Amplification of local fields in disordered metallic structures

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Abstract. Amplification of higher-order multipole optical fields can exist for a nanometre-size object emitting in a complex metallic environment. Frequencies and symmetries which would not be normally observed in the far-field, because of their weakness, become activated by the interactions of the object with the local collective plasmon resonances of the immediate environment (and its inhomogeneities). This idea can provide a simple and purely electromagnetic explanation to some of the most puzzling aspects of fluctuations and activation of forbidden modes observed in some types of spectroscopies involving metallic nanostructures, such as surface-enhanced Raman scattering.

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1. Introduction

We consider the possibility of amplifying local fields from an emitting object in the nanometre-size range (such as a macromolecule) surrounded by a complex metallic environment with inhomogeneities on the same order of length scales. Emissions normally not seen in the far-field become activated by a combination of symmetry reduction of the local field (produced by the inhomogeneities of the topology where the emitter is sitting) and interactions with the local-plasmon resonances.

For more than 10 years [1] there has been renewed interest at the interface between classical electrodynamics and highly disordered and/or metallic media. This has been fuelled by the interest in photonic crystals and light localization [2, 3], but also by the more recent proposals of perfect lensing [4]. The idea that the local evanescent fields can be amplified and refocused to reconstruct an image beyond the diffraction limit has generated a great deal of controversy in the literature [5]–[7]: a simple example of how subtle the effects of local fields (LF) in the proximity of metals can be. There has been also renewed interest in the optical properties of random dielectric media [8] (where light stimulation can be achieved [9]) and in time-dependent phenomena where giant transient local fields have been proposed to exist [10].

Pendry’s idea of a super-lens [4] is based on the effect of a metallic sheet on the evanescent field of an object at the wavelength where the index of refraction \( n \) is \( \approx -1 \). Imaging is more restricted than spectroscopy. We can measure the spectral content of an object even if its image has been completely destroyed; this is because imaging (spectroscopy) depends on spatial (temporal) frequencies. A typical example is the use of a scrambler in between two lenses forming an image of an object on to the entrance slit of a spectrometer. The spectral content can be measured still, while the image is completely destroyed.

The problem we study here is, in a way, in the same category as the super-lens problem, but we do not deal with the more difficult issue of the exponential evanescent field. We study instead the multipolar radiation of an emitter interacting strongly with a local (disordered) metallic environment at different frequencies. We will generalize several possibilities from this idea later.

2. Basic aspects

We start with an academic problem in electromagnetic emission to highlight the principal aspects. Consider an isolated dipole \( \vec{p}_0 \), emitting at frequency \( \omega \) and wavevector \( k = 2\pi/\lambda \). In the direction of maximum emission the electric field in the radiation zone at distance \( r \) is [11] \( E \approx k^2 \exp(ikr)/r \). Consider now two dipoles in antiphase separated by a distance \( 2a \ll \lambda \ll r \). Since \( a/r \ll ka \), we expand to lowest order in \( ka \). The field in the same direction is now \( E \approx 2i(ka)k^2 \exp(ikr)/r \). The emitted intensities for both cases are in the ratio \( \approx (a/\lambda)^2 \). For a typical wavelength in the visible \( \sim 500 \) nm, and a separation between dipoles in the range of macromolecular scales \( \sim 1–5 \) nm), the emission can be 4–5 orders of magnitude smaller. The reason is simple; two dipoles in antiphase appear from far away like a quadrupole. Another possible argument leading to the same result is as follows: the integrated power emitted by a dipole is of the order of \( P_d \sim k^4 p_0^2 \), while for the quadrupole \( P_q \sim k^6 Q^2 \), where \( Q \) is of the order of any of the quadrupole moment tensor components \( \neq 0 \). But if the quadrupole is built from the contribution of two dipoles separated by a typical distance \( a \), then \( Q \) is of the order of \( \sim p_0 a \), i.e. \( P_q/P_d \sim (a/\lambda)^2 \) as before.
Figure 1. Examples of change in the multipolar character of the emission by polarizable objects near the emitter. (a) A dipole in front of a metallic surface, emitting at frequencies $\omega \ll \omega_p$ (quasi-static), emits essentially as a quadrupole in the far field, due to the presence of the image. (b) A net polarization $p_i$ is generated in a cell approaching a finite-size quadrupole represented by $p_1$ and $p_2$; the presence of a net $p_i$ will change the character of the far-field emission from quadrupolar to dipolar.

