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Spheroidal particle plasmons in amplifying media

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ABSTRACT The effect of a surrounding gain medium on the localized surface plasmon resonance in spheroidal metal particles is analyzed in the quasi-static limit of the Maxwell equations. It is shown that the gain required to create a singularity in the dynamic polarizability of the particle is significantly lower for non-spherical spheroids than for spheres, and can be as low as several hundred inverse centimeters for noble metals in the near infrared region of the spectrum. Resonant aspect ratios and gain values are calculated as a function of frequency for various metals. The use of non-spherically shaped nano-particles, along with gains achievable in semiconductors and dyes, can result in surface enhanced Raman scattering (SERS) signals which are dramatically enhanced.

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1 Introduction

Interaction of light with small metallic particles has recently become the focus of significant research efforts despite the fact that the basic phenomena have been recognized and described almost one and a half century ago [1]. Nanoplasmonics has emerged, as a result of a continuing drive towards miniaturization in optics and electronics, spurred by new synthetic chemical techniques of producing small particles in a variety of shapes quickly and inexpensively [2], as well as by the demand for new detection capabilities in the areas of chemical and biological ultra-high sensitivity detection, including single-molecule sensing [3].

Localized surface plasmon resonances in metallic nanoparticles and the associated electromagnetic field enhancement present a number of interesting possibilities when the particles are combined with an amplifying host medium. The effect of amplification on traveling surface plasmons in thin films has been recently studied both experimentally and theoretically [4, 5]. This system exhibits a response typical of evanescent wave coupling to a gain medium such as optical fibers with amplification in the cladding. In addition, it has been proposed that an inverted medium within close proximity to a plasmon supporting structure can act as a pump source for plasmon excitation through resonant energy transfer [6, 7]. This effect, called a SPASER in analogy to LASER, is a threshold process which occurs only at or above a critical value of energy transfer rate from the gain medium to the plasmon mode at plasmon resonance. SPASER action occurs where there is a symmetry allowed coupling between the plasmon mode and the gain medium even in the absence of external driving field.

Recent work by Lawandy [8, 9] has shown that a metal particle with a surrounding medium that has a precise value of gain at the particle interface, results in a singularity in the dynamic polarizability, and hence the electric field amplitudes within and close to the particle when a driving field is present. The enhancement of fields described by this effect is present so long as both the metal and the gain medium couple to the field and does not rely on coupling between the two media as in a SPASER. The energy transfer that is described in [8, 9] occurs through the applied field rather than directly from one media to the other. Furthermore, we show that this effect is diminished for gain greater than the critical value, in contrast to the pumping rate mechanism in [6]. Finally, as in [8, 9], we show that for spheroidal particles the specific gain depends on the entire losses of the metallic particle, rather than only those associated with collective electron motion.

We discuss the effect in the framework of the classical Mie–Gans formalism in the case of metallic spheroids. With oblate or prolate geometries, the effect of aspect ratio on the gain required for achieving this resonance singularity is studied for both longitudinal and transverse orientation of the spheroids, and shown to be nearly two orders of magnitude lower for prolate spheroids as compared to that of spheres. This lower gain requirement by high aspect ratio nanoparticles presents an experimentally achievable possibility for gigantic enhancements in surface enhanced Raman scattering (SERS) based assays and detection platforms [9].

2 Localized surface plasmon resonance in spheroidal nano-particles

In the small particle limit, where the electric and magnetic fields decouple, the essential parameter used to describe fields and scattering cross-sections of a sphere is the

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polarizability given by:

$$\alpha = 4\pi r^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}\,. \tag{1}$$

Here r is the radius of the sphere, ε_1 and ε_2 are the dielectric functions of the sphere and the surrounding medium respectively. The localized surface plasmon resonance conditions are commonly defined as cancellation of the real part of the denominator in (1). While the imaginary part of the denominator is small, this residual term prevents the appearance of a singularity in (1) and leads to the well studied enhancement of fields observed in such systems.

