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Analyzing the scattering properties of coupled metallic nanoparticles

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We apply the boundary element method to the analysis of the plasmon response of systems that consist of coupled metallic nanoscatterers. For systems made of two or more objects, the response depends strongly on the individual particle behavior as well as on the separation distance and on the configuration of the particles relative to the illumination direction. By analyzing the behavior of these systems, we determine the smallest interaction distance at which the particles can be considered decoupled. We discriminate the two cases of particle systems consisting of scatterers with the same and different resonance wavelengths.

1. INTRODUCTION

By illuminating a material comprising metallic nanoparticles and microparticles at a well-defined wavelength, it is possible to excite a collective oscillation of the electrons in the material that is in resonance with the driven wave field.[1] These plasmon resonances appear in the blue and green part of the spectrum for metallic materials such as gold and silver.[2] When a plasmon is excited, a large scattering cross section (SCS) and a strong near-field amplitude can be observed. The visual result of this effect has been known for centuries since artisans began incorporating metallic particles into ceramics to give them beautiful iridescent reflections.[3] Except for the special case of a circular cylinder or a sphere where Mie theory can be applied, the exact wavelength for which the plasmon resonance is excited cannot be determined analytically. The condition for plasmon excitation of a circular cylinder is a real part of the dielectric constant that equals -1. In the case of a sphere the condition is a real part of the dielectric constant of -2 assuming air as the ambient media.[4] For certain wavelengths silver and gold fulfill this condition to a good approximation. The remaining imaginary part of the dielectric constant will lead principally to a damping, a broadening, and a slight redshift in the SCS. For objects that deviate from this simple geometry, such a quasi-analytical condition can no longer be assumed.[5] Consequently various efforts have been made to analyze the scattering properties and to determine rigorously the plasmon response of arbitrarily shaped microparticles by using a broad range of different numerical techniques. Among others, the discrete-dipole approximation,[6] the Green's dyadic function,[7] and the generalized multiple-multipole method[8] have been successfully applied. We will use the boundary element method[9] for the numerical treatment of resonant metallic nanoparticles, and we will concentrate on the influence of the plasmon response where the system consists of two or more scatterers with small separation distances. This method is chosen because it formulates the question as a surface problem, which reduces the computational effort in comparison with other methods. The method is a direct numerical solution of the boundary integral equation that is derived from Maxwell's equations.[10] Except for a discretized sampling of the surface of the particles, no approximations are made, and the field retardation within the particles especially is fully taken into account. The basic equations of the method and all the necessary parameters that describe the problem are given in Appendix A.

The systems of particles in close proximity that we consider here can play a major role in an application such as surface-enhanced Raman spectroscopy.[11] Ideally the molecules under consideration are placed directly between two metallic particles. By choosing proper system parameters, a surface plasmon is excited. The surface plasmon will lead to a large SCS and a high near-field amplitude. The enhancement of the amplitude can be dramatic, with the point of the highest near-field being directly between the two particles.[12] If the molecule is positioned directly at this "hot spot" and exposed to the large near field, its Raman cross section will be likewise dramatically enhanced. The enhancement allows detection of even single molecules.

Another interesting application of coupled metallic nanoparticles is their use for light guiding on a length scale significantly below the diffraction limit.[13–15] The basic idea is to arrange the particles in a chain or other form appropriate to fulfill an optical function such as bending or beam splitting.[16] The first particle in the chain is excited at a resonant wavelength. This particle is coupled evanescently to the subsequent one, and energy is transferred between the particles, resulting in light guiding. The process is highly efficient because the near field is resonantly enhanced in the vicinity of the particles as a result of the plasmon excitation. Such a coupling between particles has already been proven experimentally by using a scanning near-field optical microscope tip as a spatially highly confined light source.[17]

For an experimental investigation of the properties of coupled particles in a controlled manner, structures written by an electron beam[18] and suspended particles centrifuged onto glass have been used.[19] It was shown experimentally that the SCS is redshifted and broadened if the separation between the particles is reduced.

The case of two coupled circular cylinders has been analyzed theoretically with the Green's dyadic function by Kottmann and Martin.[12,20] Generally, they found that if particles are in close proximity, the response of the entire system is broadened and redshifted. Coupling effects will become dominant, and the two objects will show a characteristic scattering response that deviates strongly from the response of a single object. If the particles are in very close proximity, a second well-distinguished resonance appears at higher wavelengths. With an increase in the separation distance, the pronounced interaction of the particles will be reduced, and above a certain distance the response of the coupled particles will converge to the response of a single-particle system; they can then be treated as decoupled.