We want to show now that a quadrupole-like emitter with finite dimensions can produce intensities which can be as high as, and sometimes larger than, a dipole emission in the far-field when it is immersed in a complex, inhomogeneous, metallic environment. It is interesting first to understand qualitatively the reasons why two dipoles in antiphase separated by a few nm, resembling a quadrupole-like structure at long distances, will feel the inhomogeneities of the environment on a nm-size scale. This can certainly happen at the interstices and cavities of colloidal clusters, which are by themselves built by individual colloidal particles in the 5–20 nm range. The two dipoles forming an effective quadrupole, for example, can couple slightly differently to their local environments producing an asymmetry which is not intrinsic of the pure quadrupole emission. In addition, there is the symmetry and extent of the local-plasmon excitation to which the emitter is coupled. What counts for the final pattern and intensity of emission in the far field is not the emitter itself, but the object defined by the emitter and all its interactions with the environment.

To clarify a few basic issues, we first address the following question: can the multipolar character of the emitter be changed by close interactions with metals or highly polarizable media? The answer to this question is positive and we show two simple examples of change of multipolarity in both directions in figure 1. Figure 1(a) shows the canonical example of a dipole emitting very close to a metallic interface. If we are looking at frequencies well below the plasma frequency ($\omega_p$) and if the separation distance is very small to ignore retardation effects, the image follows adiabatically the dipole and the radiation in the far-field looks essentially quadrupolar in nature. Note also that this cancellation does not happen for the dipole being perpendicular to the surface (where it is enhanced). This highlights the intrinsic geometrical nature of the coupling between the emission and the surrounding media. The opposite is also true: a dipolar component to the emitted radiation in the far-field can be induced in a quadrupole by the proximity of a polarizable object like a metallic colloidal particle. This is again schematically depicted in figure 1(b). Assuming that the polarizable object approaching the quadrupole can be treated as a single cell (in the spirit of the discrete-dipole approximation explained in the next section),
there is an asymmetry in the polarization induced by both dipoles on it. The reason for the latter is the different distances to $p_1$ and $p_2$ and the different retardations. Accordingly, there will be a net polarization $p_i$ which will change (and dominate) the character of the emission in the far-field from pure quadrupolar to dipolar. The strong asymmetry to the contribution of $p_i$ by the two dipoles is only possible because the polarizable object is of a dimension comparable to the spatial dimensions of the quadrupole.

The main conclusion we would like to carry into the next section is that the multipolarity and, in general, symmetry of the radiation produced by an emitter with a finite size in a polarizable medium will depend on the details of the coupling to the local environment.

3. The discrete-dipole approximation (DDA)

We work with an extremely simplified system to prove the point. Plotting electromagnetic intensity distributions inside a disordered cluster is generally difficult in three dimensions, and one has to resort to images along several specific planes to convey a general impression. Instead, we choose to work with a two-dimensional disordered cluster of colloidal particles, which shows essentially the same qualitative phenomenon. None of these conditions are relevant for the point we want to raise.

The electromagnetic properties of nm-sized metallic structures (disordered or otherwise) are typically very complex and one must resort to approximations which are case-dependent. Even periodic-ordered structures are substantially much more complicated than the corresponding dielectric cases, because of the frequency dependence of the dielectric function [12]. We work here with a modified version of the DDA of Purcell and Pennypacker [13]–[15]. We give minimum details here and the reader is referred to the original articles [13]–[15]; we only emphasize the modifications of the method where appropriate.