In the case of resonant amplification in the surrounding medium, the full resonance conditions for the case of a spherical particle and in the small particle limit will be defined as follows:

$$\begin{cases} \mathrm{Re}\,\varepsilon_1 = -2\mathrm{Re}\,\varepsilon_2 \\ \mathrm{Im}\,\varepsilon_1 = -2\mathrm{Im}\,\varepsilon_2 \end{cases} . \tag{2}$$

The meaning of these conditions is that, due to introduction of the precise amount of gain into the host medium, the imaginary part of the denominator in (1) becomes zero as well. The resulting singularity must be removed with the inclusion of higher-order terms in the scattering coefficients, as is discussed by Kerker et al. in the context of SERS [10], and is described in more detail in Sect. 3 below. The remaining part of this section, however, is dedicated to obtaining resonance conditions similar to (2) for more general shape of particles, specifically, for spheroidal particles.

Consider a spheroidal particle of length a along the symmetry axis, and $b = c$ perpendicular to the symmetry axis in external electric field. The aspect ratio of the spheroid is defined as $\mathrm{AR} = a/b$, where $\mathrm{AR} > 1$ corresponds to a prolate spheroid, $\mathrm{AR} < 1$ to an oblate spheroid, and $\mathrm{AR} = 1$ to a sphere. The polarizability of such a particle in a field parallel to one of its principal axes ($i = 1, 2, 3$) is derived in [11]:

$$\alpha_i = 4\pi abc \frac{\varepsilon_1 - \varepsilon_2}{3\varepsilon_2 + 3L_i(\varepsilon_1 - \varepsilon_2)}\,, \tag{3}$$

where the geometrical factor L_1 that corresponds to the symmetry axis in (3) is expressed in terms of the eccentricity, e, for prolate spheroids by [11]:

$$L_i = \frac{1-e^2}{e^2}\left(-1 + \frac{1}{2e}\ln\frac{1+e}{1-e}\right)\,, \text{ and}$$

$$e = \left(1 - \frac{b^2}{a^2}\right)^{\frac{1}{2}}\,. \tag{4}$$

The corresponding case for oblate spheroids, according to [11], is:

$$L_i = \frac{1}{2e^2}\left(\frac{1-e^2}{e^2}\right)^{\frac{1}{2}}\left(\frac{\pi}{2} - \arctan\left(\frac{1-e^2}{e^2}\right)^{\frac{1}{2}}\right) - \frac{1-e^2}{2e^2}$$

$$\text{and}\quad e = \left(1 - \frac{a^2}{b^2}\right)^{\frac{1}{2}}\,. \tag{5}$$

The other two geometrical factors L_2 and L_3 are obtained by symmetry arguments as: $L_2 = L_3 = (1 - L_1)/2$.

Introducing a new set of particle shape parameters $p_i = (1 - L_i)/L_i$, (3) can be rewritten as

$$\alpha_i = \frac{4\pi}{3}\frac{abc}{L_i}\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + p_i\varepsilon_2}\,. \tag{6}$$

The complete resonance conditions for a spheroid then follow from this last equation and are given by:

$$\begin{cases} \mathrm{Re}\,\varepsilon_1 = -p_i\mathrm{Re}\,\varepsilon_2 \\ \mathrm{Im}\,\varepsilon_1 = -p_i\mathrm{Im}\,\varepsilon_2\,. \end{cases} \tag{7}$$

In the case of a sphere ($L_i = 1/3$) $p = 2$, and for all other aspect ratios $2 < p < \infty$. Equations (7) are utilized below in Sect. 4, where resonance conditions for specific metals are calculated.

3 Estimate of enhancement at complete resonance

In this section we estimate the local electric field enhancement factor in the case when both equations in (2) are satisfied, rather than only the first equation. To begin with, it should be noted that polarizability expressions (1) and (6) are valid only in the small particle limit, thus neglecting electrodynamic effects (dynamic polarizability and radiation damping), and only when the denominator of the respective expression is not too small. This follows from Mie theory, which derives scattering cross section C_{sca} by way of the so called scattering coefficients a_n and b_n:

$$C_{\mathrm{sca}} = \frac{\lambda^2}{2\pi}\sum_{n=1}^{\infty}(2n+1)\left\{|a_n|^2 + |b_n|^2\right\}\,, \tag{8}$$

and relates the latter to physical quantities such as polarizability. For a small particle, the first scattering coefficient a_1 prevails, proportional to both polarizability and scattered electric field [12], and after expansion to second-order in scattering size parameter x (circumference of the particle in units of wavelength), becomes [10]:

$$a_i = -\mathrm{i}\frac{2}{3}x^3\frac{m^2 - 1 - x^2(m^4-1)/10}{m^2 + 2 + x^2(10 - 9m^2 - m^4)/10}\,, \tag{9}$$

where m is the relative index of the particle.

