



**Universidad de Cantabria**

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Facultad de Ciencias

**ON LIGHT SCATTERING BY NANOPARTICLES WITH  
CONVENTIONAL AND NON-CONVENTIONAL  
OPTICAL PROPERTIES**

PH.D. THESIS

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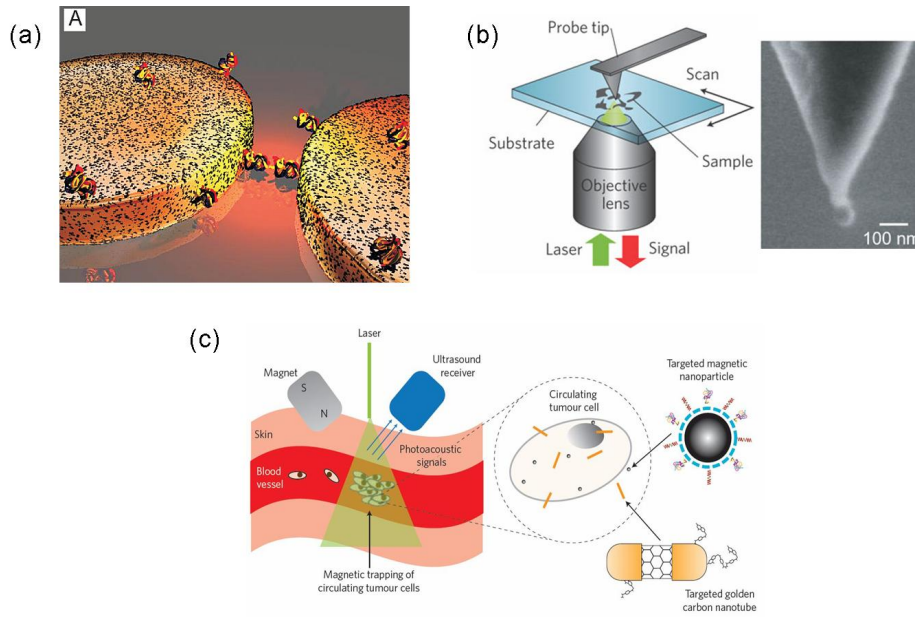
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## Dependence of the Directional Conditions: From the Near to the Far-Field

*"El idealismo aumenta en proporción directa de la distancia que nos separa del problema."  
—John Galsworthy, 1867-1933, novelista y dramaturgo inglés*

### 5.1. Introduction

Several devices, treatments and/or applications make use of the optical properties of metallic nanoparticles due to their ability to sustain localized plasmon resonances. S. Aćimović et al. [5] proposed a nano-biosensor using two chemically modified gold nanodisks as a first step to single-molecule detection (Figure 5.1(a)). S. Kawata and co-workers showed in [67] the design of a near-field microscope which uses the plasmonic behavior of a silver nanoparticle stuck to the probe tip to observe sub-diffraction limit details (Figure 5.1(b)). In addition, magnetic properties, sometimes present in these nanoparticles, are very interesting and useful and some authors have used them for cancer treatments [83, 56]. In [147], the author describes a cancer treatment that employs magnetic nanoparticles and chemically modified



**Figure 5.1:** Examples of some applications based on the scattering properties of nanoparticles. (a) Nano-biosensor described in [5], (b) Design of a near-field microscope as it was exposed in [67] and (c) scheme of a technique to control and to treat certain cancers [147]

golden carbon nanotubes attached to the tumor cells (Figure 5.1(c)). The use of a laser, a magnet and an ultrasound receiver allows them to monitor and to heat the malign cells and kill them. The characteristics of each of these applications could be improved drastically if we were able to control the direction in which nanoparticles scatter light. In other words, tune the optical constants of nanoparticles in such a way that they fulfill directional conditions as those stated by Kerker et al in [69] such as we described previously.

Although optical constants fulfilling these directional conditions can not be obtained with natural occurring materials, some researchers have demonstrated the possibility to create new engineered materials or *metamaterials* which show those interesting values for  $\epsilon$  and  $\mu$ . Two recent examples illustrating this, are the ones presented by A. Alù and N. Engheta [8] and by N.A. Mirin and N.J. Halas [99]. In the first case, the authors presented a system of six silver nanoparticles which sustain electric and magnetic plasmon resonances, this is,  $\epsilon \approx -2$  or  $\mu \approx -2$  at different frequencies. The second one analyzed experimentally nanoparticles with a certain geometry called "*nanocups*". These nanoparticles show electric and magnetic plasmon resonances as well. In general, these nanostructures or nanoparticles are much smaller than the incident wavelength and thus, can be modeled as a simple spherical nanoparticle with effective optical constants as we have seen in the results shown in previous chapters.

Light scattering in the near-field is also a crucial point for these applications. However, the directional behaviors have only been studied in the far-field region; that is for observation distances from the scatterer much larger than the incident wavelength. In order to extend the study to the near-field region, this chapter is devoted to the evolution of the angular distribution of the scattered intensity by a nanoparticle with optical constants fulfilling the directional conditions proposed by Kerker et al [69] as a function of the distance from the particle's surface. With this type of analysis, we want to understand better the behavior of light scattering under the directional conditions for the optical constants either in the near- and in the far-field and the evolution from one region to the other.

