Universidad de Cantabria

Facultad de Ciencias

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

PH.D. THESIS

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Design of a Negative-Refractive-Index (NRI) System

"La ciencia, a pesar de sus progresos increíbles, no puede ni podrá nunca explicarlo todo. Cada vez ganará nuevas zonas a lo que hoy parece inexplicable."
—Gregorio Marañon, 1887-1960 ,médico y escritor español

7.1. Introduction

In this research, we have analyzed and described new and interesting features of light scattering by small particles whose optical constants (ϵ and μ) belong to a non-conventional range ($\mu \neq 1$, either positive or negative). We have shown that resonances, both electric and magnetic, either dipolar or quadrupolar, can be excited leading to a strong enhancement of the scattered intensity. Special attention has been paid to materials that could present a permittivity and a permeability such that $\epsilon = \mu = -2$. The excitation of the electric and magnetic dipolar resonances produces spectacular values of the scattered intensity. Directionality in light scattering can also be observed for these particular values of the optical constants. This pair of optical parameters fulfils *Kerker's conditions*[69] for the zero-backward and the zero-forward light scattering. While the first effect can be observed, the second one does not appear due to the strong enhancement generated by the dipolar resonances. For this reason, and as was described before, this pair (ϵ, μ) represents an exception for the zero-forward condition proposed by Kerker et al [11].

Nanoparticles with resonant permittivity ($\epsilon = -2$) for a stated value of λ are common and can be found using metals. Recently, the researchers N. Mirin and N. Halas have shown that also resonant magnetic nanoparticles can be obtained [99] by "playing" with the geometry and, because its geometry, a dipolar magnetic resonance is excited. These particles have been called "*nanocups*" due to their similarity with a cup. Nevertheless, the fabrication of a nanoparticle with ϵ and μ negative and both equal to -2 is still out of reach. Only a nanostructured material, a metamaterial, can exhibit these optical parameters. The inner structure of this kind of materials is usually quite complex. C. Holloway *et al.* showed in their work [53] that an array of magnetodielectric particles embedded in a matrix presents effective double-negative optical constants and analyzed their reflection and transmission properties [54].

Inspired by these works, we tried to develop our own design of a system with double negative and resonant optical parameters, that is ($\epsilon = \mu = -2$). Here, we present a numerical study of an array, similar to those studied in [53], composed of two kinds of nanoparticles: the first kind being resonant electric and the second kind being resonant magnetic. As it will be shown, the effective optical constants of the array are in the double-negative range including a minimum in the backward scattering amplitude. We have used the lack of backscattering to identify the double-negative resonant behavior, by analyzing it as function of different geometrical parameters of the array.

7.2. Description of the System: Geometrical Configurations and Illumination Conditions

Using the *Coupled Electric and Magnetic Dipole Method* (CEMDM) described in the previous chapter, we have analyzed the scattering patterns for a simple array made of four spherical particles in a square lattice (see Figure 7.1). The particles are of two kinds: on one hand we have purely electric with an electric permittivity close to the dipolar resonant