We focus this study on the analysis of systems that consist of two or more coupled cylinders of circular or elliptical geometrical cross section, which is done to the best of the authors' knowledge for the first time. We will determine the distance at which such a pair of particles can be treated as decoupled. In theory, no sharp change between coupled and decoupled particles exists. In formulating criteria for the discrimination between coupled and decoupled particles, we first require the effective suppression of the excitation of plasmons that are associated with the coupled geometry and that have no equivalent in the spectrum of either of the single particles involved in the system. This is probably the most import criterion if, e.g., the metallic nanoparticles are to be used in an optical data storage system as proposed by Ditlbacher *et al.*,[21] in which the spectrum of the reflected light within a diffraction-limited spot is analyzed. In this spot, particles with different geometries are placed, and analyzing the plasmon peaks in the spectrum reveals the existence of the particles. For such a system it is of vital importance that no additional peaks appear; as they would indicate the presence of particles that do not actually exist. As a second, weaker, criterion we have used the accordance of the plasmon wavelengths in the coupled system with their counterparts in each of the single-particle systems.

In Section 2 we will apply the boundary element method to a system of two silver circular or elliptical cylinders. For prediction of the behavior, the dielectric constant experimentally determined and published by Johnson and Christy[22] is used. The elliptical cylinders will support two different resonance wavelengths when they are illuminated along the two principal axes. The resonance wavelengths are determined principally by the axis ratio. By rotating one of the elliptical cylinders 90° relative to the other, the two objects are resonantly detuned. For the same illumination direction, their resonance wavelength is different. We will show that the interaction of these two particles is less pronounced even at small separation distances. Finally, we will analyze the SCS of a larger number of elliptical particles that have different resonance wavelengths.

2. ANALYSIS OF TWO OBJECTS WITH THE SAME RESONANCE WAVELENGTH

A. Circular Cylinder

For the investigation of the principal behavior we have analyzed the scattering response of two circular cylinders ($r = 25\,\mathrm{nm}$) for various separation distances. As a general remark, all the separation differences that are given in the text are the surface–surface separations of the particles. A plasmon can be excited only if the light is TM polarized, meaning that the magnetic field vector oscillates parallel to the cylinder. The generation of a surface charge requires an electric field normal to the surface. Because in two-dimensional geometry the magnetic field has only a single component for TM polarization, we show for simplicity in all the corresponding figures the near-field amplitude of the magnetic field necessary to visualize the excited plasmons.

For a clear relation between the arrangement of the particles and the illumination direction, we will give the angle of illumination. This angle is defined between the normal to the center–center line between the particles and the wave vector of the illuminating beam. An illumination direction of 0° means that the normal to the center–center line is parallel to the direction of the incoming wave; 90° means that the normal is perpendicular to the wave vector of the illuminating beam. In the figures, which show the amplitude distribution of the magnetic field in the near field of the particles, we have added an arrow that shows the direction of the wave vector of the illuminating beam.

Figure 1 shows the SCS of two circular cylinders at a separation distance of 5 nm for three different illumination directions. The resonance condition for a circular cylinder is a real part in the dielectric constant of -1. Such a condition is approximately fulfilled for silver at 340 nm. Independent of the illumination direction we have a local maximum in the SCS at approximately this resonance wavelength, which is the dipole excitation wavelength for the single cylinder. Additionally, a sec-

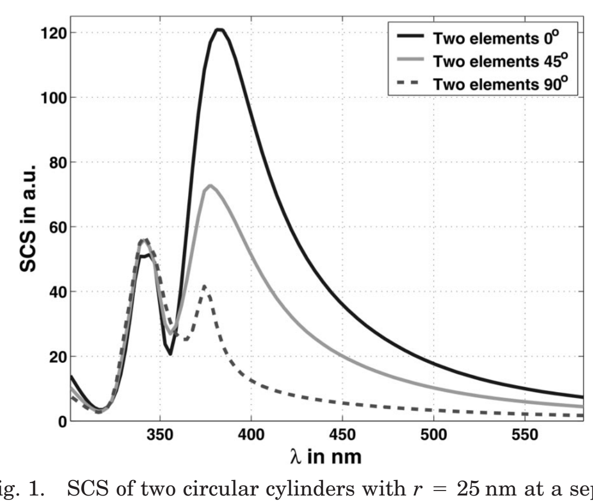

Fig. 1. SCS of two circular cylinders with $r = 25\,\mathrm{nm}$ at a separation distance of $d = 5$ nm.