A given structure is divided into small cells with characteristic dimension $d$ ($d \ll \lambda$, $\lambda$ is the wavelength of light). The polarization at the $i$th cell $\vec{P}_i$ is

$$\vec{P}_i = \alpha_i \vec{E}_i^\text{tot},$$

(1)

where $\alpha_i$ is the local scalar polarizability and $\vec{E}_i^\text{tot}$ the total electric field at site $i$, given by

$$\vec{E}_i^\text{tot} = \vec{E}_i^0 + \vec{E}_i^\text{dip},$$

(2)

where $\vec{E}_i^\text{dip}$ is the field produced by all other dipoles with $j \neq i$, and $\vec{E}_i^0$ is the field of the source driving the polarizations, which is produced (unlike the conventional DDA case) by either a local dipole or a quadrupole inside the cluster with wavevector $k = 2\pi/\lambda$ and frequency $\omega$. The electric field at cell $i$ produced by all the other cells is [15]

$$\vec{E}_i^\text{dip} = -\sum_{j \neq i} \hat{A}_{ij} \cdot \vec{P}_j,$$

(3)

with

$$\hat{A}_{ij} \cdot \vec{P}_j = \frac{e^{ikr_{ij}}}{r_{ij}^3} \left[ k^2 \vec{r}_{ij} \times (\vec{r}_{ij} \times \vec{P}_j) + \frac{(1 - ikr_{ij})}{r_{ij}^2} (r_{ij}^2 \vec{P}_j - 3 \vec{r}_{ij} (\vec{r}_{ij} \cdot \vec{P}_j)) \right],$$

(4)
where $r_{ij} = |\mathbf{r}_{ij}|$ ($i \neq j$) is the distance between cells $i$ and $j$, respectively. The solution of the $3N \times 3N$ linear inhomogeneous equations

$$\alpha^{-1} \mathbf{P}_i + \sum_{j \neq i} \mathbf{A}_{ij} \cdot \mathbf{P}_j = \mathbf{E}_0^i,$$

(5)

allows the answer to the problem. All the fields have a $e^{-i\omega t}$ time dependence.

Accordingly, the only variation in the implementation of the method is in the form of the source field $\mathbf{E}_0^i$, which is normally assumed to be an incident plane wave in the original method to study scattering problems [13]. Here $\mathbf{E}_0^i$ is the full electric field of two dipoles, either in phase or in antiphase, including all terms proportional to $1/r$, $1/r^2$ and $1/r^3$ and their corresponding geometrical dephasings [11].

The first question to address in the DDA is: what should we consider as an elemental cell for the method? A single colloidal particle in the 5–10 nm range can be considered as a single DDA cell, as long as we are not interested in the field distributions at extremely short distances (like direct contact with the colloidal particles, for example). If we do, an individual colloidal particle may have to be subdivided into further cells to accurately represent the field, or we may have to change to a method that considers explicitly the multipolar character of the near field, like the one developed by Rojas and Claro [16]. In fact, the two methods, one in the limit of infinite multipoles given in [13] and the other involving an infinite number of DDA cells in [13], should be exactly equivalent.

Rojas and Claro have shown [16], however, that for moderate densities the dipole approximation (essentially equivalent to considering each colloidal particle as a single DDA cell) can be safely used. We work here in that limit. The polarizability $\alpha$ is obtained from the measured dielectric function $\epsilon(\omega)$ of Ag through ellipsometry [17] by assuming a Clausius–Mossotti relation of the type [11]

$$\alpha = \frac{3V(\epsilon(\omega) - 1)}{4\pi(\epsilon(\omega) + 2)},$$

(6)

where $V$ is the volume of an individual DDA cell.