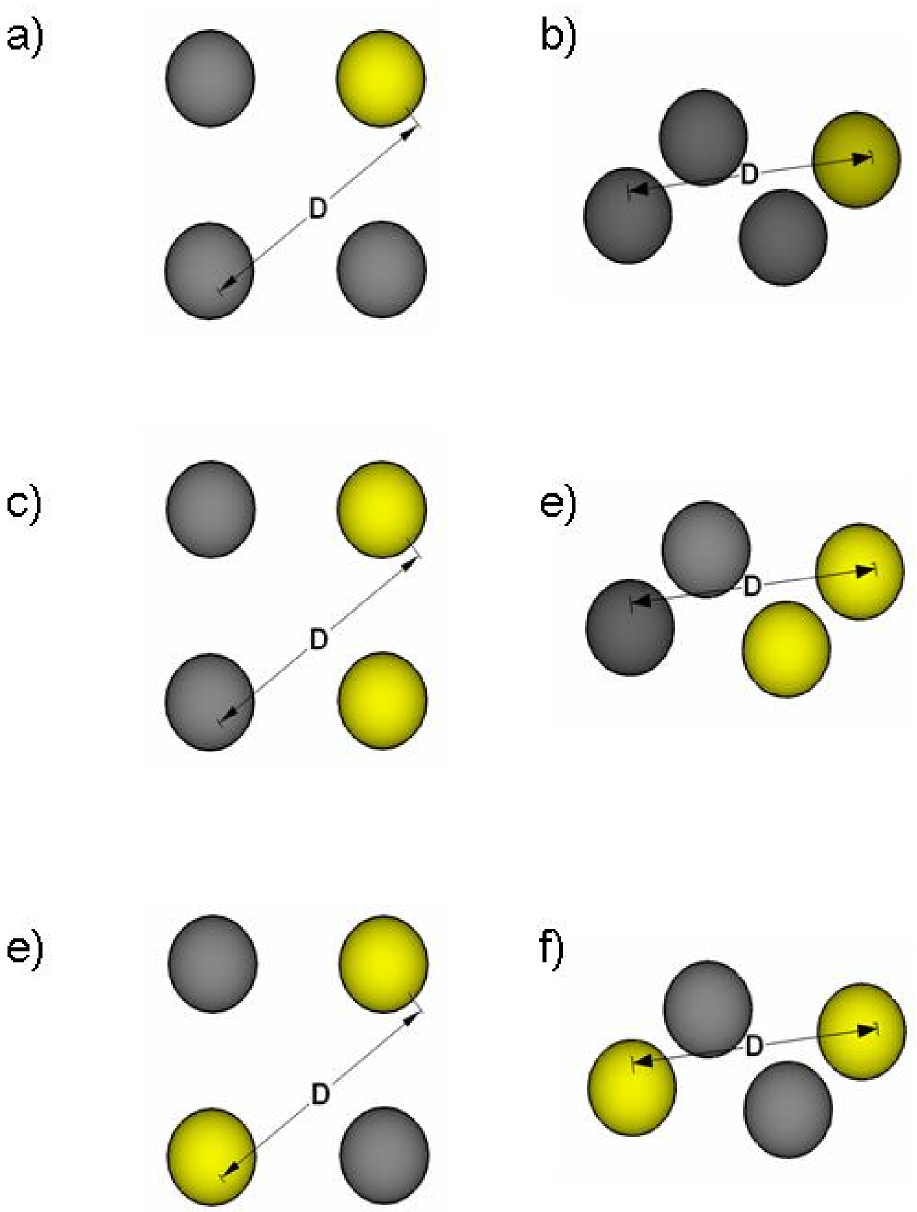

Figure 7.1: Different configurations of an array of four particles forming a square lattice. They are made of two kinds of particles: the dark ones are purely electric ($\epsilon = -2.01, \mu = 1$) while the yellow ones are purely magnetic ($\epsilon = 1, \mu = -2.01$). All of them have radius $R = 0.01\lambda$. The value D gives the distances between them. The particles are located in the scattering plane (left column) or in a plane perpendicular to it (right column).

value, that is $(\epsilon, \mu) = (-2.01, 1))$ which we call "electric" particles; on the other hand we have the "magnetic" particles which have only magnetic properties near the dipolar magnetic resonance $(\epsilon, \mu) = (1, -2.01)$. These values for the electric permittivity and the magnetic permeability are chosen such that the electric or the magnetic dipolar resonances are excited producing a high scattered intensity, but avoiding divergent polarizabilities, as would happen if ϵ or μ were exactly equal to -2. However, similar results to those shown here, but with much smaller values of the scattered intensity, can be obtained for arbitrary values of ϵ and μ under the condition that the permittivity of the electric particles and the permeability of the magnetic particles are equal.

In Figure 7.1, we show the different configurations we have considered. As can be seen, different combinations of electric and magnetic particles were analyzed. In every case the particles are much smaller than the incident wavelength ($R = 0.01\lambda$). The diagonal of the square is considered as the lattice parameter, determining the distance between the particles. The total system is illuminated by a linearly polarized plane wave. Both polarizations, with the incident electric field parallel (TM or P polarization) or normal (TE or S polarization) to the scattering plane are considered. The array is placed in the scattering plane (left panel of Figure 7.1) or in a plane perpendicular to it (right panel of Figure 7.1). When only one particle, either electric or magnetic, is different from the rest (Figure 7.1(a) and (b)), the overall light scattering is independent on its position in the array. For this reason we only report results for one specific location of the particle.

The polar distribution of the scattered intensity for each case described in Figure 7.1 is shown in Figure 7.2. Some interesting features can be observed, in particular the possibility to inhibit light scattering at certain directions. However, we have focused our attention only on the cases (e) and (f) because they show a deep minimum in the backward direction similar to Kerker's condition [69]. In Figure 7.3 the scattering patterns of one of these configurations (case (f)) is compared with the one for an isolated particle of the same size as the subunits of the array ($R = 0.01\lambda$) and optical constants fulfilling the zero-backward scattering condition ($\epsilon = -2.01, \mu = -2.01$). The similarity is clearly visible. Also the polar distributions for an isolated particle, either electric or magnetic, as those composing the array is shown in the figure. Then, we can conclude that these two array configurations behave as a double-negative system, scattering as a double-negative particle with electric permittivity equal to that of the electric particles and magnetic permeability equal to that of the magnetic particles. These particular configurations are composed by four particles on a plane normal to the incident direction, of which two particles are "electric" and two "magnetic". The electric particles are in the corners of the same side and the magnetic ones in the corners of the other