## 5.2. Theoretical overview: Is it possible to use the Dipolar Approximation?

Until now, we have considered the Mie theory for the analysis of the scattering properties of a nanoparticle in the far-field. This particle was considered much smaller than the incident wavelength, and for this reason only the first four coefficients ( $a_1, b_1, a_2$  and  $b_2$ ) were considered. However, for several of the analyzed situations the dipolar contributions were dominant and light scattering by particles was reproduced by taking only the two first coefficients ( $a_1$  and  $b_1$ ). Under this assumption, the particle could be represented as a superposition of two dipoles ( $R \rightarrow 0$ ), one electric and one magnetic. This involves an important simplification of calculations. For this reason, in order to analyze the evolution of the scattered intensity by these particles from the near to the far field region, we have considered particles as a combination of two dipoles following the theory widely explained in [105] and that is called *Coupled Electric and Magnetic Dipole Method* (CEMDM). This method, that is briefly explained here, will be described in detail later.

By assuming the scatterer as two superposed dipoles (one electric and one magnetic), the scattered electric and magnetic fields will be the sum of those produced by an electric dipole and those produced by a magnetic dipole at a distance  $d$  and in a direction  $\vec{n}$  [57]

$$\vec{E}_p = \frac{1}{4\pi\epsilon_0} \left[ \vec{p} \frac{e^{ikd}}{d} \left( k^2 - \frac{1}{d^2} + \frac{ik}{d} \right) + \vec{n} (\vec{n} \cdot \vec{p}) \frac{e^{ikd}}{d} \left( -k^2 + \frac{3}{d^2} - \frac{3ik}{d} \right) \right] \quad (5.1)$$

$$\vec{H}_p = \frac{1}{4\pi(\mu_0\epsilon_0^{1/2})} \left[ (\vec{n} \times \vec{p}) \frac{e^{ikd}}{d} \left( k^2 + \frac{ik}{d} \right) \right] \quad (5.2)$$

$$\vec{E}_m = -\frac{1}{4\pi} \left( \frac{\mu_0}{\epsilon_0} \right)^{1/2} \left[ (\vec{n} \times \vec{m}) \frac{e^{ikd}}{d} \left( k^2 + \frac{ik}{d} \right) \right] \quad (5.3)$$

$$\vec{H}_m = \frac{1}{4\pi} \left[ \vec{m} \frac{e^{ikd}}{d} \left( k^2 - \frac{1}{d^2} + \frac{ik}{d} \right) + \vec{n} (\vec{n} \cdot \vec{m}) \frac{e^{ikd}}{d} \left( -k^2 + \frac{3}{d^2} - \frac{3ik}{d} \right) \right] \quad (5.4)$$

where the electric dipole is represented by the electric dipolar moment ( $\vec{p}$ ) and the magnetic one by the magnetic dipolar moment ( $\vec{m}$ ). These moments are related with the incident field ( $\vec{E}_0$  and  $\vec{H}_0$ ), considered here as a plane wave, in the following way

$$\vec{p} = \epsilon_0 \alpha_E \vec{E}_0 \quad (5.5)$$

$$\vec{m} = \alpha_H \vec{H}_0 \quad (5.6)$$

being  $\alpha_E$  and  $\alpha_H$  the electric and magnetic polarizability, respectively. As we are considering dipolar particles, only the two first Mie coefficients,  $a_1$  and  $b_1$  are not negligible. The polarizabilities can be written as a function of these coefficients as follows

$$\alpha_E = \frac{3i}{2k^3} a_1 \quad (5.7)$$

$$\alpha_H = \frac{3i}{2k^3} b_1 \quad (5.8)$$

As was explained in (2.56) and (2.57), the Mie coefficients can be even simplified under the dipolar approximation. The electric and the magnetic polarizabilities are then given by the Clausius-Mossotti relation

