Scattering and absorption of light by periodic and nearly periodic metallodielectric structures

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Abstract. We consider the effect of different approximations to the dielectric function of a silver sphere on the absorption of light by two-dimensional and three-dimensional periodic and non-periodic arrays of non-overlapping silver spheres in a host dielectric medium. We present also some results on the band structure and the absorption coefficient of light by photonic crystals consisting of non-overlapping silver-coated spheres in a dielectric medium.

Keywords: photonic crystals, disorder, absorption, metallic particles.

Metallic particles, say spheres with diameters between 50 Å and a few thousand Å, distributed periodically or randomly on an insulating substrate [two-dimensional (2D) systems], or many layers of such particles [three-dimensional (3D) systems], have interesting optical properties and have been studied for a long time (Abelès et al., 1984). In recent years it has become possible to prepare such systems which are well defined (they are periodic arrangements of same spheres) and have remarkable optical properties. Depending on the size and distribution of the spheres, they can be very good absorbers of light (Taleb et al., 1999), or photonic crystals operating as non-absorbing mirrors within a certain frequency range of the electromagnetic (EM) spectrum (Zhang et al., 2000).

For a theoretical analysis of the optical properties of such systems, it is often necessary to go beyond the effective-medium treatment described by the Maxwell Garnett (MG) approximation (Bohren and Huffman, 1983). When the interparticle distance and (or) the size of the particles become(s)comparable with the wavelength of the EM radiation, or when the fractional volume occupied by the spheres is larger than 0.3 or so, the MG theory breaks down and one needs to solve Maxwell’s equations accurately for a proper description of the optical properties of these systems. In recent years, and mainly in relation

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to the study of photonic crystals, a number of methods have been developed which allow one to do so (Soukoulis, 1996).

Using our method of calculation (Modinos, 1987; Stefanou et al., 1992), we calculated the optical properties of periodic systems: 2D arrays of metallic spheres on a substrate (Stefanou and Modinos, 1991) and thicker slabs consisting of many layers of spheres (Yannopapas et al., 1999). We have also studied the effect of moderate disorder on the optical properties of the above systems, using a variation of the coherent potential approximation (CPA) (Stefanou and Modinos, 1993; Modinos et al., 2000). In most of the above papers we have assumed that the metallic spheres are plasma spheres, i.e. the optical properties of the isolated (single) sphere are described by a dielectric function

$$
\epsilon_p(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\tau)}
$$

(1)

where $\omega_p$ stands for the bulk plasma frequency of the metal and $\tau$ is the relaxation time of the conduction-band electrons. In the present paper we examine more closely the role of the optical properties of the single sphere in the determination of the optical properties of the composite system.

The dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i \epsilon_2(\omega)$ for bulk silver has been determined experimentally by Johnson and Christy (Johnson and Christy, 1972) over the range from $\hbar\omega = 0.64$ eV to $\hbar\omega = 6.60$ eV. With $\hbar\tau^{-1} = \hbar\tau_{b}^{-1} = 0.02$ eV and $\hbar\omega_p = 9.2$ eV [which is obtained from the well known formula: $\omega_p^2 = (4\pi e^2 n)/m$], Eq. (1) reproduces satisfactorily the experimentally determined $\epsilon_1(\omega)$ over the whole of the above frequency range, and the experimentally determined $\epsilon_2(\omega)$ at low frequencies ($\hbar\omega < 1.5$ eV). $\tau_b$ refers to the collision time of conduction-band electrons in the bulk metal; the collision time of an electron in a sphere of radius $S$ may be approximated by: $\tau^{-1} = \tau_b^{-1} + v_F S^{-1}$, where $v_F$ is the average velocity of an electron at the Fermi surface. For silver $v_F = 1.4 \cdot 10^6$ m/sec, so that for a sphere of radius $S = 50$ Å, using $\hbar\tau_{b}^{-1} = 0.02$ eV, we obtain $\hbar\tau^{-1} = 0.2$ eV. Therefore, a more realistic description of the dielectric function of a silver sphere would be (Abelès et al., 1984)

$$
\epsilon_S(\omega) = \epsilon(\omega) + \frac{\omega_p^2}{\omega(\omega + i\tau_{b}^{-1})} - \frac{\omega_p^2}{\omega(\omega + i\tau^{-1})}
$$

(2)

where $\epsilon(\omega)$ is the experimentally determined dielectric function of bulk silver. We note that $\epsilon_S(\omega)$ as given above, is different from the approximation to the dielectric function of the silver sphere obtained from Eq. (1) with $\hbar\omega_p = 9.2$ eV and $\hbar\tau^{-1} = 0.2$ eV only because
the imaginary part of the dielectric function is not represented well by Eq. (1) for \( \hbar \omega > 1.5 \text{ eV} \). We shall refer to Eq. (1), as the plasmonic approximation, to distinguish it from the more realistic representation of Eq. (2).