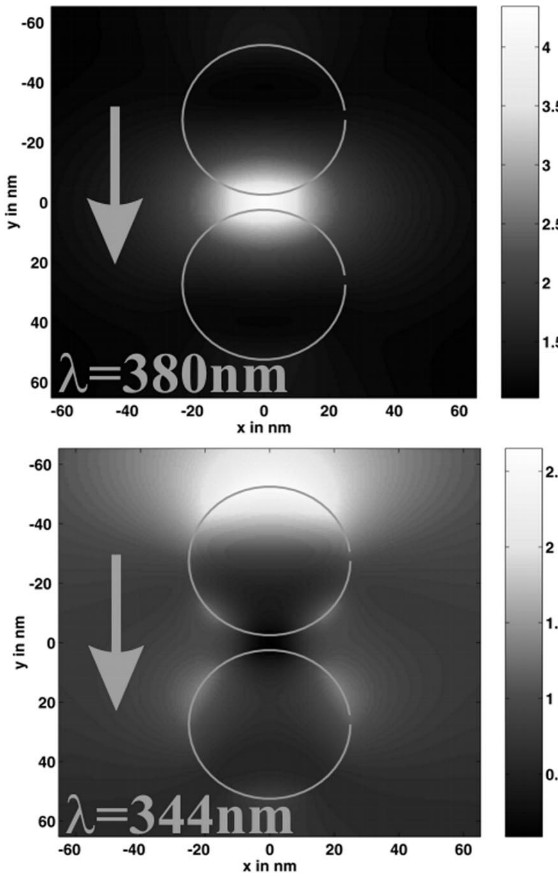

Fig. 2. Near-field amplitude of the magnetic field for plasmons excited at two circular cylinders with $r = 25$ nm at a separation distance of $d = 5$ nm.

ond plasmon is excited at a wavelength that is redshifted relative to the dipole wavelength (≈380 nm). These resonances are clearly attributed to the coupling effect of the neighboring particles. The interaction is less pronounced for the illumination direction of 90°. In such a configuration the field inside each of the two particles does not oscillate in phase because the retardation of the incoming wave, and the coupling between the particles is less pronounced than in the case of illumination at 0°. The wave vector for this illumination direction is perpendicular to the line joining the two particles, and the scattered fields inside the particles oscillate in phase.[12] This plasmon is the fundamental mode of the two-particle configuration. The field amplitude has its highest value directly between the two particles for this plasmon. In Fig. 2 we show the field distributions of the excited plasmons for an illumination direction of 90°. By increasing the separation, the interaction is reduced. Figure 3 shows the SCS at a separation of 5 nm, 25 nm, and 75 nm in comparison with the SCS of a single particle (multiplied by a factor of two) for two different illumination directions (as indicated in the inset of the figure). It can be seen clearly that both SCSs at a separation distance of 75 nm are comparable with the SCS of the single particle. The particles can be treated as decoupled for this separation distance. A further effect on the SCS is a broadening and a marginal damping. Figure 4 shows the near-field amplitude at the maximum of the SCS for an illumination direction of 0°.

This maximum in the SCS correlates with the excitation of a dipole, and the two local maxima in the amplitude can be seen. Nonetheless, an influence of the neighboring scatterer still remains that results in a slight distortion of the field from the axisymmetric distribution across the particle with respect to the illumination direction.

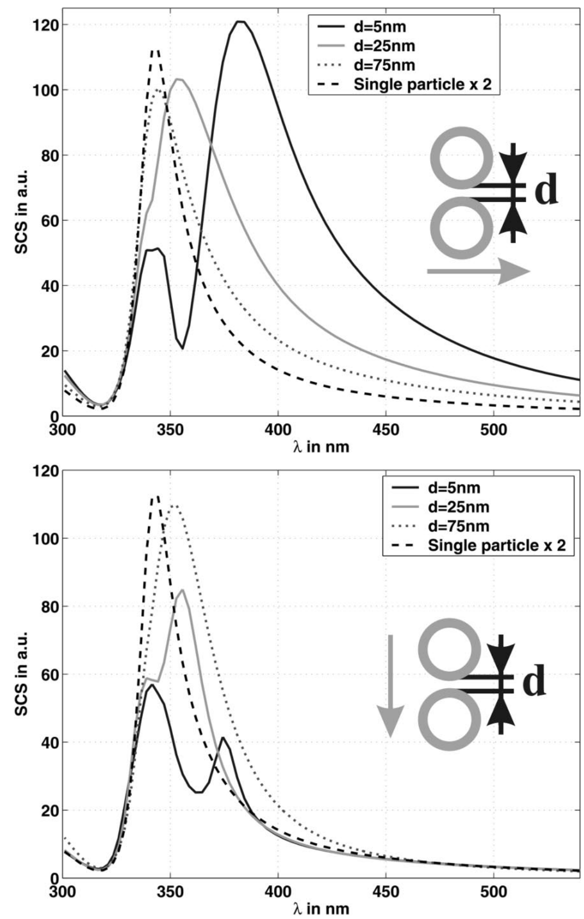

Fig. 3. SCS of two circular cylinders with $r = 25$ nm at different separation distances for an illumination direction of 0° in the upper figure and 90° in the lower figure.