$$\alpha_E = 4\pi a^3 \frac{\epsilon - 1}{\epsilon + 2} \quad (5.9)$$

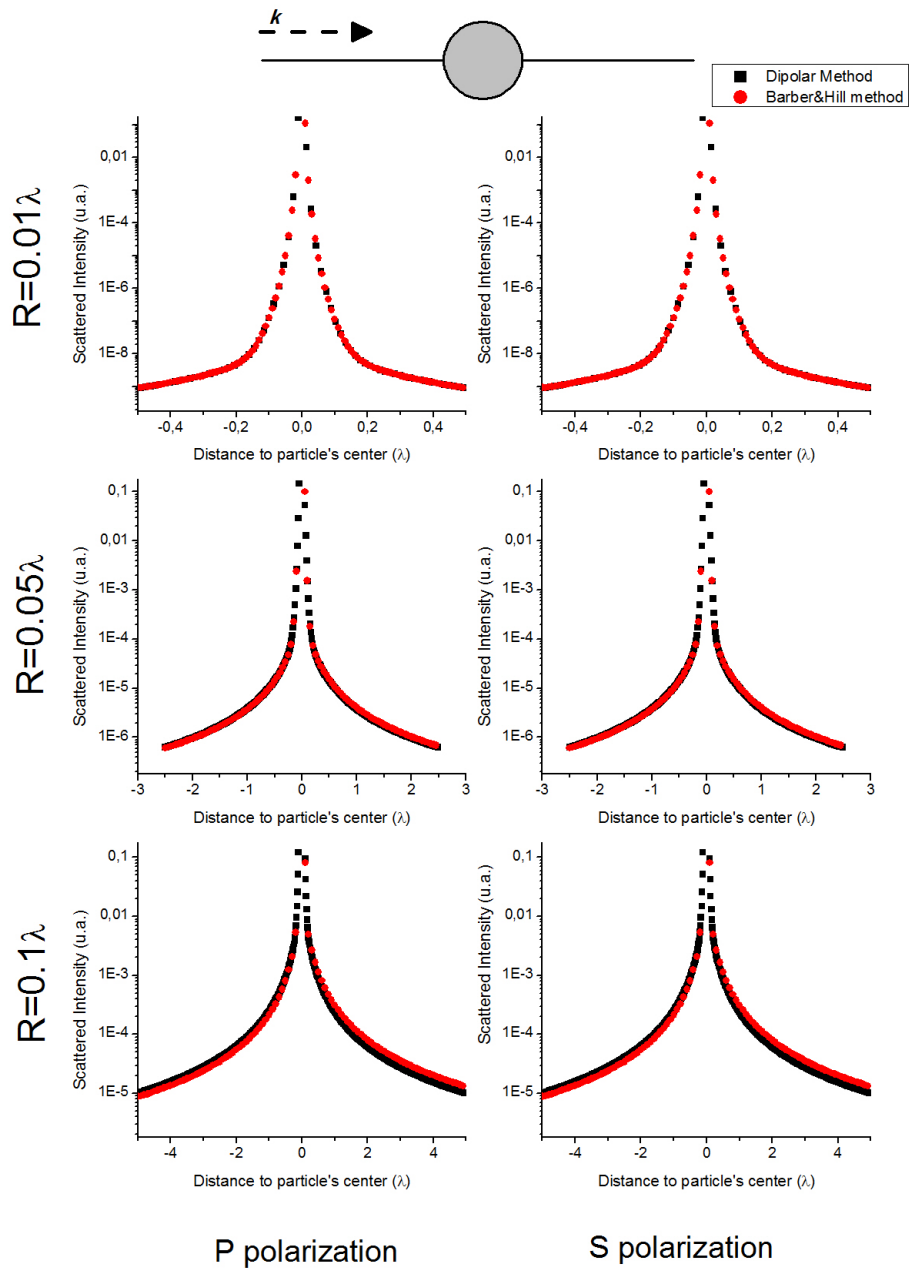
$$\alpha_H = 4\pi a^3 \frac{\mu - 1}{\mu + 2} \quad (5.10)$$

As we already explained, the expressions of the Clausius-Mossotti relation do not verify the Optical Theorem. Then the extinction efficiency has to be calculated using other expressions. If we want to apply the Optical Theorem, the radiative correction [28] must be included to the expressions of the polarizabilities.

In order to show the validity of this approximation, we have compared the scattered intensity by a particle calculated using the *CEMDM* and an exact method with a code developed by Barber and Hill [13] which implements the Mie theory.

In Figure 5.2 the scattered intensity by a dielectric and isolated nanoparticle ( $\epsilon = 3, \mu = 1$ ) is calculated along a line parallel to the incident direction and crossing the particle at its center (see inset in Figure 5.2). Three different particle sizes have been considered in the nanometric range for the visible part of the spectrum. Two methods are compared in this plot: the approximate method and the exact one. The approximate one considers the nanoparticle, as an electric dipole ( $\mu = 1$ ) using the expression described previously, (5.1)-(5.4). The exact method was developed by Barber and Hill using the Mie theory and it is described in their book [13]. Following the characteristics of this last computational method, the distance ranges are fixed to 50 times the radius of the particle, where the negative values correspond with the backward direction and the positive ones with the forward direction. Both polarizations have also been considered. Results for a P incident polarization are plotted in the left panel while those for an S incident polarization are plotted in the right panel of the figure. As can be seen, the dipolar method reproduces accurately the near-field light scattering by an isolated nanoparticle with particle sizes  $R < 0.05\lambda$ . For larger radii, the differences between the two considered methods start to appear, especially in the forward direction. This is because orders higher than the dipolar one become important. These orders are considered in the exact method but not in the dipolar approximation.

This results allow us to warrant that the expressions of the scattered field given by equations (5.1), (5.2), (5.3) and (5.4), reproduce accurately the scattered field of a particle while  $R < 0.05\lambda$ . This eases the calculations with respect to the Mie theory.