We consider a crystal of identical silver spheres centered on the sites of an fcc lattice, with lattice constant \( a \). We view the crystal as a stack of layers (planes of spheres) parallel to the (001) surface (which we assume parallel to the \( xy \) plane). For any given \( \mathbf{k}_\parallel = (k_x, k_y) \), we can calculate the real frequency lines: \( k_z = k_z(\omega, \mathbf{k}_\parallel) \). For any given \( \mathbf{k}_\parallel \), there may be, for a few frequency lines, regions of \( \omega \) over which \( k_z \) is real. These regions define the frequency bands of the EM field in the infinite crystal. In the absence of absorption (\( \tau = \infty \)) the band structure of a photonic crystal consisting of silver spheres in a non-absorbing host medium is determined solely by the real part of the dielectric function and is, therefore, the same whether we use Eq. (1) or Eq. (2) to describe the spheres. In Fig. 1a we show the band structure, for \( \mathbf{k}_\parallel = 0 \) [normal to the (001) surface], for a crystal where the fractional volume occupied by the spheres \( f = 0.3 \). The broken lines show the bands that are obtained using the MG approximation. The flat bands, which are not obtained in the effective-medium treatment, derive from \( 2^l \)-pole resonances \( (l > 1) \) of the individual spheres. Next to the band structure, in Fig. 1b, we show the transmission coefficient of light incident normally on a slab of the crystal consisting of 16 planes of
Figure 2. Absorbance of light incident normally on a 129-layers thick slab of the crystal described in the caption of Fig. 1, except that $\hbar \tau^{-1} = 0.2$ eV. The solid (broken) line is obtained with the realistic (plasmonic) dielectric function of the silver spheres.

spheres parallel to the (001) surface. The medium on either side of the slab has the same dielectric constant $\epsilon = 2.37$ as between the spheres of the slab. We see that the exact results agree with those of the MG treatment except in the region of the multipolar bands which, in the present case, are prominent as they fall within the frequency gap of the MG band structure. A detailed discussion of the band structure shown in Fig. 1 can be found elsewhere (Yannopapas et al., 1999).

We now turn our attention to the absorption coefficient of light which involves the imaginary part of the dielectric function of the silver spheres which, as we have seen, differs from that of plasma spheres. In Fig. 2 we show the absorption coefficient of light incident normally on a slab of the above crystal, 129-layers thick. The dip in the absorbance, in the region from $\hbar \omega \approx 3.2$ eV to $\hbar \omega \approx 5.2$ eV, corresponds to the frequency gap of the dipolar bands shown in Fig. 1a, and two relatively small peaks at about $\hbar \omega \approx 4.5$ eV are obviously the result of weak absorption by the multipolar bands, at about the same frequency, shown in Fig. 1a. When the more realistic approximation of Eq. (2) is used, the dip shrinks and with it disappears the fine structure associated with the multipolar bands, as shown by the solid line of Fig. 2. We note that the shrinking is effected asymmetrically and that the minimum of absorption now occurs at a lower frequency. We may add that the result represented by the solid line of Fig. 2 does not differ significantly from that obtained from the MG theory, when we use in the latter the dielectric function of Eq. (2). This, however, is not generally true.

In Fig. 3 we compare the absorbance by different systems as calculated using the plasmonic approximation for the single sphere with more realistic results based on Eq. (2). The two top diagrams, (a) and
Figure 3. Absorbance of light incident normally on a (001) slab of an fcc crystal of silver spheres ($S = 50$ Å, $\hbar\omega_p = 9.2$ eV, $\hbar\tau^{-1} = 0.2$ eV) in gelatine ($\epsilon = 2.37$). Slab of one layer: (a) plasmonic, (b) realistic dielectric function. Slab of 129 layers: (c) plasmonic, (d) realistic dielectric function. Solid lines: random occupancy of 75% of the lattice sites. Broken lines: ordered system with the same volume (surface) coverage by the spheres [30% (43%)] as for the disordered 3D(2D) system.