Normally, for a sufficiently small particle the quadratic terms in (9) are neglected. At plasmon resonance, where $\mathrm{Re}(\varepsilon_1 + 2\varepsilon_2) = Re(m^2 + 2) = 0$, the only term remaining in the denominator is the imaginary part of $m^2 + 2$, resulting in (1). In this case we obtain:

$$a_1^{\mathrm{normal}} = \mathrm{i}\frac{2}{3}x^3\frac{m^2 - 1}{\mathrm{Im}\,(m^2+2)}\,. \tag{10}$$

However, when the imaginary part of $m^2 + 2$ becomes zero as well ("complete" resonance), i.e., $m^2 + 2 = 0$, the quadratic term in the denominator of (9) must be retained. Then substitution of $m^2 = -2$ into (9) gives:

$$a_1^{\mathrm{complete}} = \mathrm{i}\frac{2}{3}x^3\frac{-3}{12x^2/5} = \mathrm{i}\frac{5}{6}x\,. \tag{11}$$

The enhancement factor for the radial component of the scattered electric field, which is proportional to a_1 [12], is then given by

$$\frac{E_{\mathrm{r}}^{\mathrm{complete}}}{E_{\mathrm{r}}^{\mathrm{normal}}}=\frac{a_1^{\mathrm{complete}}}{a_1^{\mathrm{normal}}}=-\frac{5}{4}\frac{\mathrm{iIm}(m^2+2)}{(m^2-1)}\frac{1}{x^2}\,. \tag{12}$$

Thus, local field enhancement in the case of complete resonance in the electrostatic limit, relative to the case of a passive dielectric external medium is of the order of $1/x^2\sim(\lambda/r)^2$, r is the particle radius. For the case of a typical metallic particle of radius $r=5$ nm and λ in the visible range, this gives the extra enhancement factor of the local electric field of $\sim 10^4$ – the result of the second equality in (2) becoming true. This equation determines the required value of gain, which depends on the particular type of metal and gain medium.

This new regime of full resonance SERS (FRSERS) would have many applications for ultra sensitive chemical and biological assays, potentially eliminating polymerase chain reaction steps in some genomics applications. Other phenomena that could also be enhanced include light localization and random lasers.

It should be noted here that when the exact solutions for the scattering coefficients in Mie theory are used, the singularity reappears, but at a slightly higher gain and at frequencies which are red-shifted by the dynamical correction terms [13]. On the other hand, Raman scattering involves two fields of different frequencies separated by the Stokes shift, so placing Raman emission at the exact full resonance will result in an infinite field and require an infinite pump rate for the gain medium. Thus the value of the extra enhancement factor calculated in (12) is to provide what we believe is a practical sense for the magnitudes which exist even when exact resonance is not achievable between the Raman pump, Raman emission and the gain medium.

4 Complete resonance for spheroids in gain medium

In this section, we analyze the case of a spheroidal metal particle in a gain medium and determine conditions under which the complete resonance condition is achieved. The host medium is described by a mixture of a "solvent" with a constant across the resonance index of refraction n_0 and a dilute "dye" described by a symmetric Lorentzian gain line centered at ω_0 and having a line width $\Delta\omega$, given by:

$$g(\omega)=\frac{\Delta\omega}{(\omega-\omega_0)^2+\left(\frac{\Delta\omega}{2}\right)^2}\,. \tag{13}$$

The entire dielectric function of the host medium, therefore, can be written as

$$\varepsilon_2=n_0^2+4\pi(\chi'+\mathrm{i}\chi'')\,, \tag{14}$$

where χ' and χ'' are the real and imaginary parts of the dielectric susceptibility of the "dye".