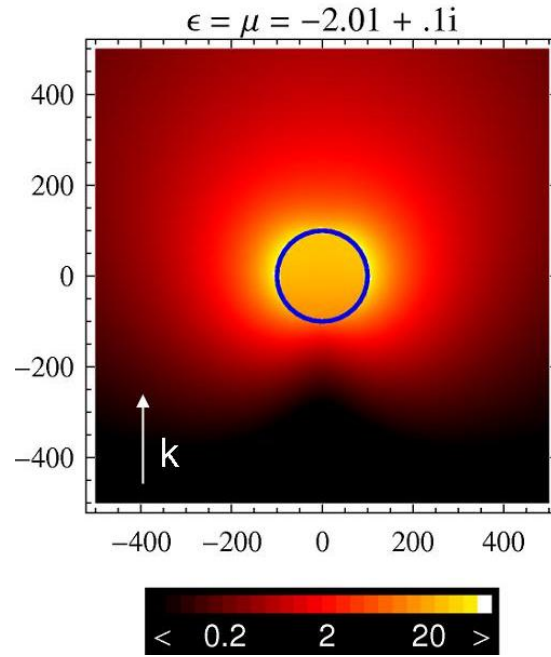
**Figure 5.2:** Scattered intensity by an isolated particle with optical constants ( $\epsilon = 3, \mu = 1$ ) along an axis parallel to the incident direction (see inset) for three different particle sizes. An approximate (black squares) and an exact (red circles) method are compared. Both incident polarizations have been considered: parallel (left panel) and perpendicular (right panel) to the scattering plane.

### 5.3. Evolution of the Scattered Intensity from the Near- to the Far-field Region under Directional Conditions

In Figure 5.3, we show the spatial distribution of the scattered intensity by a nanoparticle ( $R = 0.01\lambda$ ) with optical constants  $(\epsilon, \mu) = (-2.01 + 0.1i, -2.01 + 0.1i)$  fulfilling the zero-backward scattering condition. The values for  $\epsilon$  and  $\mu$  are chosen close to the electric and magnetic resonances because the main interest of this kind of nanoparticle is based on their resonant behavior. The resonant values were not used because the singularities introduce infinite values into the calculations which is problematic in order to make the numerical process converge. A small absorption has also been included in order to make the calculations more realistic. Nevertheless, the scattering behavior does not change with or without small absorption and only small differences in the results can be observed. That is why in what follows only lossless particles are considered. A polarization with the incident electric field parallel to the scattering plane has been considered. It can be seen that the distribution of the scattered intensity far from particle surface follows the directional scattering behavior with an abrupt minimum (dark zone) in the backward direction. However, as the observer approaches the particle's surface, the backward intensity becomes higher and even comparable to the one in the forward direction. This evolution is analyzed, in more detail, in Figure 5.4. In this figure, we plot the scattering diagrams measured at different distances from an isolated particle with a radius  $R = 0.01\lambda$  and optical constants satisfying the zero-forward (left panel) or the zero-backward condition (right panel). The incident field is polarized either parallel (P-polarization) or perpendicular (S-polarization) to the scattering plane. The distances at which we have measured the scattered intensity are increased from the surface of the particle ( $d = 0.01\lambda$ ) to  $d = 1\lambda$  in order to observe the evolution of the directional behavior from the immediate surroundings of the particle to distances far away from it.

For distances far from the particle and almost in the far-field region ( $d = 1\lambda$ ), the scattered intensity shows a directional distribution very similar to the one shown in Figures 4.2 and 4.1, where the far-field scattered intensity of a dipole-like particle which optical constants satisfied the zero-backward and the zero-forward conditions, respectively, are plotted. As the observer approaches the particle, the directional distribution tends to disappear, as can be seen in the third and second rows of Figure 5.4. The evolution with the distance is

