imaginary part $\varepsilon''(\omega)$ of dielectric permittivity is neglected. This imaginary part of permittivity is fully accounted for in the analysis of excitation of plasmon modes by incident optical radiation, which has been carried out in Ref. 21. It is demonstrated there that $\varepsilon''(\omega)$ determines the lifetime of plasmon modes as well as the strength of plasmon resonance fields in the case of resonance and off-resonance excitations. In particular, the analytical formulas derived in Ref. 21 show that the efficiency of plasmon resonance excitation is controlled by the ratio $\varepsilon'(\omega)/\varepsilon''(\omega)$.

The plasmon resonance analysis based on formulas (1)-(4)presumes the validity of the electrostatic approximation and local in space constitutive relations. It is apparent that this approach is limited from "below" and "above." In other words, this approach is valid for intermediate dimensions of nanoparticles. It is of interest, of course, to evaluate the limit of applicability of this approach from "below" by using the quantum-mechanical treatment of plasmon resonances. Such treatment has been undertaken in Ref. 22 for nanowires with elliptical cross sections and compared with analytical results from Ref. 5 based on the electrostatic approach. It is demonstrated in Ref. 22 that the electrostatic approach is quite accurate provided that cross-sectional dimensions exceed 8 nm. Another (empirical) way to evaluate the validity of electrostatic approach from "below" is to compare the numerical and analytical results of the electrostatic analysis with experimental data. It has been shown in Ref. 23 that for spherical gold nanoparticles with dimensions above 5 nm plasmon resonances occur at the wavelength of about 520 nm consistent with the electrostatic approach. To evaluate the validity of electrostatic approach from "above," the radiation corrections can be used. This approach and its experimental testing are discussed in the paper.

B. Radiation corrections

Next, we shall discuss radiation corrections to the electrostatic approximation defined by formulas (1)–(4). These radiation corrections can be mathematically treated as perturbations with respect to a small parameter β which is defined as the ratio of the particle dimension to the free-space wavelengths:

$$\beta = \omega \sqrt{\mu_0 \varepsilon_0} d, \tag{5}$$

where d is the nanoparticle diameter, i.e., the maximum distance between any two points M and Q on S. According to perturbation theory, the resonance permittivities are expressed as a series in β ,

$$\varepsilon_k = \varepsilon_k^{(0)} + \beta \varepsilon_k^{(1)} + \beta^2 \varepsilon_k^{(2)} + \cdots.$$
 (6)

It has been shown that for any shape of nanoparticle the first-order radiation correction $\varepsilon_k^{(1)}$ is equal to zero,⁶

$$\varepsilon_k^{(1)} = 0. \tag{7}$$

For the second-order radiation correction $\varepsilon_k^{(2)}$ the following formula has been derived:⁶

$$\varepsilon_{k}^{(2)} = \frac{\left(\varepsilon_{0} - \varepsilon_{k}^{(0)}\right) \oint_{S} \tau_{k}^{(0)}(Q) \vec{n}_{Q} \cdot \vec{a}_{k}(Q) dS_{Q}}{\oint_{S} \tau_{k}^{(0)}(Q) \vec{n}_{Q} \cdot \vec{E}_{k}^{(0)}(Q) dS_{Q}}, \qquad (8)$$

where $\vec{E}_k^{(0)}(Q)$ and $\vec{a}_k(Q)$ are defined as

$$\vec{E}_k^{(0)}(Q) = \frac{1}{4\pi\varepsilon_0} \oint_S \sigma_k^{(0)}(M) \frac{\vec{r}_{MQ}}{r_{MQ}^3} dS_M, \tag{9}$$

$$\vec{a}_k(Q) = \frac{\varepsilon_0 - \varepsilon_k^{(0)}}{8\pi\varepsilon_0} \oint_S \frac{\left[\vec{n}_M \times \vec{E}_k^{(0)}(M)\right] \times \vec{r}_{MQ}}{r_{MQ}} dS_M.$$
(10)