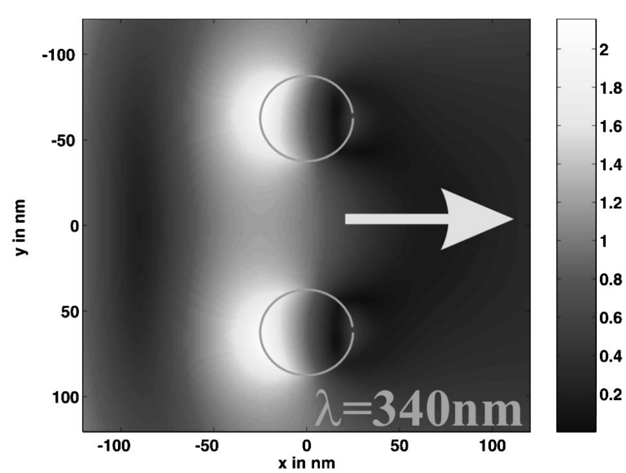

Fig. 4. Near-field amplitude of the magnetic field for a plasmon excited at two circular cylinders with $r = 25$ nm at a separation distance of $d = 75$ nm.

B. Elliptical Cylinder

Similar investigations can be carried out for elliptical cylinders. These particles will have a resonance at two different wavelengths that for small particles $r \ll \lambda$ depends only on the axis ratio. Illuminating the particles at an angle relative to the principal axis will excite both plasmons but with a somewhat lower strength.[9] The strength is related to the projection of the incoming wave front on the two principal axes. If the two elliptical cylinders in the system have the same alignment relative to the illumination direction, it is assumed that the interaction is likewise enhanced as in the case of the circular cylinders, because the resonance wavelength is the same for the two elliptical objects.

Figure 5 shows the SCS of two elliptical particles ($r_1 = 10\,\text{nm}$, $r_2 = 20\,\text{nm}$) for the illumination directions of 0° and 90° relative to the major axis, the latter of which corresponds to an illumination direction along the minor axis, for three different separation distances (5, 10, and 80 nm). The geometrical arrangement is shown in the inset of Fig. 5. Please note that the y scale is now a logarithmic one. For a separation distance of 5 nm two well-pronounced maxima exist for an illumination direction of 0°. By comparing the response of the coupled system with that of a single particle it becomes obvious that the plasmon at 335 nm is related to the wavelength for which the dipole is excited in the single elliptical particle by illuminating such a particle along its major axis. When a second particle is present in the setup, this wavelength is slightly redshifted relative to the resonance wavelength of the single particle. Additionally, the second plasmon is excited at a higher wavelength of 390 nm if the particles are in close proximity. Increasing the separation distance results in a strong decrease and a blueshift in the second plasmon. In such a scattering configuration the fields inside the particles oscillate in phase, and the interaction is enhanced in a way similar to that of the circular cylinders. On the other hand, with the illumination along the line joining the two particles, the interaction becomes much weaker. A strong plasmon is excited at ≈360 nm, corresponding to the plasmon of the single particle under illumination along the short axis. For a separation distance of 5 nm an additional plasmon is weakly excited at 430 nm. With an increase in the distance between the particles, this resonance wavelength is shifted toward the resonance wavelength of the single particle. Because its strength is small compared with the strength of the dipole excitation, the dipole contribution dominates the entire SCS, and the signature of the second plasmon vanishes.