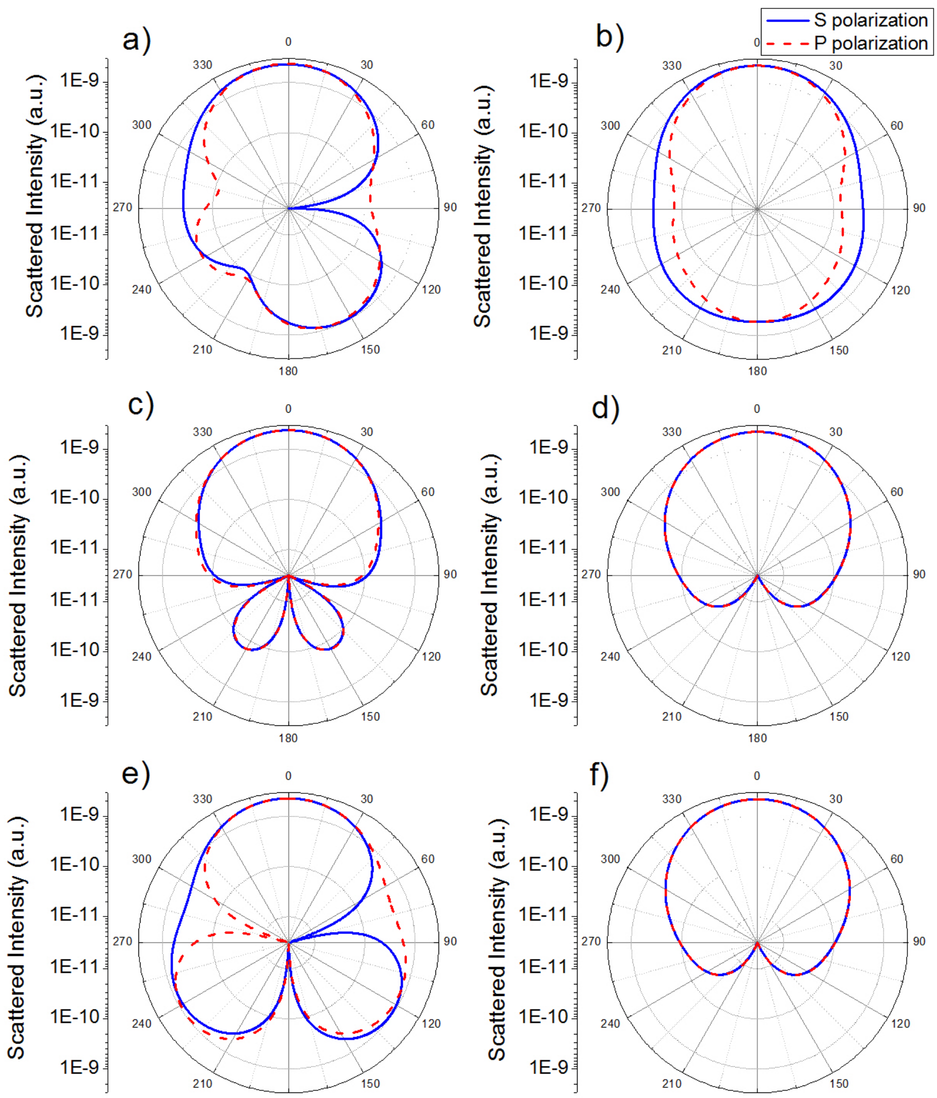

Figure 7.2: Scattering patterns of an array of four particles in the different configurations shown in figure 7.1. Both incident polarizations, parallel (P) and perpendicular (S) to the scattering plane, are considered. The lattice parameter is $D = 0.5\lambda$

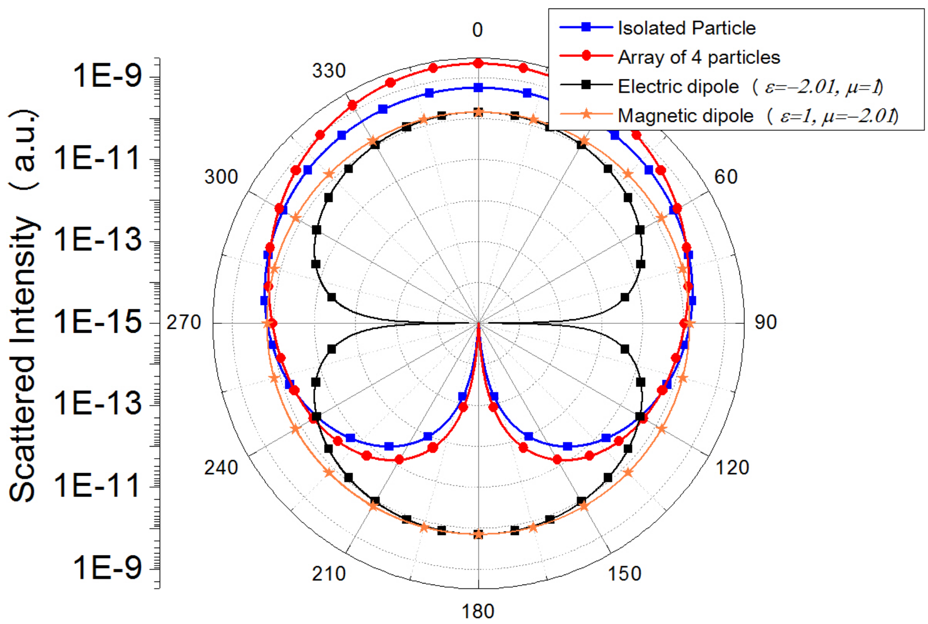

Figure 7.3: Comparison of the scattering pattern for an isolated double-negative and resonant particle ($\epsilon = \mu = -2.01$) with radius $R = 0.01\lambda$ and for an array of electric ($\epsilon = -2.01, \mu = 1$) and magnetic ($\epsilon = 1, \mu = -2.01$) particles ($R = 0.01\lambda$) following the geometrical characteristics shown in Figure 7.1(f). Also the scattering patterns for an electric ($\epsilon = -2.01, \mu = 1$) and a magnetic ($\epsilon = 1, \mu = -2.01$) dipole have been included. The incident field was considered linearly polarized with the electric field parallel to the scattering plane (P polarization).

side (Figure 7.1(e)). For the other configuration, the electric and the magnetic particles are placed alternatively in the corners (Figure 7.1(f)). In both cases, the positions of the particles result in the compensation of the electric and the magnetic contributions in the backward direction, producing the pronounced minimum in that direction. These results follow those presented by C. Holloway *et al.* [53] with the difference that our array exhibits a scattering behavior similar to the double-resonant and double-negative case ($\epsilon = -2.01, \mu = -2.01$). The minimum backward scattering is a characteristic feature that is easy to identify. For this reason we will use it to characterize the deviation of the array's behavior from the double-resonant and double-negative properties with changing geometrical parameters.

7.2.1. Dependence on the Particle Distance

The scattering pattern of both array configurations described in Figure 7.1 (e) and (f) changes as the distance, *D*, between the particles is modified. The results of this modification are shown in Figures 7.4 and 7.5 where the polar distribution of the scattered intensity is plotted for both geometrical configurations described in Figure 7.1(e) and Figure 7.1(f), respectively, for several values of the distance parameter *D*.

The "alternate"-configuration (Figure 7.1(f)) shows a more stable behavior with interparticle distance than the one represented in Figure 7.1(e). While the minimum in the first case is well-defined and the angular range is broad for every distance (Figure 7.5), in the second case (Figure 7.4) the minimum in the backward direction depends strongly on *D*. Even for small distances there is scattering in the backward direction for this array. The angular range at which the minimum can be observed is quite sensitive with decreasing *D*. Hence, we can conclude that only the case described in Figure 7.1(f) is stable. In what follows we shall call it the "alternate" configuration. The minimum-backscattering range in the first case depends also on *D*. It is around $30°$ in width, centered on $180°$, for the small and large distance and it reaches a maximum width at $D = \lambda$ with a value equal to $60°$.