### 4. Results

Figure 2 shows the basic geometry of the problem we study. Two dipoles ($p_0$) separated by 5 nm at the centre of a plane are made to radiate with their dipole moments perpendicular to the plane itself. The dipoles are either in phase or in antiphase with each other, simulating a dipole or quadrupole emission problem. The dipoles will be immersed in a cluster of Ag colloidal particles afterwards (avoiding direct overlap with the dipoles themselves) and their emission patterns and intensities compared. We observe only the field patterns on the plane of the figure for ease of representation. The situation is schematically depicted in figure 2, where the case of two in-phase and in-antiphase emitting dipoles is shown together with their corresponding far-field emissions. For the two in-phase dipoles, the emission in the perpendicular plane presents concentric patterns equivalent to an effective dipole $p = 2p_0$ in the far-field, while for the antiphase case (quadrupole) there is a characteristic $l = 2$, $m = \pm 2$ quadrupolar emission pattern in the plane [11]. The intensity in the far-field is much lower by a factor $\sim (a/\lambda)^2$ in this latter case, as pointed out before.
Figure 2. Emission of two dipoles on the plane. The dipoles are perpendicular to the plane itself, separated by a small distance compared to $\lambda$, and either in-phase or out-of-phase with each other. The far-field patterns are shown at the bottom of the figure. For the in-phase situation on the right, the emission looks like a single dipole of magnitude $p = 2p_0$, with concentric emission waves in the plane. For the out-of-phase situation on the left, the overall pattern is weaker, due to the influence of $(a/\lambda)^2$, and also has an angular dependence typical of a $l = 2$, $m = \pm 2$ quadrupolar emission. Both figures at the bottom are plotted in the same intensity range with a logarithmic intensity scale where red is intense and blue is weak. The patterns are calculated for a separation between dipoles of 5 nm and $\lambda = 633$ nm, in an area of $1 \times 1 \mu m^2$.

We now observe the far-field emission at very long distances from the emitter ($r = 50 \mu m$) for both in-phase and antiphase configurations when the emitter is surrounded by a cluster of metallic colloidal particles (each 10 nm in diameter). The cluster is generated with 60 colloidal particles (each of which is taken as a single DDA cell) within an area of $100 \times 100 \mathrm{nm}^2$ around the emitter, avoiding direct overlap with the dipoles and among themselves. The 180 $\times$ 180 system of equations (5) is solved and the intensity in the far-field computed. The process is repeated for many randomly generated clusters. Figure 3 displays the situation for the dipole and quadrupole-like cases for 1000 randomly generated clusters. The spikes in the plots represent clusters in which there is a strong coupling of the emitter with the local environment of plasmon resonances resulting in a high far-field intensity in that specific direction. Comparing the dipolar and quadrupolar cases, we observe that fluctuations in the far-fields for both cases are comparable in intensity. Actually, there are configurations in which the quadrupolar arrangement emits more than the dipolar one, as seen from the far-field.

The far-field patterns reveal, accordingly, anomalously large intensities for configurations with weak intrinsic emissions, but they do not say much about their origin. To this end, it is interesting to observe the field patterns in full, at different length scales. This is done in figure 4 for two quadrupole-like emitters in two cases where the far-field emission is either low or high; and we show the intensity patterns at three different length scales. The far-field pattern for low emission is somewhat distorted but its basic quadrupole nature can be easily seen from the far
Figure 3. Far-field intensity for two dipoles in phase (a) and in antiphase (b) at a fixed position. The intensity is monitored at a distance of 50 µm along the horizontal direction in the previous figure. The calculation is performed at a photon energy corresponding to 633 nm (1.96 eV). A randomly generated cluster of 60 colloidal particles (avoiding direct overlap) is surrounding the emitter in both cases. The figures show the results for $10^3$ clusters. The spikes in the intensities seen in the far fields are a manifestation of strong coupling of the emitter with local inhomogeneities of the cluster. The intensity of the antiphase configuration (simulating a quadrupole) is comparable to or larger than that of a dipole emission in many cases.