Thus, in order to compute the second-order radiation corrections $\varepsilon_k^{(2)}$ for resonance values of the nanoparticle permittivity, first boundary integral equations (1) and (4) are solved to find $\varepsilon_k^{(0)}$, $\sigma_k^{(0)}(Q)$, and $\tau_k^{(0)}(Q)$. Using $\sigma_k^{(0)}(Q)$ and

formulas (9) and (10), $\vec{E}_k^{(0)}(Q)$ and $\vec{a}_k(Q)$ are computed. Finally, using formula (8), $\varepsilon_k^{(2)}$ is calculated. After $\varepsilon_k^{(2)}$ is found, the resonance values of the nanoparticle permittivity are computed as follows:

$$\varepsilon_k = \varepsilon_k^{(0)} + \beta^2 \varepsilon_k^{(2)}. \tag{11}$$

The resonance frequencies of the plasmon modes can be computed from the equation

$$\varepsilon'(\omega_k) - \beta^2(\omega_k)\varepsilon_k^{(2)} = \varepsilon_k^{(0)}.$$
 (12)

C. Computational details

The computational method described above has been software implemented. The boundary integral equations (1) and (4) are discretized by partitioning the surface of the particle into triangular or square patches and are solved by using ARPACK eigenvalue solvers implemented in MATLAB. After solving the eigenvalue problem, the dipole plasmon modes are identified through computing the dipole moments of the eigenmodes by using the formula

$$\vec{p}_k^{(0)} = \oint_S \vec{r}_Q \sigma_k^{(0)}(Q) dS_Q.$$
(13)

It is important to mention that, to calculate the dipole moment strength of each plasmon mode, $\sigma_k^{(0)}$ and $\tau_k^{(0)}$ have to be properly normalized.⁶ Subsequently, formulas (8)–(10) are discretized and computed for each dipole mode and by using (12) the resonance frequencies of the plasmon modes are determined. In this work, the numerical calculations have been performed with 5120 and 12,288 triangular surface patches per single sphere particle and single ring particle, respectively, and with 38,400 square surface patches per single cube particle. The dielectric constants of water and glass have been set to $1.77\varepsilon_0$ and $2.25\varepsilon_0$, respectively.

III. EXPERIMENTAL DETAILS

Silver nanocubes were synthesized by the polyol reduction method.²⁴⁻²⁶ 15 mg CuCl₂ were dissolved in 2.5 mL 1,5pentanediol (PDOH) and the solution was aged for 10 days. 100 mg AgNO₃ were dissolved in 5 mL PDOH and 20 μ L of the aged CuCl₂ solution were added. This mixture was sonicated for 90 min to yield a light orange solution (Ag solution). Separately, 200 mg polyvinylpyrrolidone 55K (Sigma-Aldrich) were dissolved in 10 mL PDOH (PVP solution). In a round-bottom flask, 5 mL of PDOH were heated in an oil bath set to 190 °C. The Ag solution was injected in 125 μ L aliquots at regular intervals. The PVP solution was added dropwise between injections at a rate of ~160 μ L min⁻¹. The size of the nanocubes was controlled by adjusting the number of Ag solution injections and the time intervals between injections. Electron micrographs were taken using a Hitachi SU-70 FE-SEM. UV-vis-NIR spectra were recorded by diluting the reaction product in deionized water, using a Hitachi U-2910 spectrometer. Absorption maxima were determined by fitting each spectrum to a sum of two to six Lorentzian peak functions using Origin8.