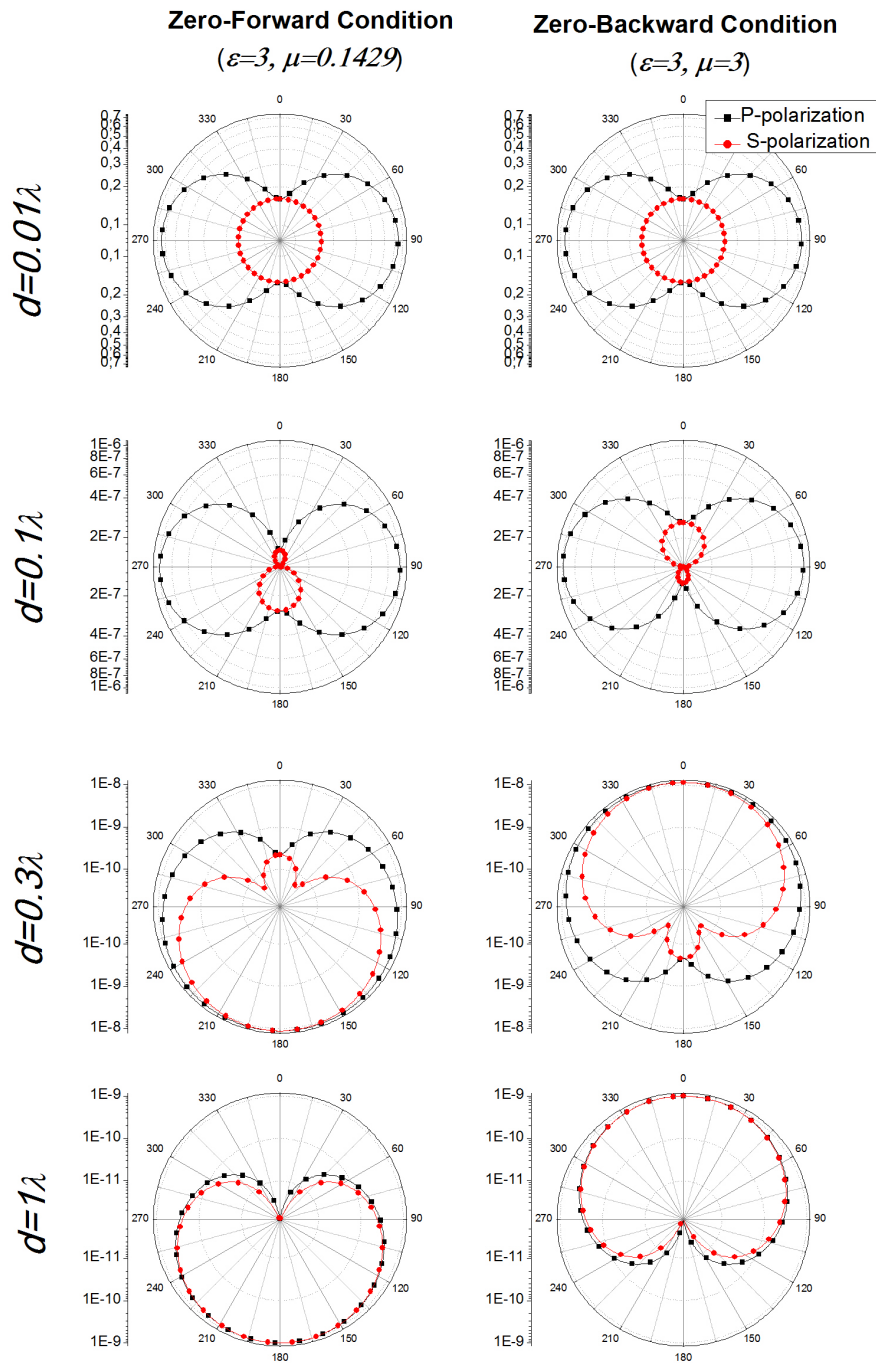




**Figure 5.3:** Distribution of the scattered intensity (in arbitrary units) of a nanoparticle ( $R = 0.01\lambda$ ) with optical constants  $(\epsilon, \mu) = (-2.01 + 0.1i, -2.01 + 0.1i)$  fulfilling the zero-backward scattering condition.

smooth, tending to the scattered intensity behavior on the particle's surface. The behavior close to the particles, even on their surfaces (first row of Figure 5.4) is the same as the one for an electric dipole in the near-field. In fact, the scattering pattern for the P-polarization has the typical "eight-shape" parallel to the electric field vector while for the S-polarization, it is isotropic [108]. While the differences between the distribution for each orthogonal polarization are almost null in the far-field, as it was stated in a previous chapter, the scattering intensity close to the particle has a different angular distribution depending on the incident polarization. When moving from far to short distances, differences between both orthogonal polarizations appear in the scattering diagrams.

The explanation for this can be deduced from the equation of the scattered electric field produced by an electric and a magnetic dipole (see equations (5.1) and (5.3)). Substituting the expressions for the dipolar moments (equations (5.5) and (5.6)) and then calculating the scattered intensity in the two interesting directions: the forward,  $\vec{n} = (0, 0, 1)$  and the backward direction  $\vec{n} = (0, 0, -1)$ ; we obtain the following expressions as a function of the distance to the observer ( $d$ ), the particle size ( $R$ ), the optical constants  $(\epsilon, \mu)$  and the incident wavenumber ( $k$ ).



**Figure 5.4:** Polar scattering diagrams measured at different distances from an isolated particle with  $R = 0.01\lambda$  and optical constants satisfying the zero-forward (left) or the zero-backward condition (right). Both incident polarizations, parallel (P-polarization) and perpendicular (S-polarization) to the scattering plane have been considered.

- Forward Direction

$$I(0^\circ) = \left| \frac{e^{ikd}}{d} R^3 \left[ \left( k^2 + \frac{ik}{d} \right) \left[ \frac{\epsilon - 1}{\epsilon + 2} + \frac{\mu - 1}{\mu + 2} \right] + \frac{ik}{d} \left( \frac{\epsilon - 1}{\epsilon + 2} \right) \right] \right|^2 \quad (5.11)$$