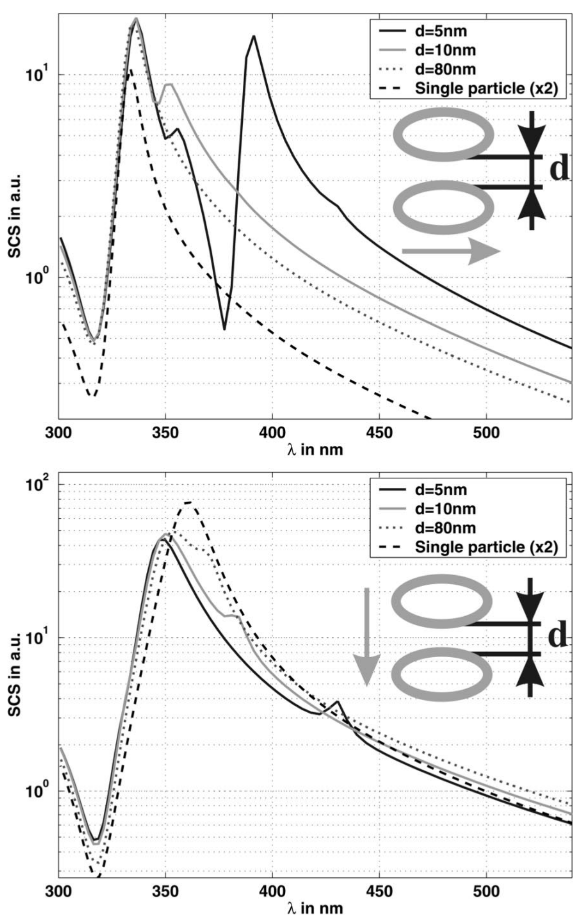

Fig. 5. SCS of two elliptical cylinders with $r_1 = 10\,\text{nm}$ and $r_2 = 20\,\text{nm}$ at different separation distances for an illumination direction of 0° in the upper figure and 90° in the lower figure.

By comparing this strength with that of the fundamental plasmon, we can see that it is always enhanced at an illumination direction of 0° as a result of the in-phase oscillation of the field inside the particles. The dipole strength at an illumination direction of 90° is always lower than the strength for the single particle.

For both illumination directions the system can be treated as decoupled at a separation distance of 80 nm.

3. ANALYSIS OF TWO OBJECTS WITH DIFFERENT RESONANCE WAVELENGTHS

For the analysis of particles with different resonance wavelengths, we use elliptical particles with different axis ratios. The axis ratio is the ratio of the radius of the particle that is perpendicular to the wave vector of the illuminating beam to the radius of the particle that is parallel to the wave vector.

Figure 6 shows the SCS of two elliptical particles that have again a radius of $r_1 = 10\,\text{nm}$ for the minor axis and $r_2 = 20\,\text{nm}$ for the major axis. They have a relative rotation of their axes of 90° such that by illuminating the particles at an angle of 0°, one of the particles has a resonance wavelength at 360 nm (axis ratio 2/1) and the other particle has a resonance wavelength at 335 nm (axis ratio 1/2). The SCS is shown for three different separation distances (5 nm, 10 nm, and 35 nm) and again for two illumination directions. In addition, the sum of the SCS for the two principal axes is shown in the figures. The exact geometry is shown in the inset of Fig. 6. It can be seen that even for small separation no significant additional plasmon is excited. The only remaining influence of a neighboring particle on the SCS is a redshift of the entire SCS of ≈20 nm for a separation distance of 5 nm. Additionally, the plasmon response is damped upon illuminating the system parallel to the two particles and enhanced if the particles are perpendicular to the illumination direction, for the reasons outlined in Section 2. The plasmon resonance is broader for an illumination direc-

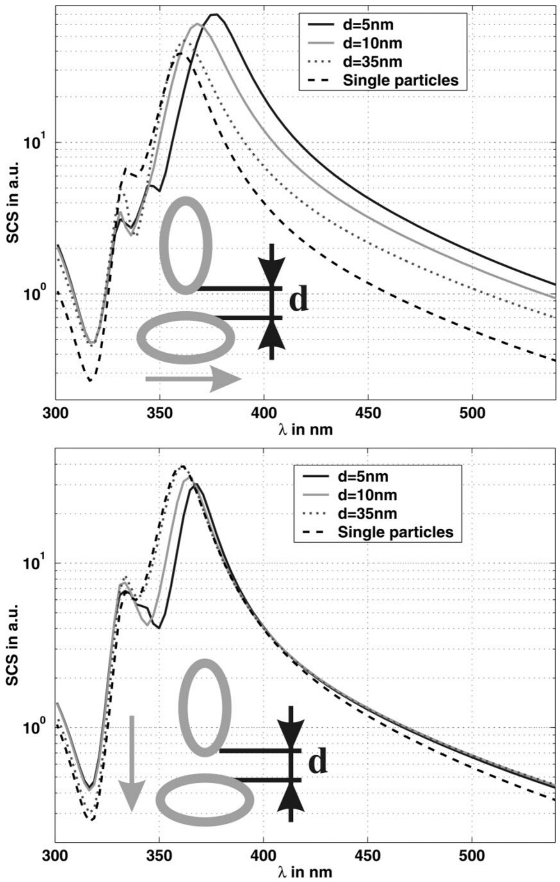

Fig. 6. SCS of two elliptical cylinders with $r_1 = 10$ nm and $r_2 = 20$ nm that have a relative rotation of 90° at different separations for an illumination direction of 0° in the upper figure and 90° in the lower figure.

tion of 0°. This is the only remaining signature of a perturbation. Increasing the separation distance reduces both effects in their characteristic strength, and already at a separation of 35 nm the SCS of the coupled system is comparable with the SCS of the two single systems. For an explanation of this behavior Fig. 7 shows the near-field distribution of the coupled particles at the two resonance wavelengths (334 nm and 362 nm). Obviously, the particles behave as if nearly transparent at wavelengths for which they are not resonant. Neither particle will produce a significant portion of scattered light that could perturb the other. As a consequence, one particle can act as if it were alone, and the SCS will converge to the SCS of the two single particles even for small separation distances. They are effectively resonantly detuned.