7.2.2. Dependence on Possible Rotations of the System

One of the main practical problems with this kind of systems is the alignment of the array. In order to analyze its tolerance to perturbations on the alignment, we have considered in-plane rotations of the array around an axis parallel to the incident direction going through the center of the lattice. The scattered intensity, in semi-logarithmic scale, for the rotated arrays is shown in Figure 7.6. These rotated arrays are obtained by turning the original "al-

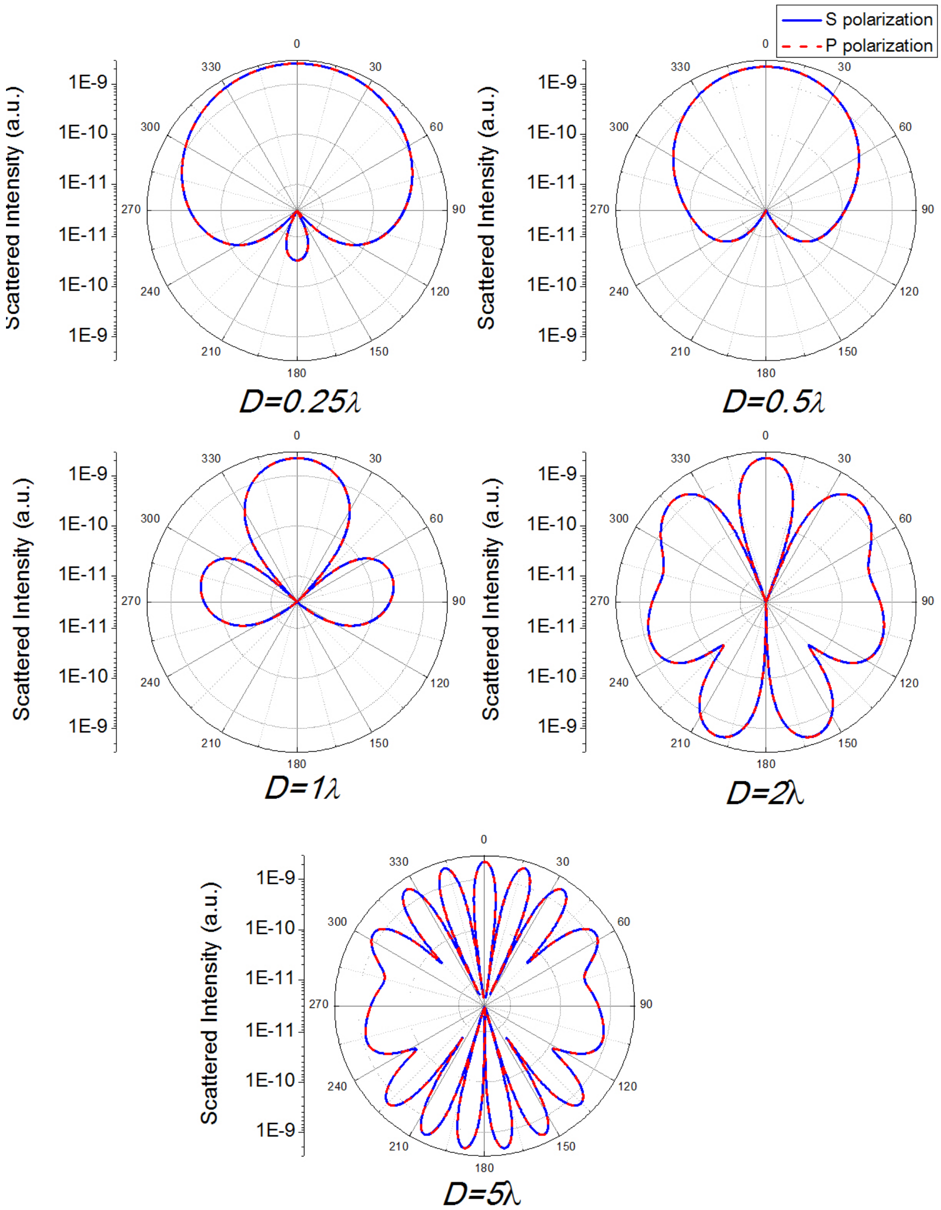

Figure 7.4: Polar light scattering diagram by an array similar to the one described in figure 7.1(e) for several distances between the particles (*D* expressed in units of wavelength). Both incident polarizations, parallel (P) and perpendicular (S) to the scattering plane are considered.