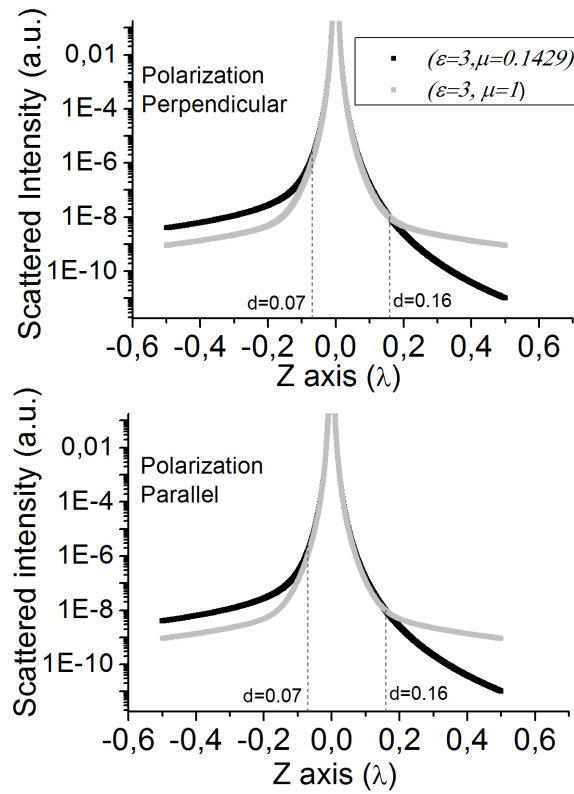
- Backward Direction

$$I(180^\circ) = \left| \frac{e^{ikd}}{d} R^3 \left[ \left( k^2 + \frac{ik}{d} \right) \left[ \frac{\epsilon - 1}{\epsilon + 2} - \frac{\mu - 1}{\mu + 2} \right] + \frac{ik}{d} \left( \frac{\epsilon - 1}{\epsilon + 2} \right) \right] \right|^2 \quad (5.12)$$

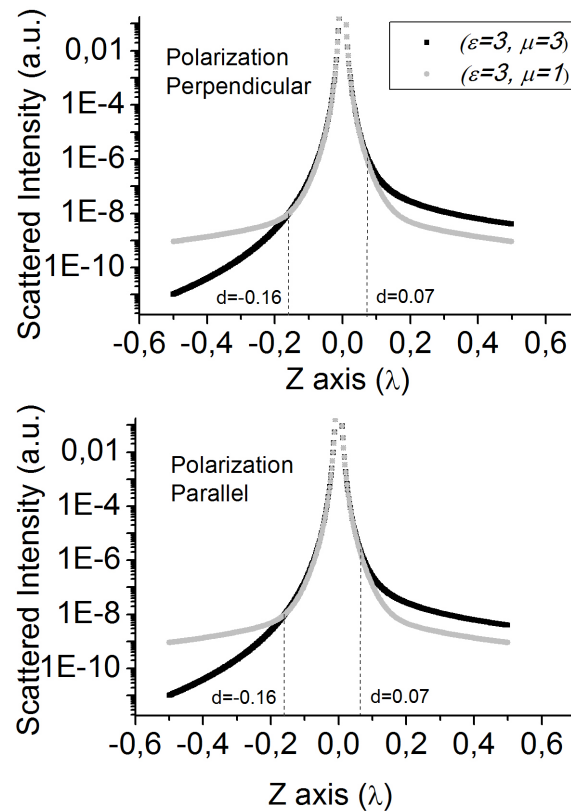
The previous equations are formed by the sum of two terms. The first one depends on the electric and magnetic properties of the scatterer. It is easy to demonstrate that when the optical constants of the particle verifies one of Kerker's conditions, the first term of the equations is zero. On the other hand, the second term of both expressions only depends on the electric properties ( $\epsilon$ ) and it can not be canceled, except when  $\epsilon = 1$ . The fact that this remaining term only has an electric response is the reason for which the scattered intensity distribution close to the surface of a particle with optical constants fulfilling one of the Kerker's conditions resembles the electric dipolar behavior (see first row of Figure 5.4)

We now study in more detail the evolution from the dipolar scattering pattern to a more directional behavior, such as we observed in Figure 5.4. In order to estimate a distance from the center of the scatterer, at which the scattering behavior starts to differ from the dipolar distribution, we have calculated the scattered intensity by a particle with directional optical constants ( $\epsilon$  and  $\mu$  fulfilling one of the Kerker conditions) along a line from the backward to the forward direction (parallel to the incident direction,  $z$ -axis) and crossing the particle's centre. Figures 5.5 and 5.6 show the scattering intensity by a particle ( $R = 0.01\lambda$ ) with optical constants satisfying the zero-forward and the zero-backward scattering conditions, respectively, as a function of the distance from the scatterer in a direction parallel to the incident one (see inset Figure 5.2). Incident polarization parallel (top) and perpendicular (bottom) to the scattering plane have been considered in both cases. As we want to observe the evolution of the differences between the directional and the dipolar behavior as a function of the observation distance, we have included, for comparison, the scattered intensity by a similar particle but with conventional optical constants, this is, with the same electric permittivity but with magnetic permeability equal to 1 ( $\epsilon = 3, \mu = 1$ ) showing an electric dipolar behavior.