4. ANALYSIS OF VARIOUS OBJECTS WITH DIFFERENT RESONANCE WAVELENGTHS

The possibility of tuning the resonance wavelength of elliptical particles raises the prospect of calculating a set of particles with plasmons that can cover a broad range of wavelengths. Additionally, varying the absolute size of the particles while keeping the axis ratio constant can change the scattering strength of the particles in a controlled manner. For small particles within the electrostatic approximation the scattering strength will scale with the fourth power of the radius. For larger particles the phase retardation of the field inside the particle cannot be neglected, and the scattering strength will saturate. In addition, the wavelength for which the plasmon resonance is excited will increase, and the FWHM of the SCS will be increased. By using these properties it is possible to design particles such that their SCS becomes clearly distinguishable in the spectral domain, and the strength of the scattering signal is approximately the same for all the particles. The SCS for a set of nine silver particles that have different resonance wavelengths and approximately the same strength is shown in Fig. 8. For completeness Table 1 shows the exact radii of each elliptical particle. It is possible to tune the resonance wavelength over a range of ≈200 nm.

For an analysis of incoherent superposition we use only four of the particles because each element should show a clear spectral signature. This incoherent superpositioned SCS of the four particles is shown in Fig. 9. The particles that were used in the calculation had axis ratios of 40/5, 30/5, 20/5, and 5/10. The different elliptical particles drawn in the figure show the geometry of the particle that is associated with the corresponding plasmon wavelength.

Figure 10 shows the SCS of the four coupled particles as a function of surface–surface distance for an illumination direction perpendicular to the particle chain. The

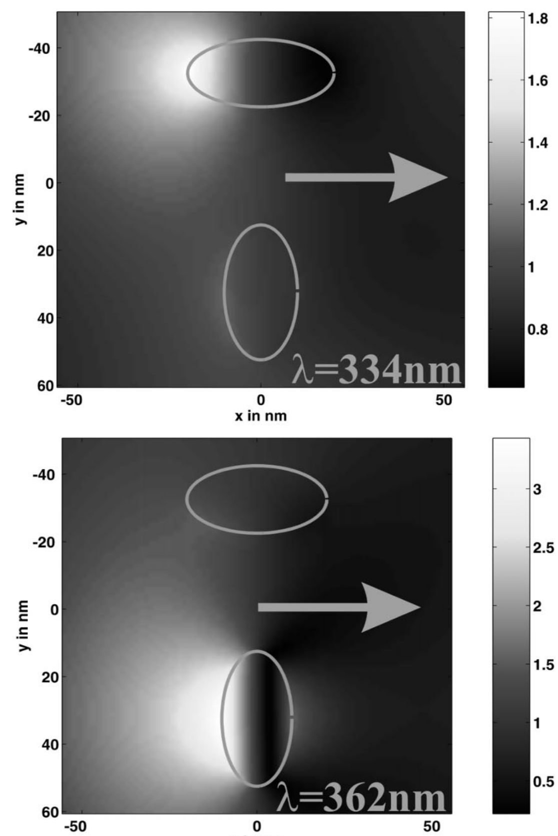

Fig. 7. Near-field amplitude of the magnetic field for plasmons excited at two elliptical cylinders with $r_1 = 10$ nm and $r_1 = 20$ nm at a separation distance of $d = 35$ nm for two different wavelengths.

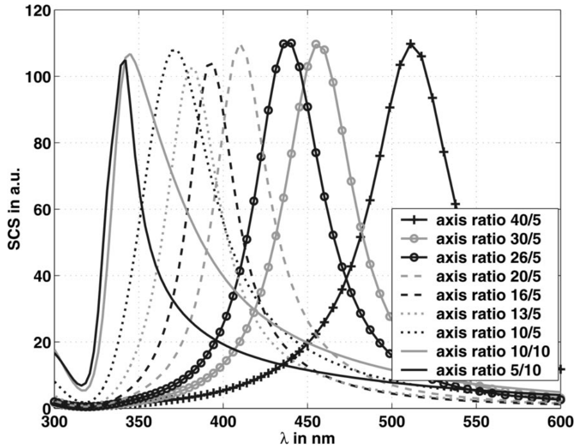

Fig. 8. SCS of nine elliptical cylinders as a function of the axis ratio.