It is worth mentioning that the statistics of emitted intensities in figure 3 will be, in general, linked to the statistics with which the clusters are built. In the end, the probability of finding dimers, trimers, etc, and clusters with different topological characteristics is nothing but a manifestation of the particle–particle correlation function for their position. In many situations found experimentally, however, almost all possibilities can exist depending on whether the plasmon resonances come from dried (fixed) clusters, clusters that form sporadically in liquid with varying degrees of aggregation depending on the mutual screening of colloidal particles, collapsed clusters in the liquid produced by an aggregating agent (KCl or NaCl), etc. For our
Figure 4. Field distributions on the plane for low (left) and high (right) emission quadrupoles. We display the intensity patterns at three different length scales $1 \times 1 \mu m^2$ (top), $50 \times 50 \text{nm}^2$ (centre) and $30 \times 30 \text{nm}^2$ (bottom), displaying characteristic features of the far, intermediate and short fields, respectively. The separation of the dipoles is $5 \text{nm}$ and $\lambda = 633 \text{nm}$ as before. All graphs are plotted in the same intensity range with a logarithmic scale of colours from blue (low) to red (high). The far-field pattern of a low-emission case is still essentially quadrupolar in nature, while the high-emission case recovers a dipolar component. The short-range field for the high-emission quadrupole reveals a region of highly connected (through their interactions) colloidal particles, which amplify any small asymmetry in the neighbourhood of the quadrupole. See the text for further details.

purposes here, it is important to show that the effect can exist in some types of clusters. The variety of situations found experimentally would then make their appearance almost inevitable.

5. Discussion

The examples shown in the previous section have been chosen deliberately to highlight the problem of (i) symmetry reduction and (ii) coupling to the environment of different types of emitters. But the problem is, in fact, very general. What the examples really show is that, essentially, any non-emitting or weakly emitting configuration can be activated given the proper combination of geometry and local-plasmon resonances.

We now address the question: is there any experimental situation where a breakdown of selection rules and amplification of forbidden signals can be seen in a complex metallic environment? The literature of surface-enhanced Raman scattering (SERS) is plagued with examples of selection rule breakdowns [18]–[21], and this is precisely one of the main issues we would like to highlight in the present paper. An inelastic scattering technique like Raman implies an internal conversion of frequencies of some sort (typically vibrations in the case of molecules). In the Plazeck picture of the scattering process [22], the re-emitted field has its origin in the variations of the electronic bond polarizabilities under the presence of an internal
vibration. Each molecular bond can be thought of as a small dipole re-emitting the Stokes or anti-Stokes field with an overall pattern and symmetry intrinsic of the eigenvector of a specific vibration. These re-emissions and their symmetries combine in the far-field to create a Raman active/inactive or silent mode. The source of the secondary (Raman) radiation is very local, it is the molecule itself, and in this context it is evident why the presence of an inhomogeneous metallic environment might affect the Raman emission.