IV. RESULTS AND DISCUSSION

A. Comparison with Mie theory and experimental data

Section II succinctly details a computational method for determination of plasmon resonance frequencies of nanoparticles given their shape and dispersion relation $\varepsilon(\omega)$. In this section, we first discuss the accuracy of this method in modeling a number of particle shapes with increasing complexity. First, it is important to mention that the presented computational methodology is consistent with the analytical results for spherical nanoparticles that follow from the Mie theory. According to the Mie theory, the resonance permittivity for the first three (spatially uniform) dipole plasmon modes is given by the formula²⁷

$$\varepsilon_1 = -\left(2 + \frac{3}{5}\beta^2\right)\varepsilon_0 = -\left(2 + \frac{3}{5}\omega^2\mu_0\varepsilon_0d^2\right)\varepsilon_0,\qquad(14)$$

where *d* is the diameter of the spherical nanoparticle.

It can be shown analytically that in the case of spherical nanoparticles formula (14) can be derived from Eqs. (1)–(11). This somewhat lengthy derivation is omitted here and, instead, the comparison between computations performed by using Eq. (14) on the one hand and Eqs. (8)–(12) on the other hand is presented graphically in Figs. 2 and 3 for spherical nanoparticles in water. It is evident from Fig. 2 that the resonance permittivity decreases quadratically as the diameter increases. Due to the dispersion relation of gold and silver, a decrease in the resonance permittivity results in a redshift in the resonance wavelength of these metallic nanoparticles as their diameter increases. The calculation results of Fig. 3 also match values of plasmon resonance wavelengths for spherical nanoparticles of different diameters calculated in Ref. 7 as well as experimental results from Ref. 28.

To further illustrate the accuracy of radiation corrections given by formulas (8)–(12) for different shapes of nanoparticles, Tables I–III present the results of computations of second-order radiation corrections for resonance wavelengths of dipole plasmon modes of gold nanorings placed on glass substrates, silver nanocubes immersed in water and silver



FIG. 2. (Color online) Comparison between the calculation of the resonance permittivity of the dipole plasmon modes using secondorder radiation corrections (open circles) and the Mie theory (solid line) for spherical nanoparticles in water as a function of nanosphere dimension.



FIG. 3. (Color online) Comparison of the calculated dipole plasmon resonance wavelength of spherical nanoparticles in water computed by using second-order radiation corrections (open circles) and the Mie theory (solid line). Data presented for (a) silver and (b) gold dispersion relations.

nanocubes placed on glass substrates, respectively.²⁹ The corresponding inner radii for ring 1, ring 2 and ring 3 in Table I are 46, 50, and 51 nm, whereas the heights and outer radii are 40 and 60 nm, respectively for all rings. The edge length of the nanocubes in Tables II and III is 36 nm. It is evident from the presented data that the second-order radiation corrections result in a better agreement with experimental data than the results based on purely electrostatic analysis. The largest discrepancy between the calculated and experimental data is observed in the case of the thinnest ring (ring 3). The plausible explanation for this discrepancy can be related to the technical challenges associated with writing sub-10-nm features by electron-beam lithography and characterizing their dimensions by scanning electron microscopy (SEM). This point of view is consistent with the observation that a difference in thickness of 1 nm between ring 2 and ring 3 results in almost the same redshift in the resonance wavelength as in the case of ring 1 and ring 2 that differ in thickness by 4 nm. Additionally, the large linewidth of the extinction peak for ring 3 (see Ref. 30) suggests that there are significant dimension variations among the nanostructures within the ring 3 ensemble.

B. Radiation corrections for dipole plasmon modes in silver nanocubes

A more detailed examination of the radiation correction theory has been performed by comparing calculated results with experimental data collected from ensembles of silver

TABLE I. Calculated and measured resonance wavelengths of gold nanorings placed on a glass substrate.

Resonance wavelength (nm)	Ring 1 (thickest)	Ring 2	Ring 3 (thinnest)
Electrostatic calculations	940	1102	1159
Second-order corrections	987	1156	1214
Experimental data (Ref. 30)	1000	1180	1350

TABLE II. Calculated and measured resonance wavelengths of silver nanocubes immersed in water.