Table 1. Radii of the Analyzed Particles

Axis Ratio	1/2	1	2/1	13/5	16/5	20/5	26/5	30/5	40/5
r_1 (nm)	35	41	39.0	33.8	32.3	34.0	36.3	36.5	40
r_2 (nm)	70	41	19.5	13.0	10.1	8.5	7.0	6.1	5

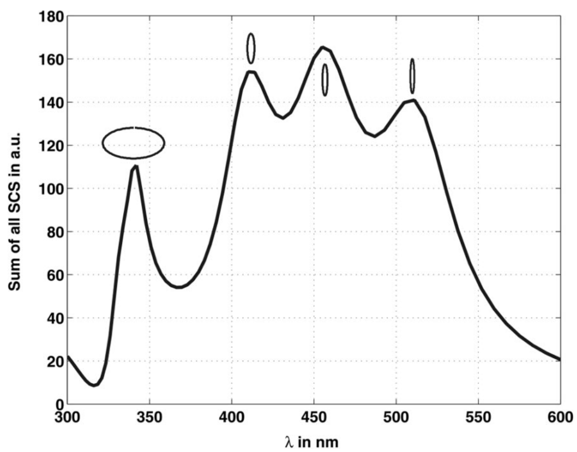

Fig. 9. Incoherent superposition of the SCS of four elliptical cylinders.

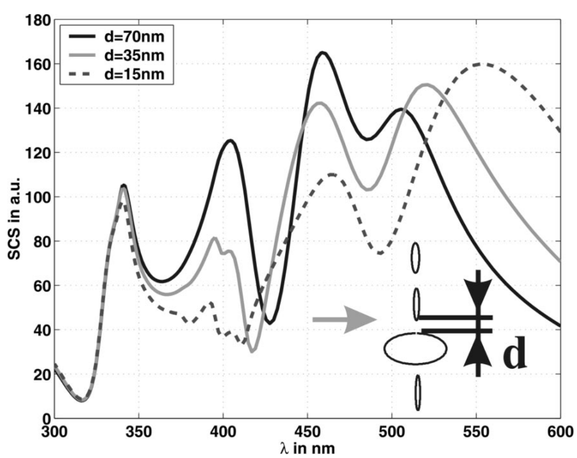

Fig. 10. SCS for four coupled silver elliptical cylinders for different separation distances.

axis ratios of the particles were 40/5, 5/10, 30/5, and 20/5. Similar responses have been obtained with other arrangements.

It can be seen that as long as the particles have a large separation (70 nm) all the maxima in the SCS are well defined, and each of the four particles clearly reveals its existence by leaving a signature in the common SCS. By reducing the distance between the particles, the entire SCS becomes redshifted and slightly damped. Nevertheless, at a separation of 35 nm all particles can be discriminated in the SCS. An additional decrease of the particle distance will further redshift the spectra. This is especially well pronounced for particles with a higher axis ratio. The coupling effects among neighboring particles play a dominant role, and the spectral peaks are no longer precisely resolved. We conclude that the smallest interaction distance from which coupled particle systems can be treated as decoupled is ≈35 nm for systems where the plasmon resonance wavelengths are different.

5. CONCLUSIONS

In the present work we have applied the boundary element method to analyze the influence on the SCS of metallic nanoparticles when they are perturbed by additional particles. Generally, the coupling effects are stronger if the particles are arranged in a plane perpendicular to the illumination direction, because in such a geometry the scattered field emanating from the particles is in phase, which leads to enhancement of the interaction. In contrast, the effects are less pronounced if the particles are arranged parallel to the illumination direction, because the oscillating scattered fields from the particles are out of phase.

For all particles that are in close proximity, an additional plasmon resonance is excited that has no equivalent in the single-particle case. By increasing the distance between the particles the interaction is less pronounced, the strength of this additional plasmon is reduced, and beyond a certain separation distance the particles can be treated as decoupled. This separation distance depends strongly on the plasmon wavelength for the two particles that are involved. If the particles have their resonance at the same wavelength, the particles have to be separated by at least 75 nm.

If the particles are resonantly detuned, which means that their plasmon resonances are at different wavelengths, the interaction is less pronounced. In this case the only alteration that can be observed in the resulting SCS is a broadening and a slight redshift of the SCS. Both are more pronounced for an illumination direction perpendicular to the particle arrangement.