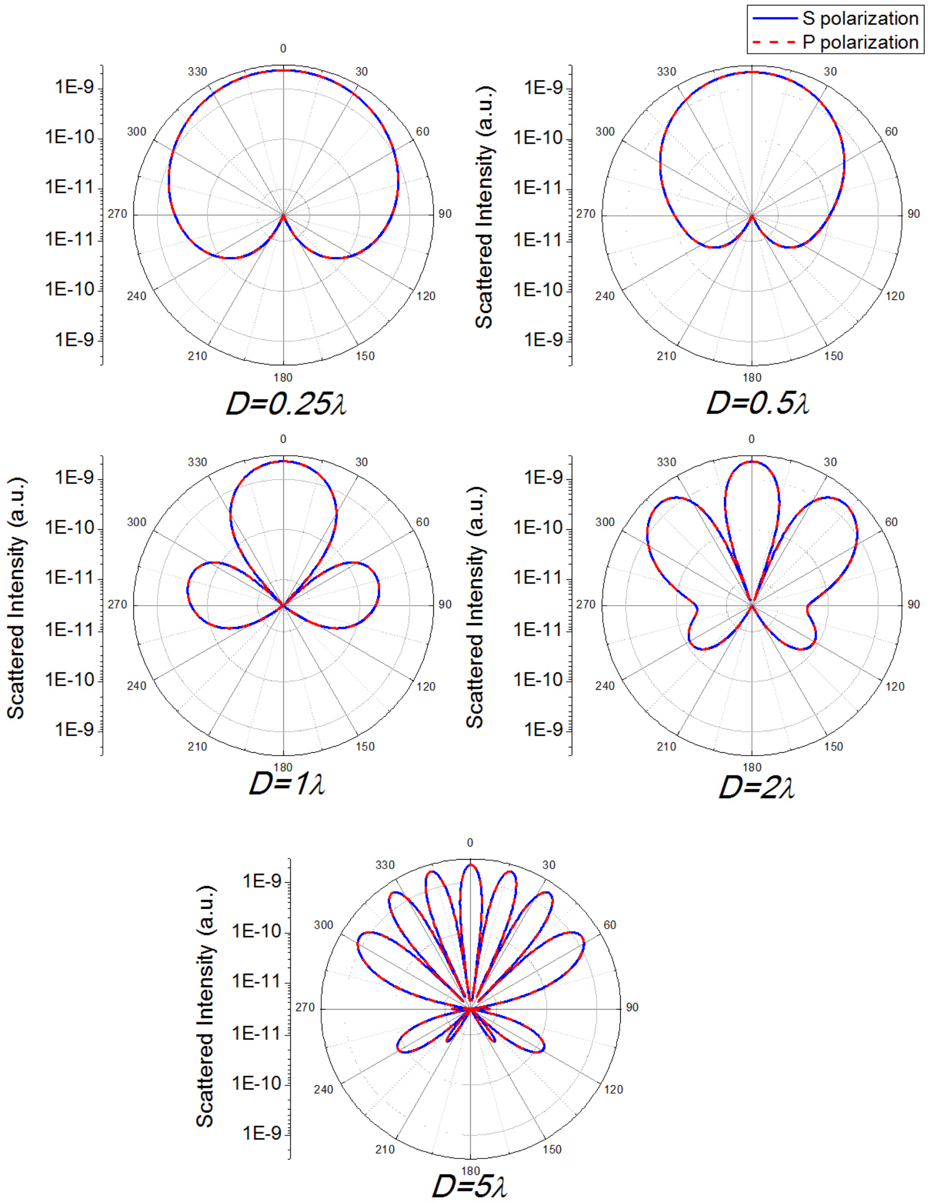

Figure 7.5: Polar distributions of light scattering by an array similar to the one described in figure 7.1(f) for several distances between the particles (*D* expressed in units of wavelength). Both incident polarizations, parallel (P) and perpendicular (S) to the scattering plane are considered.

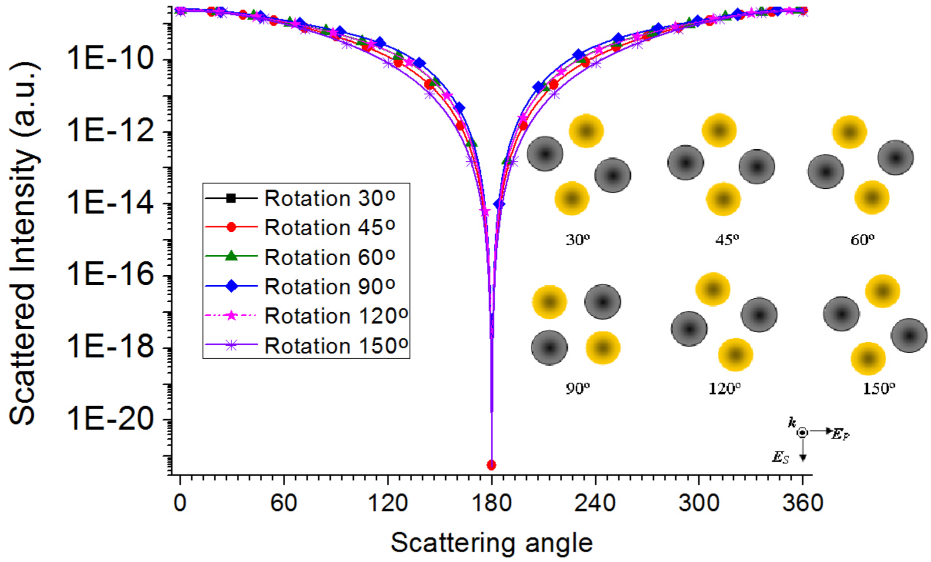

Figure 7.6: Scattered intensity for different arrays rotated around an axis parallel to the incident direction. The incident polarization is perpendicular to the scattering plane. The other polarization gives similar results. A scheme of the rotated arrays is included in the inset.

ternate" array around the axis as is shown in the inset of the figure. The distance between the particles is $D = 0.25\lambda$ and the incident wave is linearly polarized perpendicular to the scattering plane (S polarization). The system has a similar scattering behavior for both normal polarizations, as a particle fulfilling the zero-backward condition. It can be seen that the minimum backscattering is still clearly present under any rotation of the system. Only small differences can be observed for scattering angles around $90°$ and $270°$, due to the different geometrical configuration felt by the electric field at those angles. For example for the original array ($0°$) the electric field does not see any particle in the scattering plane at $90°$, but under a $45°$ rotation, the electric field sees a particle at this angle (see inset Figure 7.6). In spite of these small differences, we can conclude that the minimum scattering observed in the backward direction is almost independent of the position of the array in the normal plane. Any experimental misalignment would not change the scattering behavior of the array.

As we have shown in previous chapters, light scattering by small particles with electric and magnetic optical properties, fulfilling Kerker's conditions depends on the particle size. Its influence is limited to the sharpness of the minimum, but not on the shape. The pairs (ϵ, μ) satisfying the conditions are shifted slightly. Since the considered array behaves as a unique particle, we suppose that the dependence of it on the particle size will be very similar. As

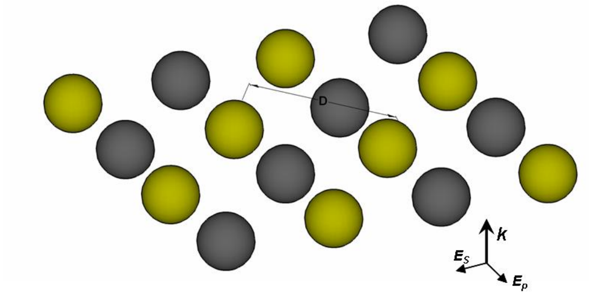

Figure 7.7: Scheme of an array with 16 nanoparticles ($R = 0.01\lambda$), either electric (dark) or magnetic (yellow) following the arrangement described previously.

the particle size increases, the minimum in the scattered intensity by the array at backward direction becomes less abrupt and the optical constants would have to be modified to obtain the sharpest minimum.

7.3. Extension of the Alternate-Array

The previous results are limited to a small number of particles. However, this array configuration can be used as a unit cell to generate a large composition with electric and magnetic particles as described in Figure 7.1(f), presenting similar scattering properties. As an example, we have studied an array composed by 16 particles, either electric or magnetic, placed as in the alternate array (Figure 7.7). As before, the array is placed on a plane that is perpendicular to the incident beam and the distance between the particles is fixed through the diagonal of the square (D). The incident beam is a linearly polarized plane wave. Both polarizations are considered: parallel (P) and perpendicular (S) to the scattering plane.