Resonance wavelength (nm)	High-frequency mode	Low-frequency mode
Electrostatic calculations	405	454
Second-order corrections	420	478
Experimental data (Ref. 31)	432	500

nanocubes in aqueous suspensions (see details in Sec. III). Until recently, 32,33 fine control of the size of the resulting silver nanocubes has been a challenging task. In our synthesis protocol, control over the mean size of the nanocubes was achieved by adjusting the timing of the additions of the silver ions and the polymeric surfactant to the reaction mixture. We have successfully prepared monodispersed suspensions of silver nanocubes 50-150 nm in edge length. Larger mean sizes of silver cubes could be achieved, yet the size distribution is thus far unsatisfactory for those preparations. The monodispersed silver nanocubes were characterized by scanning electron microscopy (SEM) and by UV-vis-NIR absorption in aqueous suspensions (Fig. 4). SEM images of the silver nanoparticles indicate that the vast majority of the particles in the as-made suspension have a cubic shape and a common size [Fig. 4(a)]. The optical absorption spectrum of the nanocubes in water displays a number of absorption maxima in the wavelength range 300–900 nm. As shown in Fig. 4(b), the location of these absorption maxima is size dependent. An increase in the size, and thus in the contribution of retardation effects, leads to a redshift in the absorption maxima.³⁴ In particular, the absorption band with the longest wavelength shifts from ~ 450 to \sim 750 nm as the mean size of the cubes increases from 50 to 150 nm. This absorption peak becomes broad and relatively less intense as the cube size increases. The interpretation of the spectra of plasmonic nanocubes has not been consistent across the literature because of the scarcity of size controlled samples, the spectral sensitivity to the sharpness of the corners of the cubes, and the need to include radiation effects in theoretical modeling.^{16,25,33,35–37} Theoretical modeling demonstrates that dipole resonance modes supported by the silver nanocubes are the origin of the features seen in the absorption spectra. The peaks (maxima) in the extinction spectra are identified with the resonance wavelengths of different plasmon modes. These values and their dependence on cube size can be predicted theoretically as long as radiation corrections are included. Using Eqs. (1)–(4) we have calculated $\varepsilon_k^{(0)}$, $\sigma_k^{(0)}$, and $\tau_k^{(0)}$ for the numerous plasmon resonance modes of metal nanocubes in the quasistatic approximation. Several of these

TABLE III. Calculated and measured resonance wavelengths of silver nanocubes placed on a glass substrate.

Resonance wavelength (nm)	High-frequency mode	Low-frequency mode
Electrostatic calculations	383	421
Second-order corrections	410	443
Experimental data (Ref. 31)	395	457



FIG. 4. (Color online) (a) SEM image of an ensemble of silver nanocubes (NCs). Scale bar: 500 nm. (b) Absorption spectra of seven types of silver nanocubes (in water). As the size of the nanocube increases, the absorption peaks due to plasmon resonances shift to longer wavelengths as highlighted by dashed lines. (c) A small nanocube with rounded corners. (d) A large nanocube with sharp corners.

modes are dipolar in nature, while the rest are of higher multipole characteristics. As will be shown, it is sufficient to consider just the dipole modes to interpret the absorption spectra of nanocubes suspended in water. We have identified the resonance modes with the strongest dipole moments (Table IV). In the case of silver nanocubes in water, these plasmon resonances, denoted D1-D8, occur at 468, 427, 405, 399, 398, 375, 339, and 332 nm, respectively, in the electrostatic limit. In Fig. 5, the surface charge density distribution functions $[\sigma_k^{(0)}(Q)]$ corresponding to each of the eight modes are displayed. The color in these density maps represents the local amplitude of the charge density oscillation, as well as its relative sign. It can be appreciated that these modes can couple strongly to electromagnetic wave excitations due to the antisymmetric (dipole) distribution of charges along one of the main axes of the cubic system.

TABLE IV. Calculated resonance permittivities, resonance wavelengths, and dipole moments for dipole modes D1–D8, for a single silver nanocube in water.