We have shown that the resonance wavelength for elliptical particles is tunable over a broad wavelength range merely by changing the axis ratio. The strength of the scattering signal can be tuned by changing the overall size of the geometrical cross section. A set of nine elliptical cylinders was presented that have clearly distinguishable resonance wavelengths and approximately the same scattering strength. The collective response of four of these elliptical cylinders was analyzed again for different particle distances. We found that a separation of 35 nm is necessary for the treatment of the system as an uncoupled one, which means that all the particles can be spectrally resolved.

APPENDIX A

We assume that the system consists of M homogenous scatterers with a dielectric constant ϵ_{I_m}. The objects are described by their contour C_m and their normal $\hat{n}_{I_m}$, and they are illuminated with an arbitrary wave field $u_0^{\text{inc}}(\rho)$ from a region with a homogenous permittivity ϵ_0. ρ is an observation point in the $x-y$ plane. If the field is TE polarized, $u(\rho)$ denotes the $E_z(\rho)$ component of the electromagnetic field, and $u(\rho)$ denotes the $H_z(\rho)$ component if the field is TM polarized. The total field $u^{\text{tot}}(\rho)$ can be written as a superposition of the illuminating field $u_0^{\text{inc}}(\rho)$ and the scattered field from each of the particles $u_m^{\text{sc}}(\rho)$. The normal derivatives of the different fields with respect to the boundary are denoted by $v_0^{\text{inc}}(\rho)$, $v_m^{\text{sc}}(\rho)$, and $v^{\text{tot}}(\rho)$. It is assumed that the materials are nonmagnetic; i.e., the relative permeability is $\mu_r = 1$.

In the interior region of each particle the total field is a solution of a homogenous wave equation; in the exterior region the total field is a solution of an inhomogeneous wave equation. The boundary integral equations can be derived by applying Green's second identity[10] to these Helmholtz equations. For a particle m they read as

$$
\begin{aligned}
0 = {} & u_m^{\text{sc}}(\rho_m) + \int_{C_m} \Bigg[u_m^{\text{sc}}(\rho'_m) \frac{\partial G_{I_m}(\rho_m, \rho'_m)}{\partial \hat{n}_{I_m}} \\
& - p_{I_m} G_{I_m}(\rho_m, \rho'_m) v_m^{\text{sc}}(\rho'_m) \Bigg] \mathrm{d}l' \\
& + u_m^{\text{inc}}(\rho) + \int_{C_m} \Bigg[u_m^{\text{inc}}(\rho'_m) \frac{\partial G_{I_m}(\rho_m, \rho'_m)}{\partial \hat{n}_{I_m}} \\
& - p_{I_m} G_{I_m}(\rho_m, \rho'_m) v_m^{\text{inc}}(\rho'_m) \Bigg] \mathrm{d}l' \quad \text{for } \rho \in I, \\
0 = {} & u_m^{\text{sc}}(\rho_m) + \int_{C_m} \Bigg[u_m^{\text{sc}}(\rho') \frac{\partial G_O(\rho_m, \rho'_m)}{\partial \hat{n}_{O_m}} \\
& + p_O G_O(\rho_m, \rho'_m) v_m^{\text{sc}}(\rho'_m) \Bigg] \mathrm{d}l' \quad \text{for } \rho \in O. \qquad \text{(A1)}
\end{aligned}
$$

$G_{I_m}(\rho_m, \rho'_m)$ and $G_O(\rho_m, \rho'_m)$ are Green's functions related to the field inside and outside the objects. $p_{I_m,O}$ is a parameter that depends on the polarization; it equals unity if the field is TE polarized and $\epsilon_{I_m,O}$ if the field is TM polarized. The incident wave field on particle m, $u_m^{\text{inc}}(\rho)$, is a superposition of the illuminating wave field $u_0^{\text{inc}}(\rho_m)$ and the scattered contribution from all the other particles in the system. It reads as

$$
\begin{aligned}
u_m^{\text{inc}}(\rho_m) = {} & u_0^{\text{inc}}(\rho_m) + \sum_{n \neq m} \int_{C_n} \Bigg[u_n^{\text{sc}}(\rho'_n) \frac{\partial G_O(\rho_m, \rho'_n)}{\partial \hat{n}_{I_n}} \\
& - p_O G_O(\rho_m, \rho'_n) v_n^{\text{sc}}(\rho'_n) \Bigg] \mathrm{d}l'. \qquad \text{(A2)}
\end{aligned}
$$

By expanding the field and its derivative normal to the surface for each of the particles in terms of linear interpolation functions, a system of linear equations can be derived that is solved by standard matrix techniques for the unknown field components of all the particles in parallel.[9]

Once the scattered field and its derivative along the surface are known, the entire field outside the particles can be calculated with an equation similar to Eq. (A2).

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