In order to analyze the resonance conditions (7) as a function of the particle shape p, and the surrounding medium properties, we note that (7) can be recast as:

$$\begin{cases}\dfrac{\mathrm{Re}\,\varepsilon_1}{\mathrm{Im}\,\varepsilon_1}=\dfrac{\mathrm{Re}\,\varepsilon_2}{\mathrm{Im}\,\varepsilon_2}\\[2mm] \dfrac{\mathrm{Re}\,\varepsilon_1}{\mathrm{Re}\,\varepsilon_2}<-2\,.\end{cases} \tag{15}$$

The advantage of rewriting resonance conditions in this form is in its straight forward graphical interpretation. The left-hand side of the first equation in (15) depends only on the dielectric properties of the particle, while the corresponding right-hand side is determined only by the host medium. The latter can be readily obtained for the case of the specified gain medium (13) and is given by:

$$\frac{\mathrm{Re}\,\varepsilon_2}{\mathrm{Im}\,\varepsilon_2}=\frac{n_0^2}{4\pi\chi''}+\frac{\chi'}{\chi''}=\frac{n_0\omega}{\pi\alpha c}\left[\frac{(\omega_0-\omega)^2}{\Delta\omega^2}+\frac{1}{4}\right]+2\frac{(\omega_0-\omega)}{\Delta\omega} \tag{16}$$

where α is the gain coefficient and we have used the well established relation between α and χ'' given by:

$$\chi''(\omega)=\alpha\frac{cn_0}{4}\frac{\Delta\omega}{\omega}g(\omega)\,, \tag{17}$$

where $g(\omega)$ is given by (13).

The left-hand side of the first equation in (15) can be computed by means of parameterization of compounded experimental data by Rakić and coworkers [14], while the right-hand side, as shown by equation (16), is the third order polynomial with respect to ω. Figure 1 is a graphical representation of (15), whose solutions are provided by the intercept of the frequency curve for a metal (gold, silver, copper, or aluminum) with the gain medium frequency dependence. The values for the host medium parameters were: $\omega=2.1\times10^{15}$ Hz, $\Delta\omega=3\times10^{14}$ Hz, $n_0=1.33$, and $\alpha=500\,\mathrm{cm}^{-1}$.

This graphical representation allows a number of useful general conclusions about the resonance conditions to be made. For instance, it is easy to see that silver would allow for the lowest critical gain among the four metals shown, if the frequency of interest is greater than 3.9×10^{14} Hz, while

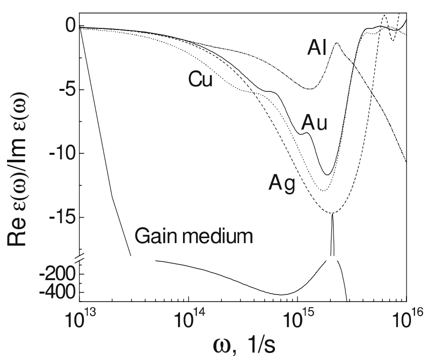

FIGURE 1 Graphical representation of resonance conditions for spheroidal nanoparticles of Au, Cu, Ag, and Al, immersed in a medium with Lorentzian gain line centered at $\omega=2.1\times10^{15}$ Hz with linewidth of $\Delta\omega=3\times10^{14}$ Hz, refractive index far from resonance $n_0=1.33$, and peak gain value of $\alpha=500\,\mathrm{cm}^{-1}$. Resonance takes place at the point of intercept between the gain medium curve and the corresponding metal curve

below that frequency copper offers the lowest critical gain. Furthermore, if the local maximum of equation(16) is below the local minimum of a metal (e.g., ~ -14.7 for silver), no solution exists at any frequency. This condition easily provides the value of gain below which there is no resonance for any frequency or particle shape.

Another observation that follows from Fig. 1 is that the solution is unique at the critical gain value, but there are two solutions corresponding to two resonances and two different aspect ratios when the curve for the gain medium is above the curve for the metal. In this case, the two resonance frequencies will be on the opposite sides of the gain line, while if the peak gain is at the critical value, the sole resonance frequency will be close to the center of the gain line.

At the center of the gain line ($\omega = \omega_0$) the gain is at its peak value and $\chi' = 0$, thus from (14), the real part of ε_2 equals n_0^2, and we can use the center frequency as a parameter. Mathematically it is equivalent to neglecting the last term in equation (16). The justification of this is that although ω_0 is not necessarily the frequency at which the resonance can be achieved under the lowest gain conditions, this frequency will be close to ω_0, due to narrow width of the gain medium peak compared to the metal frequency response profile in Fig. 1. As ω_0 varies and the peak of the gain medium curve scans through the metal dielectric function curve, the corresponding gain and particle aspect ratio can be calculated using the formalism described.