Let us summarize several aspects of SERS that can be linked to the present problem. (i) Symmetries of Raman forbidden modes are seen to be activated in macromolecules all the time and in a wide variety of situations. This aspect arises as a natural consequence in this context, as shown in the previous section. (ii) Raman spectra with forbidden modes are seen to fluctuate all the time, with time scales of the order of seconds or fractions of a second. This can be easily understood if we consider that macromolecules on a nm-size scale move and fluctuate continuously. Indirect thermal processes are mainly responsible for this, including local laser heating. This can explain why the time scale for variations is in the range of seconds, which is more typical of thermal effects rather than much faster photochemical processes. Far-field resonances allowing forbidden modes to be seen are generated continuously and at random positions while the laser is on. (iii) Smaller organic molecules like dyes do not show these fluctuations as often as macromolecules. This is an important point: both molecules are made of the same elements and they even share many functional groups. Within this framework, however, it is possible to understand why collective modes in macromolecules might be more susceptible: the difference in size is the answer. In order for the inhomogeneities of the local metallic environment to activate a forbidden symmetry in the far-field, the molecule (emitter) should extend to several nanometres in size. If not, it can be considered to be a point source from the point of view of the external field and the internal symmetry rules for emission of the isolated molecule prevail. (iv) In the present picture, the laser frequency (and consequently the frequency of the re-emitted Raman photons) should have an influence on the result. The reason is that different lasers couple differently to plasmon resonances which are (on average) localized to different spatial extents. In one of our previous studies [23], we have shown that plasmon–plasmon interactions lead to red-shifted (with respect to the intrinsic plasmon resonance) collective resonances which are more spatially localized and are the possible origin of very efficient SERS hot-spots. In general terms, we expect that the more spread-out the eigenvector or a collective plasmon, the more homogeneous it will be on a nm-size scale, and less effective to probe the inhomogeneities of the emitter. Indeed, lasers in the red-region (below the intrinsic surface plasmon resonance of Ag) normally display much higher activity of fluctuations than lasers in the green which are more directly in resonance with the surface plasmons of the colloidal particles. Note also that in the specific case of SERS, the signal is dominated by the contribution of hot-spots [23], which are small regions with high spatial localization of the order of the wavelength of light where high enhancement factors exist. In many typical situations, accordingly, the contribution from single macromolecules or a small number of molecules concentrated in these places becomes dominant, even in the presence of a larger number of molecules in the illuminated area.

In fact the Raman problem is slightly more complex. In [23], we pointed out the necessity of considering the details of the fields at both the laser and Stokes frequency. On a nm-size scale, the laser intensity itself will be inhomogeneous. Accordingly, it is the convolution of the inhomogeneities of the laser intensity itself and the re-emission pattern generated at the Raman frequency that will decide the type of signal being observed. Both conditions are sufficiently varied to allow almost any type of symmetry to be seen. It is unlikely, in addition, that the
origin of Raman fluctuations seen in SERS has only an electromagnetic origin. For example, we found in [21] that, besides the laser frequency, oxygen can activate the fluctuations and nitrogen quenches them. The same result has been found in other carbon-based macromolecules [20]. This reveals that there is, at least, an intermediate photochemical step which is not fully accounted for by a purely electromagnetic picture. This is, indeed, one of the main problems with the microscopic origin of SERS, i.e. the existence of an electromagnetic and chemical contribution which can coexist and sometimes interfere with each other. A mechanism like the one described in [21], which is a mixture of electromagnetic and chemical contributions simultaneously, has to invoked. Despite all this, the phenomenology described here can account on its own for very many simple experimental facts in a way which is natural and without any highly specialized condition. The concept of forbidden symmetry amplification by a complex metallic environment with inhomogeneities in the nm-size range remains valid in any case, irrespective of the SERS problem.

6. Conclusions

In more general terms, the results in this paper show that it might be worth revisiting our assumptions on the character of allowed or forbidden emissions in spectroscopy, and their corresponding intensities, when an active nm-sized metallic environment (with complex localized plasmon excitations) is present. The analogue of Pendry’s problem applied to spectroscopy, irrespective of the imaging capabilities, has not been exploited or even investigated to the very best of our knowledge. The results in this paper show, however, that there might be a case for it. In spectroscopies that involve a frequency down-conversion like Raman, the optical properties of the metallic environment and its plasmon resonances might be decisive for the information recovered in the far field. If local multipolar or evanescent fields at the Raman frequencies can be ‘extracted’ from the object and projected into the far-field (as in the imaging problem) it is reasonable to believe that frequencies and symmetries not normally seen under standard conditions will be observed. This could provide not only a unifying picture for the multitude of violations of Raman selection rules and activation of Raman forbidden modes seen in many cases experimentally in SERS [18], but also provide a tool for the studies of the resonances themselves. The effect on the amplification of local fields by different laser frequencies, in particular close to the super-lens condition \( n \approx -1 \) [4] require an extensive separate study which is under way and will be published elsewhere [24].

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