In Figure 7.8, we plot the polar distribution of the scattered intensity for a 16-particles array (Figure 7.7) considering several values for the distance parameter, D. As can be seen, the deep minimum in light scattering is still present in the backward direction confirming the double-negative and double-resonant behavior of the system. The angular range at which the minimum of the scattering intensity appears depends again on the particle distance. The angular width of the minimum reaches a maximum for the values of $D = 0.5\lambda$ and $D = \lambda$ with 120° around the backward direction while it is only 60° for other values of D. For a larger number of particles, due to interferential effects, the scattering patterns present a larger number of lobes and a more complex structure than the 4-particle case.

This system is even more stable than the 4-particle arrangement against geometrical mis-

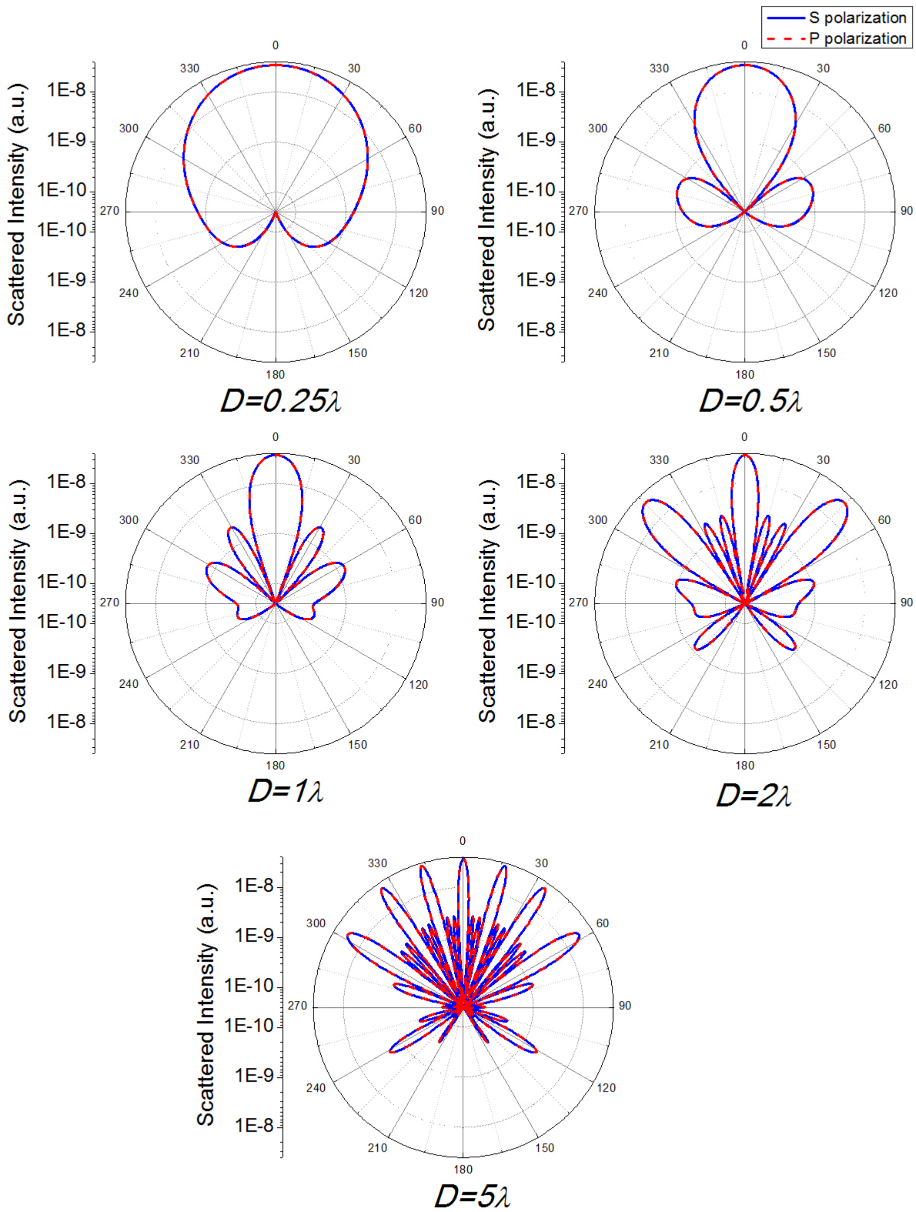

Figure 7.8: Scattering patterns, for both incident polarizations, corresponding to a 16-particles array as shown in figure 7.7 for several distances between the particles.

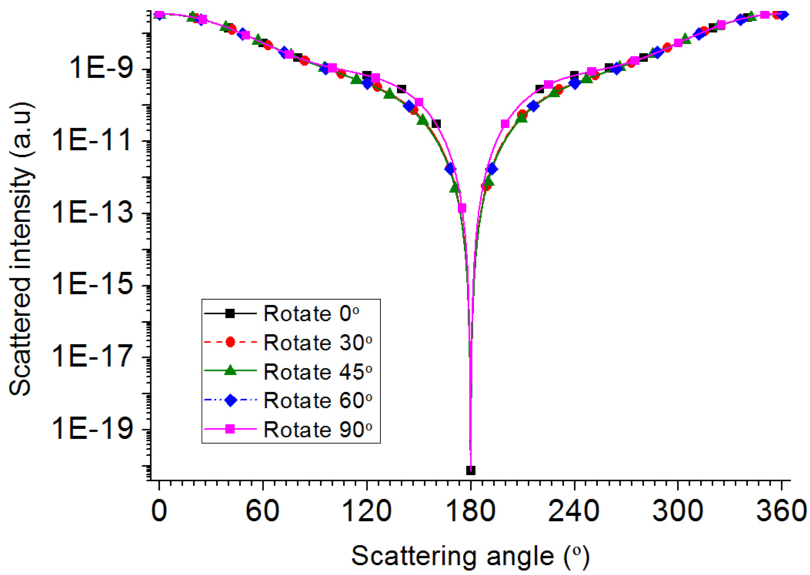

Figure 7.9: Scattering intensity, in semi-logarithmic axes, for a 16-particles alternate array with $D = 0.25\lambda$ as a function of the scattering angle and for different rotations of the system around an axis parallel to the incident direction. Only an incident S polarization is considered.