Mode	$\varepsilon_k^{(0)}/\varepsilon_0$ (water)	$2\pi c/\omega_k^{(0)}$ (water)	$\left p_{k}^{(0)} \right $ (relative)
D1	-8.0602	468.45 nm	0.9103
D2	-5.8599	426.61 nm	1.0000
D3	-4.7187	405.20 nm	0.6305
D4	-4.3716	398.99 nm	0.2749
D5	-4.2901	397.51 nm	0.1849
D6	-3.1001	374.66 nm	0.5928
D7	-1.0630	338.90 nm	0.6030
D8	-0.6858	332.06 nm	0.3915

Modes D1-D5 are part of a series of dipole plasmon modes with their charge concentrated at the corners and along the edges of the nanocubes. The modes differ in the number of nodes the charge density has along the three orthogonal edges (N_x, N_y, N_z) . Modes with more nodes and shorter spatial oscillation periods resonate at higher frequencies, yet their dipole moments are weaker. Modes D7 and D8 are dipole modes with charge density distributed over the faces of the cubes. In our experience, the computation of the eigenvalues λ_k and resonance wavelengths of the nanocubes converges faster than the computation of the surface charge density $[\sigma_k^{(0)}(Q)]$ as the number of patches used in the discretization of the surface of the cube is increased. Mapping the charge distribution becomes computationally demanding for modes with short oscillation periods. For example, by using a large number of patches for the cube (e.g., 9600 or more), more detailed spatial oscillations of the charge density along the cube edges are resolved for modes D3-D5. Thus, while our resonance wavelength calculations and charge density maps mostly coincide with peak absorbance wavelengths³⁸ and the electric-field maps presented in other works,^{38,39} previous works reported on mode D3 as having (3, 4, 4) nodes and our calculations identify the mode as having (5, 4, 4) nodes. This inconsistency on the charge distribution for mode D3 may be explained by the difference in the density of the meshes used in the calculations.



FIG. 5. (Color online) Calculated surface charge distributions for different dipole plasmon modes. Red and blue colors represent positive charges and negative charges, respectively.



FIG. 6. (Color online) Comparison between calculated (solid lines) and measured (open symbols) resonance wavelengths for five dipole plasmon modes of silver nanocubes. The " \times " symbols indicate the wavelength of the major attenuation peak in experimental data from Refs. 32 and 33.

With the dipole modes well characterized at the quasistatic limit, we now turn to discuss the effect of the size of the nanocube on the plasmon spectra. By using Eqs. (8)–(12), the second-order corrections for the resonance wavelengths were computed. The computational results for the resonance wavelengths of the five strongest dipole plasmon modes are plotted in Fig. 6 as a function of cube edge length, and are compared to our experimental results, as well as results from Refs. 32 and 33.

Figure 6 shows an overall good agreement between the predictions of the outlined radiation correction theory and the experimental data. Considering the experimental error associated with determining the resonance wavelength from the extinction spectra, particularly for overlapping absorption peaks, the size dependence of the plasmon resonance wavelengths in silver nanocubes was determined exceedingly well through the calculations without the need for fitting parameters. Note that modes D4, D5, and D8 may also contribute to the peaks at 400 and 350 nm, however, their contributions are less pronounced due to their weaker dipole moments. In Fig. 6, a nonlinear relationship between wavelength and cube size is revealed both experimentally and computationally. Previously, a linear relationship between the major plasmon resonance wavelength and the cube size was hypothesized based on results from a narrow range of sizes.³² Here, we show that a quadratic relationship between the resonance permittivity and the cube size adequately reproduces the experimental results. There is no one function that can relate the plasmon resonance wavelength to the particle size, because of the role of the dispersion relation of the material in determining the resonance wavelength.