Figure 2 shows critical gain plotted as a function of frequency in the visible and near-IR range for the same four metals – Al, Au, Cu, and Ag. The latter three metals exhibit similar behavior with critical gain decreasing as the frequency decreases into the IR region, and silver has the lowest gain requirement among the three metals. Aluminum's curve is nearly flat in the visible, thus resulting in critical gain lower than that of gold and copper below ~ 600 nm, and lower than that of silver below ~ 400 nm. Overall, the critical gain values are experimentally achievable for all metals at wavelengths longer than 1 μm.

Aspect ratio complements gain as a requisite for a resonance at a given frequency, and is plotted in Fig. 3. Panels a and b correspond to the case of the electric field directed parallel and perpendicular to the symmetry axis of the particle, respectively. Prolate spheroids have aspect ratios greater than 1, and oblate spheroids have aspect ratios less than 1. Figures 2 and 3 together provide a practical tool for evaluating resonance condition for spheroidal particles of one of the four metals in gain medium. Figure 2 allows one to specify the resonant frequency-gain pair if one of the two parameters is selected. Once frequency is known, the required aspect ratio and the orientation of the metal particle can be found from Fig. 3. Alternatively, for a given metal and particle aspect ratio, the resonance frequency can be found from Fig. 3 and used to determine the critical gain value from Fig. 2. It can be seen from Fig. 3 that in order to achieve a lower critical gain, the particle's symmetry axis must be oriented parallel to the external field. For aluminum, silver, and copper critical gains below $\sim 500\,\text{cm}^{-1}$ are sufficient if the aspect ratio is greater than ~ 7 in the case of prolate particles (needles), and less than ~ 0.04 in the case of oblate particles (film islands). Also, as seen from (17), gain requirement is inversely proportional to n_0 , thus, for example, doubling n_0 to 2.66 would result in critical gain of $\sim 250\,\text{cm}^{-1}$.

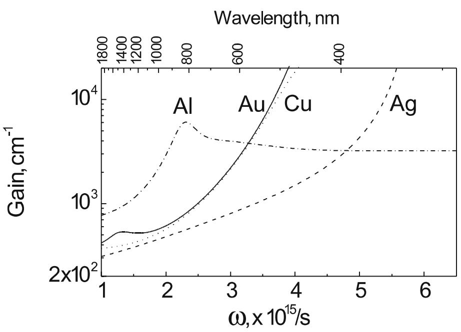

FIGURE 2 Critical gain value as a function of resonance frequency calculated for the four metals

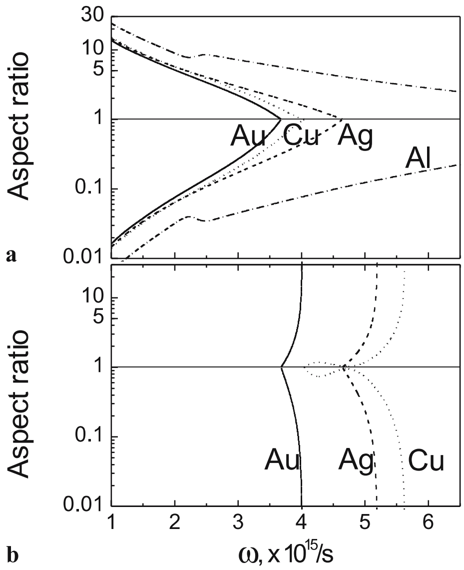

FIGURE 3 Resonant aspect ratio as a function of resonance frequency for spheroids: (**a**) symmetry axis is parallel to the external field, and (**b**) perpendicular to the external field. Aspect ratio greater than unity corresponds to prolate particles, aspect ratio less than unity corresponds to oblate particles

5 Conclusions

We analyzed the critical gain requirements for cancellation of both real and imaginary parts of the denominator in polarizability expression for spheroidal particles, leading to the localized surface plasmon resonance and local field enhancements. Four metals (Au, Cu, Ag, Al) were considered. For these metals, due to non-sphericity of the particles, the resonance can be achieved with external peak gain of less than $500\,\text{cm}^{-1}$ at wavelengths above 1 μm for particles whose symmetry axis is parallel to external field. These particles can be either rods with aspect ratios greater than 7 or discs with aspect ratio of less than 0.04. The gain is further reduced in high index semiconductor materials such as GaN where optically pumped or injected gain is possible [15, 16].

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