alignments. In Figure 7.9, the scattering intensity as a function of the scattering angle is plotted for a 16-particle alternate system with a distance parameter $D = 0.25\lambda$ and for several rotations of the system around an axis parallel to the incident direction and crossing the center of the system. The minimum in the backward direction, as can be seen, appears clearly for every rotation and without any remarkable change at other scattering angles. Differences between the original and the rotated arrays can be observed only in the range of scattering angles $[90° < \theta < 160°]$ and these differences are less pronounced than in the 4-particle case (see Figure 7.6). As it was commented before, the insensitivity of the system to any in-plane rotation is very important and helpful for possible future experimental implementations of these kind of systems.

7.3.1. Sensitivity of the Array to Mistakes in the Arrangement

The experimental techniques used to manufacture such systems could induce different kinds of errors in the arrangement. Besides, the larger an array, the higher the risk to place a particle inaccurately. The physics involved in this system is strongly linked to the position of the electric and magnetic particles in such a way that their contributions are compensated in the

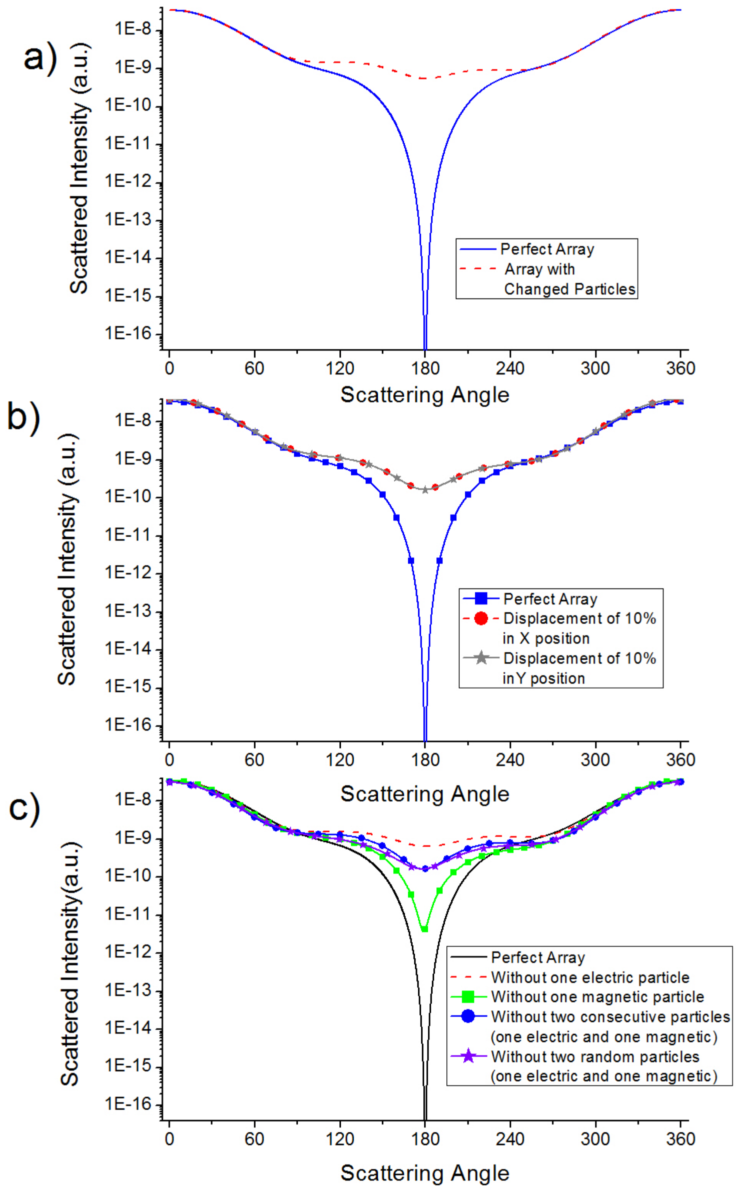

Figure 7.10: Comparison of the scattering intensity for a 16-particle array with and without placing errors. Different kinds of mistakes have been considered: (a) changing an electric particle by a magnetic one, (b) displacing one of the particles and (c) eliminating one or more particles of the array. For all of them, the incident beam is polarized with the electric field parallel to the scattering plane (P-polarization) and the distance between particles is $D = 0.25\lambda$

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backward direction. A positioning error, e.g. changing one electric particle with a magnetic one or viceversa, displacing one of the particles or even removing one or more particles from the array can destroy the compensation mechanism thereby changing the scattering behavior. In order to analyze these cases, we have considered a 16-particle array and induced each of these mistakes. The results are summarized in Figure 7.10. In it, we show the scattering intensity as a function of the scattering angle for an ideal 16-particle alternate array ($D = 0.25\lambda$) and for arrays with experimental mistakes: (a) on the particle's properties, (b) on the position of the particles and (c) when one or more particles are removed from the array.

Any of these mistakes on the arrangement destroys the minimum in the backward direction. The electric-magnetic compensation in the backward direction disappears when a simple error is induced in the array. This compensation is independent of the position of the experimental mistake.

7.3.2. Stacks of Arrays

Another interesting extension of the system consists in considering more than one layer [82]. A stack of several layers with similar or different configurations can be generated [15, 46, 16]. For this reason, we have considered a simple system composed of two layers of 16 particles one above the other and with a spacing d. Two cases have been studied: when the two layers are equal to the one shown in Figure 7.7 or when the layers are complementary. In this last case we consider that for each magnetic particle in the bottom layer, there is an electric particle in the top layer and vice versa.