A closer examination of the data suggests that there is some discrepancy between the resonance values determined computationally and experimentally for plasmon mode D1, the mode with the longest resonance wavelength and the most pronounced size dependence. The discrepancy is systematic, with the numerical calculations predicting higher wavelength values than the measured values. The discrepancy is less severe for larger cube dimensions. The sensitivity of the resonance



FIG. 7. (Color online) Comparison of the experimental absorption peak wavelengths (open symbols) with computational resonance wavelengths for silver nanocubes in water with ideal sharp corners (solid lines) and for cubes with rounded corners and edges (dotted lines).

wavelength value to the corner geometry of the nanocubes is a plausible explanation for these observations.³⁵ The corner geometry (i.e., sharpness of the corners) cannot be entirely controlled during the chemical process of nanocube growth. Because the silver nanoparticles first nucleate as spherical seeds and their faceted structures only develop at a later stage, syntheses of smaller silver nanocubes tend to result in particles with more rounded corners, as evidenced by SEM microscopy [Figs. 4(c) and 4(d)]. We anticipate that the corner geometry will have the strongest influence on the properties of mode D1 because the charge density associated with this mode is the highest at the corners of the cube (Fig. 5).¹⁶ To test this explanation, the computation of the resonance wavelength of the dipole plasmon modes was performed for nanocubes with smoothed (rounded) corners and edges. The computed resonance wavelengths for silver nanocubes with rounded corners and edges do indeed shift towards shorter wavelengths and this blueshift is more appreciable for mode D1 than for the other plasmon modes (Fig. 7). Thus, better agreement between the radiation corrections and the experimental data can be achieved by considering the radius of curvature of the corners and edges in addition to the cube size. This explanation is also supported by spectral shifts (blueshifts of ~ 10 nm in the position of the absorption peak attributed to mode D1) we have observed as a consequence of aging the silver nanocube suspensions (e.g., prolonged storage in aerated solutions that results in blunt edges). Similar spectral shifts have been reported, experimentally and theoretically, for a range of plasmonic nanoparticles whose corners were intentionally rounded or truncated.^{31,34–36,40}

The interpretation of the absorption spectra of silver nanocubes of different size has been in the past challenging and inconsistent, because of the lack of a comprehensive theoretical model and the limited set of experimental data. The interpretation of the spectra was difficult because, regardless of the size of the silver nanocubes, the strongest absorption peak is always in the range 450–550 nm. When an additional peak is observed at longer wavelengths, this absorption peak is notably weaker and exceptionally broad. As was alluded to, similarities between spectra of nanocubes of different sizes in the range 450-550 nm are quite coincidental, and tracking the most intense absorption peak ("×" symbols in Fig. 6) does not coincide with the evolution of a single plasmon mode with size. For small nanoparticles the strong sharp absorption peak relates to plasmon mode D1, while for large nanoparticles the strongest absorption is from plasmon mode D2. Li et al. have correctly identified this trend in calculated optical extinction spectra using the discrete dipole approximation (DDA) method.⁴¹ In their spectra they identified three peaks, which appear to correlate well with our modes D1, D2, and D6 and their size-dependent shifts. But the DDA method does not allow for resolving the full set of resonance modes of the structure. As for the broadening of the absorption peak associated with mode D1, particularly for large nanocubes, Cortie et al. have suggested that it originates from the distribution of sizes present in the experimental sample. Our results support this explanation. Figures 6 and 7 show that the shift in resonance wavelength is the largest for plasmon mode D1 with respect to variations in both the edge length and the radius of curvature of the cube edges. Thus, the absorption spectra of an ensemble of nanocubes with some degree of shape inhomogeneity will display a peak for mode D1 that is broader than the other peaks, and its width will increase as the mean size of the nanocubes increases. Our experimental spectra [Fig. 4(b)] show these features. An additional parameter affecting the width of the absorption peak is the quality of the resonance. Radiation loss increases with the size of the particle, and the quality of the resonance decays.