One of the main characteristics of the electric dipolar behavior, shown in Figures 5.5 and 5.6 (gray circles) is the symmetry with respect to the centre of the particle. When we



**Figure 5.5:** Scattered intensity by a nanoparticle of radius  $R = 0.01\lambda$  and optical constants ( $\epsilon = 3, \mu = 0.1429$ ) as a function of the distance from the particle surface in a direction parallel to the incident direction. For comparison, we have also included the case of a particle with ( $\epsilon = 3, \mu = 1$ ). Both incident polarizations have been considered: parallel (top) and perpendicular (bottom) to the scattering plane.



**Figure 5.6:** Scattered intensity by a nanoparticle of radius  $R = 0.01\lambda$  and optical constants  $(\epsilon = 3, \mu = 3)$  as a function of the distance from the particle surface in a direction parallel to the incident direction. For comparison, we have also included the case of a particle with  $(\epsilon = 3, \mu = 1)$ . Both incident polarizations have been considered: parallel (top) and perpendicular (bottom) to the scattering plane.

consider the particle with unconventional optical properties (optical constants satisfying the directional conditions), the behavior is more complex. For a particle with optical constants fulfilling the zero-forward scattering condition (Figure 5.5), it can be seen that for distances close to the surface of the scatterer, the scattered intensity remains symmetric as for the dipolar behavior. However, as the distance increases, the differences between the dipolar and the directional distributions tends to appear, the last one losing the symmetry. In the forward direction (positive values of  $Z$ ), we can see that when moving away from the particle's surface, the scattered intensity by the conventional and the unconventional particle, overlap. For distances larger than  $d \approx 0.16\lambda$ , light scattering by the directional particle drops exponentially. In the opposite direction ( $Z < 0$ ), the differences between the two behaviors appears for shorter distances: around  $d = 0.07\lambda$ . However, the difference is almost constant. We attribute this second change to a redistribution of the energy. As the energy in the forward direction is minimum or zero but the total energy must be conserved, the energy scattered in other directions must be increased, as can be observed for the backward direction. Kerker et al [69], as we explained in a previous chapter, stated that under the directional conditions for the optical constants, there is an TE-TM identity. This means that light scattering is similar for both incident orthogonal polarizations. In Figure 5.5, this feature can be observed, once again.

The evolution of the light scattering distribution as a function of the distance from the particle is very similar when the zero-forward or the zero-backward scattering condition is fulfilled as can be seen from the Figures 5.4, 5.5 and 5.6. Then, the previous explanations for Figure 5.5 can also be applied to Figure 5.6 considering the complementary directions. Furthermore, it can be seen that the values for the critical distances are the same for both cases.

### 5.3.1. Influence of Particle Size on the Evolution of the Scattered Intensity Distribution

As it is well known, the scattering properties of a particle are strongly dependent on its size. Directional scattering is not an exception and, as we have analyzed in [40], particle size is an important factor for particles with such unconventional optical constants. The zero-forward scattering conditions evolve with the particle size in such a way that only for small values of  $R$  it is possible to observe a minimum light scattering in that direction. As  $R$  increases, the minimum becomes less pronounced until it disappears [40]. On the contrary, the zero-backward

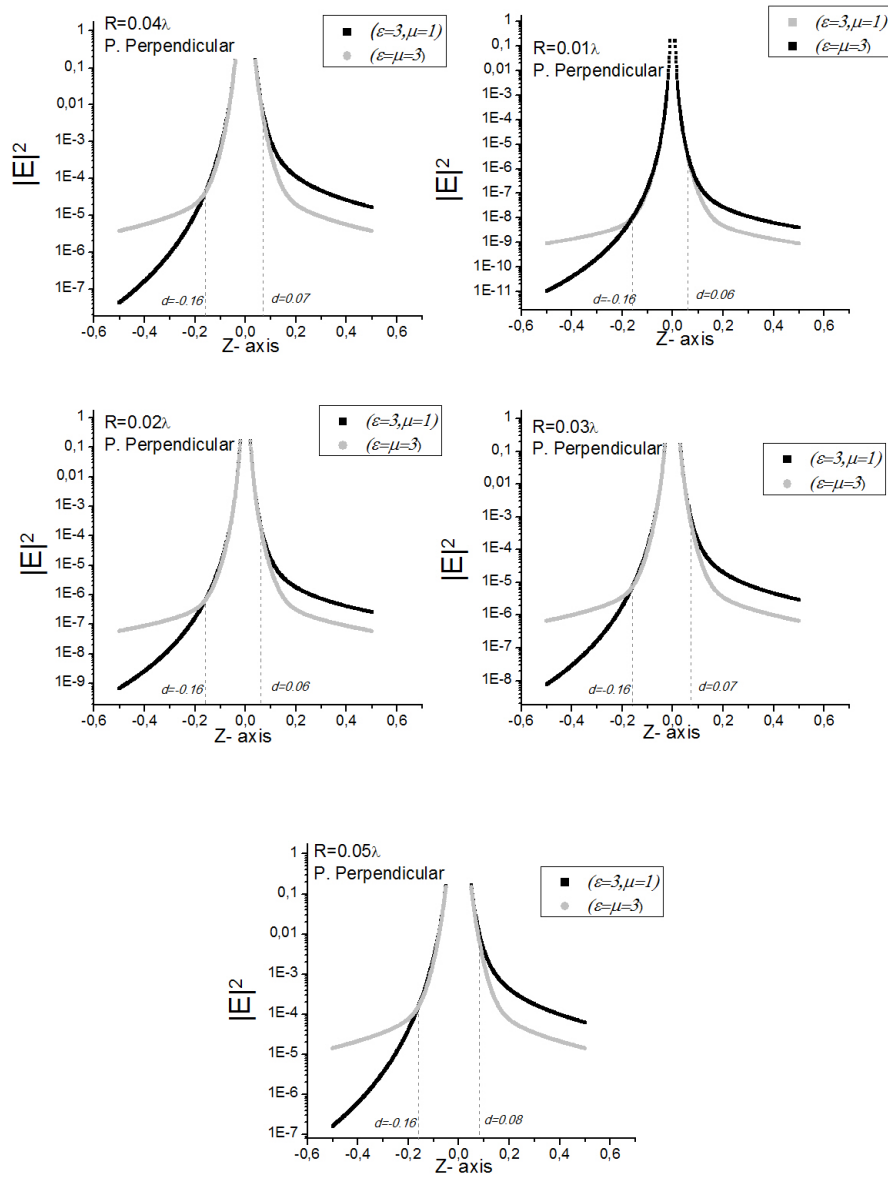
scattering condition is still valid for particles with high values of the radius. Using this, we can analyze the influence of the size effects on the evolution of the near-field distribution of the scattered electric field for particles with optical constants satisfying the zero-backward condition. In Figure 5.7, we show the scattered intensity along the  $z$ -axis (direction parallel to the incident direction) for a particle with optical constants ( $\epsilon = 3, \mu = 3$ ); that is, the particle does not scatter in the backward direction, and for several values of the particle size. As before, the conventional case ( $\epsilon = 3, \mu = 1$ ) has been included as a comparison. In this case, we have only considered a polarization parallel to the scattering plane because, as we have shown several times before, there is no differences between both polarizations.