The results of these systems are reported in Figure 7.11 where the scattering intensity is plotted as a function of the scattering angle, in semi-logarithmic scale, for both cases and a P incident polarization. The most remarkable feature in this figure is that the scattering pattern still shows the minimum backscattering. The electric and the magnetic contributions are equilibrated in the backward direction, independently of the similarity (Figure 7.11a) or not (Figure 7.11b) of the two layers. Also it is important to note that the scattered intensity at $180°$ is independent on the inter-particle (D) and inter-layer (d) distances. Their influence is only observed at other scattering angles for which interferential lobes appear. The incident polarization does not influence light scattering for this kind of geometries and similar results, shown in Figure 7.11, were obtained for an S incident polarization.

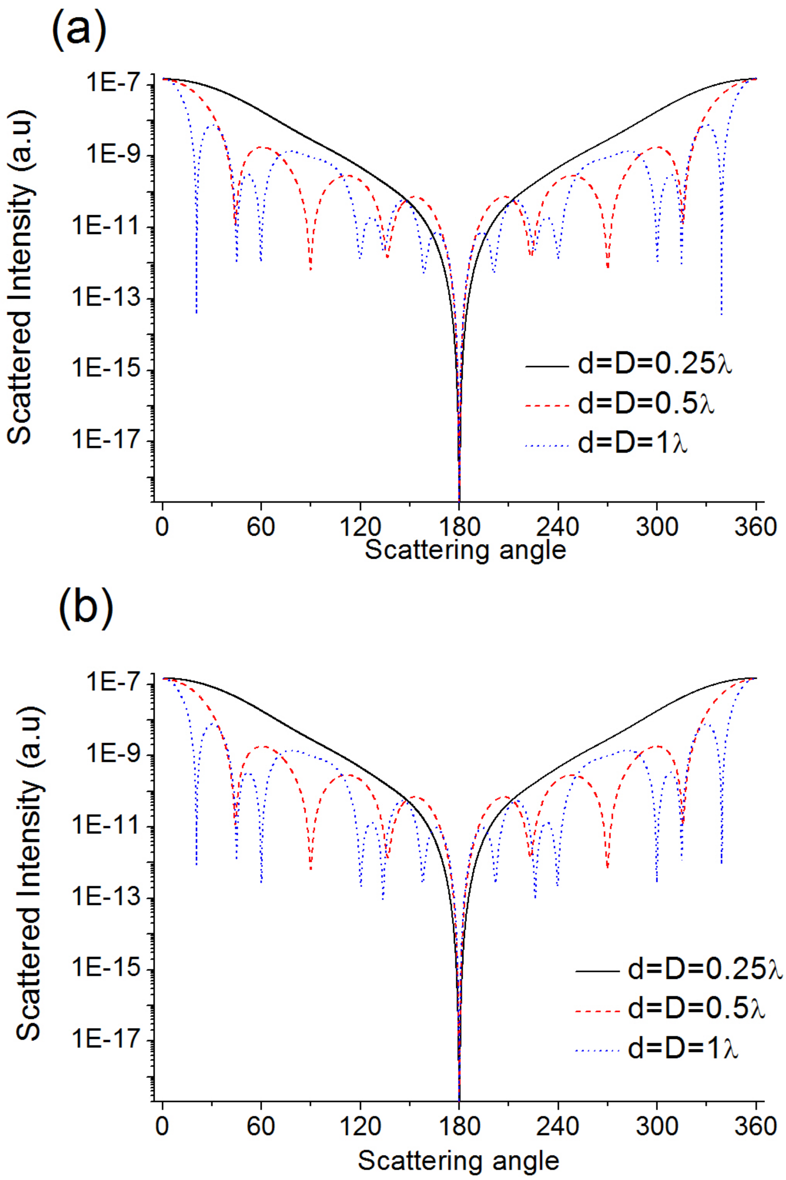

Figure 7.11: Scattered intensity as a function of the scattering angle for a system composed of (a) two arrays equal to the one showed in Figure 7.7 on top of each other and (b) two complementary arrays, one similar to Figure 7.7 and the other where an electric particle has been replaced by a magnetic one and vice versa. For both cases, the considered incident polarization is parallel to the scattering plane (P polarization). The distances between the particles (D) and the layers (d) are in units of wavelength.

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7.4. Conclusions

During this research, we have considered materials with unconventional optical properties, e.g. in the double-negative range. These values for the electric permittivity and the magnetic permeability are only obtained through the use of nanostructured materials, called *metamaterials*. Research efforts in the new field of metamaterials have grown exponentially in the last years due to their possible applications in, for instance, cloaking [135, 134, 82, 87, 66, 34]. Although the last studies have been able to create resonant magnetic nanoparticles [99], it is not yet possible to obtain metamaterials which are double-negative and double-resonant, electrically and magnetically at the same time.

In order to overcome this restriction, we have proposed the design of an arrangement composed of electric $(\epsilon, \mu) = (-2.01, 1)$ and magnetic $(\epsilon, \mu) = (1, -2.01)$ particles under certain geometrical conditions. It has been shown that the proposed system scatters like an isolated particle with a size similar to each subunit of the system and optical properties in the double-negative range: the effective electric permittivity is equal to that of the electric particles, while its magnetic permeability is that of the magnetic ones, that is $(\epsilon, \mu) = (-2.01, -2.01)$. In addition to the double resonance, one electric and one magnetic, the scattered intensity presents a minimum in the backward direction as it was predicted by Kerker et al [69]. In this work, we have demonstrated that for certain geometrical conditions, which we have called the "alternate" configuration, a minimum backscattering can be observed for an array of particles including a few or a large number of them. The lack of scattered light in the backward direction persists when more than one layer is considered. The scattering behavior of the proposed structure is independent of the inter-particle or inter-layer distances and also of any rotation of the array in the plane. However, it was observed that the minimum backscattering and then the double-negative behavior disappears when a manufacturing mistake (errors in the optical properties or position of the particles) is included. Although the system we studied in this chapter is a simple arrangement, it could be useful for the design and future implementation of double-negative systems. The interesting scattering properties of these systems could be also very interesting for the development of a new generation of devices, techniques or treatments based on the use of nanoparticles.