Figures 6 and 7 suggest that the radiation corrections are quite accurate. Indeed, it is clear from Fig. 6 that for nanocubes with diameters d about $\sqrt{3} \times 150 \simeq 260$ nm the resonance wavelengths for modes D2, D3, D6, and D7 fall below 550 nm ($\sim 2d$), and the radiation corrections predict these values accurately. In fact, this accuracy is even higher because the aqueous media makes the actual incident wavelength shorter. We note that all the features in the extinction spectra of silver nanocubes have been explained by a set of dipole resonance modes and radiation effects. Quadrupole and higher-order plasmon resonance modes (i.e., "dark modes") were not invoked, because they do not couple to electromagnetic radiation in the electrostatic limit. When the dimension of the particle is not negligible, charge oscillations on the surface of the plasmonic object acquire a position-dependent phase. In DDA and finite element method calculations, the simulated near-field intensity distribution may appear to show the symmetry of a higher-order mode.^{25,41} Strictly speaking, the concept of a resonant eigenmode with a well-defined symmetry is only valid in the electrostatic limit.

Figures 3, 6, and 7 show that resonance wavelengths increase (redshift) with the increase in nanoparticle dimensions. This may have a positive effect because the ratio of the real to imaginary parts of the permittivities of gold and silver is the largest in the 600–1000-nm wavelength range and this larger ratio leads to more strongly pronounced plasmon resonances and higher field enhancements.²¹

The presented radiation corrections may be quite useful for the calculation of resonance wavelengths for clusters



FIG. 8. (Color online) Calculated resonance wavelengths of the dominant dipole mode for face-to-face silver nanocube dimers on a glass substrate in air, with various cube edge lengths *a* and gaps *d*.

of metallic nanoparticles. The overall dimensions of such clusters may be comparable with the resonance wavelengths, requiring the inclusion of retardation effects in modeling their plasmonic response. Since nanoparticle clusters are used in various applications, for instance, in surface enhanced Raman scattering (SERS) and nonlinear optics studies, reliable and efficient simulation tools may impact progress in these fields. As an example, we present here the computational results for resonance wavelengths of face-to-face nanocube dimers on a glass substrate. The investigation of SERS in these nanocube clusters has been previously reported.^{19,20,42} Figure 8 presents the computational results for various nanocube edge lengths and various "gap-to-cube size" ratios. This figure presents the dependence of one of the resonance wavelengths on this ratio. The computational data from Fig. 8 may be useful for the extraction of interparticle separations from extinction cross-section measurements. For example, the data for 100-nm nanocube dimers indicates that dimers with gaps of 5 and 6 nm are easily distinguishable by their spectra.

V. CONCLUSION

In the paper, the radiation corrections for the analysis of plasmon resonances in nanoparticles are presented. These radiation corrections have been tested by comparing the calculation results for a single sphere with the Mie theory, and for nanorings with available experimental data. The results of the extensive study of radiation corrections for silver cubic nanoparticles of various dimensions and their comparison with measured extinction spectra of nanocube ensembles is reported. This study reveals that cubic nanoparticles have many dipole plasmon modes with distinct resonance wavelengths. For small nanocube dimensions, these wavelengths are closely clustered and the linewidth of the extinction peak of the first dipole mode D1 conceals the extinction peaks of other dipole plasmon modes. As the dimensions of the silver nanocubes are gradually increased, the resonance wavelengths of dipole plasmon modes are increased, but with different rates, which leads to their wider separation. This results in the emergence of extinction peaks of other dipole plasmon modes in ensemble absorption spectra and eventually in the dominance of the extinction peak of the second plasmon mode D2. The radiation corrections accurately describe this physical phenomenon and also reveal that the mode D2 is less sensitive to the rounding of nanocube corners and edges as well as to nanocube dimensions variations than the mode D1. This suggests that on-resonance excitation of mode D2 in an ensemble of nanocubes may be a preferable approach to a reproducible plasmonic enhancement, particularly in SERS studies.

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