From the results, we can conclude that the influence of the particle size on the evolution of the near-field distribution of the scattered intensity is not important. The main effect in the backward direction is that as  $R$  increases the differences between the conventional and the unconventional behaviors, that is, the dipolar and the directional cases, respectively, becomes larger. The distance at which we can start to observe differences between both cases in the backward direction, does not change as the particle size changes. However, the distance at which the differences appear in the opposite direction changes noticeably as  $R$  increases. Larger particle sizes could have been considered, but more exact methods than the small-particle approximation must be used.

## 5.4. Conclusions

In previous chapters we have analyzed in detail the possibility to control the directional behavior of light scattering by small particles. These studies focused on the far-field area. New applications, whose characteristics depend strongly on the directionality of the scattered intensity by the nanoparticles or nanostructures, were the motivation of those studies. However, the distribution of the scattered intensity in the near-field region is also quite important. This is specially relevant for the diagnosis or treatment of cancer where it is crucial to destroy the malign cells without damaging the healthy ones close to the tumor. This is why we concentrated in this chapter on the study of the evolution of the directional conditions, proposed by Kerker and co-workers [69], as a function of the distance to the scatterer, and looking closely to the transition from the far-field to the near-field.

The presented results show that the zero-forward and the zero-backward conditions do not produce the expected features for very short distances. While for large distances (larger than 0.16 times the incident wavelength) the angular distribution of the scattered intensity



**Figure 5.7:** Scattered intensity by a nanoparticle with optical constants ( $\epsilon = 3, \mu = 3$ ) as a function of the distance from the particle surface in a direction parallel to the incident direction for several particle sizes. For comparison, we have also included the case of a particle with ( $\epsilon = 3, \mu = 1$ ). The incident polarizations have been considered parallel to the scattering plane.



presents the directional behavior predicted by the conditions, for shorter distances it is quite different. Close to the surface of the scatterer, the scattering patterns resemble that of an electric dipole with the typical "eight-shape" for a parallel incident polarization and a "circle" (isotropic) for an incident polarization perpendicular to the scattering plane. These features are similar to the zero-forward and the zero-backward conditions for both polarizations. We have explained this behavior using the dipolar approximations. While for the expressions of the scattering intensity in the far-field under the directional conditions it is possible to obtain zeros, the same expression in the near field do not present any zero except for the trivial case ( $\epsilon = 1, \mu = 1$ ), because an electric dipolar term remains under the Kerker conditions. However, the evolution from one behavior to the other is smooth.

The forward-backward asymmetry produced by the directional conditions starts to appear even for shorter distances. For distances around  $0.07\lambda$  from the surface of the particle, the differences between the unconventional or directional and the conventional or dipolar behavior, tends to increase in the opposite direction (in the forward direction under the zero-backward condition and viceversa). These differences are caused, in our opinion, by a redistribution of the total energy. The observed features are common for both conditions, zero-forward and zero-backward, and for both incident polarizations.

Finally, we have checked the influence of the particle size on the evolution of the scattered intensity distribution from the far-field to the near-field region. The only noticeable effect is that the differences between the directional and the dipolar behavior is more important as the particle grows. The critical distances at which the differences between the two behaviors start to appear do not change with  $R$ .