(b), refer to a single plane of spheres. The broken lines correspond to an ordered arrangement: the spheres are centred on a square lattice with a lattice constant $a_0 = 135.14$ Å. The solid lines correspond to a disordered arrangement: the spheres occupy at random a fraction $c = 0.75$ of the sites of a square lattice with a lattice constant $a'_0 = a_0 \sqrt{c}$, so that the average number of spheres per unit area is the same as for the ordered arrangement. The calculation of the absorbance for the disordered arrangement was done using a CPA formalism (Stefanou and Modinos, 1993). In relation to the ordered arrangements (2D and 3D) of plasma spheres we observe that the lower-frequency peak in the absorbance, which is due to dipolar absorption by the plasma oscillations is shifted slightly toward higher frequencies and it is wider than that obtained with the more realistic approximation of Eq. (2). Fine structure in the absorbance, which occurs at about $\hbar\omega \simeq 4.5$ eV in the plasmonic approximation, and which is due to multipolar absorption by the spheres, disappears altogether with the more realistic dielectric function of Eq. (2). This appears to explain why this fine structure has not been detected experimentally (Taleb et al., 1999). Finally, the absorption coefficient increases to an almost constant value at higher frequencies, $\hbar\omega > 4$ eV, when the spheres are described by Eq. (2). In contrast the absorption coefficient diminishes to almost zero for $\hbar\omega > 4$ eV in the plasmonic approximation.
In relation to the disordered 2D system, represented by the solid lines in Figs. 3a and 3b, we note the following. In the plasmonic approximation, disorder leads to increased absorption at all frequencies. When the spheres are described by Eq. (2) disorder leads to the appearance of an additional peak at $\hbar \omega \simeq 3.2$ eV where none existed for the ordered arrangement. The dipolar peak shifts to lower frequencies by about 0.2 eV, but the absorption associated with it is reduced in contrast with what happens in the plasmonic approximation. At higher frequencies, $\hbar \omega > 4$ eV, disorder leads to some further increase in absorption.

Figs. 3c and 3d refer to a (001) fcc slab, 129-layers thick. The ordered slab is viewed as a succession of the periodic planes of spheres considered in Figs. 3a and 3b, which corresponds to $f = 0.3$. In the disordered structure the spheres occupy 75% of the sites of an fcc lattice with a lattice constant $a = 173.65$ Å so that there is on average the same volume coverage by the spheres as in the ordered structure. The absorbance of the disordered 3D structure was calculated using a CPA method (Modinos et al., 2000). The physics underlying the absorption spectra of the 3D systems has been discussed in detail elsewhere (Yannopapas et al., 1999) in relation to the ordered structure, using the plasmonic approximation, represented by the broken line in Fig. 3c. The main peaks in the said absorbance curve, at $\hbar \omega \simeq 2.28$ eV and $\hbar \omega \simeq 5.96$ eV, are dipolar in origin and are associated with the plasma resonances of the individual spheres. The interaction between the spheres and with the host medium opens up the frequency gap shown in Fig. 1, and dipolar absorption, therefore, occurs mainly at and about the edges of this gap, leading to the two peaks mentioned above. The two lesser peaks, in between the above two, exhibited by the broken line of Fig. 3c are due to multipolar absorption by corresponding bands shown in Fig. 1a. The solid line in Fig. 3c shows that, in the plasmonic approximation, disorder increases the absorbance in the region between the dipolar peaks, but it does not remove the fine structure due to multipolar peaks. If anything, it adds to it; the additional structure derives from the fact that one deals with effective non-spherical scatterers in the CPA treatment of disorder (Modinos et al., 2000). In Fig. 3d we show the absorbance by a slab of the material, the same as that of Fig. 3c, except that the spheres are now described by Eq. (2). In this case the dip in dipolar absorption, associated with the frequency gap of Fig. 1, is compressed to lower frequencies, the fine structure in the dip practically disappears and the absorption coefficient increases to near unity for $\hbar \omega > 4$ eV.

We note that introducing disorder in a 2D system leads to a considerable shift and broadening of the main absorbance peaks, but in a 3D
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Figure 4. (a): The photonic band structure normal to the (001) surface of an fcc crystal of silver-coated spheres \((S_c = 1054.8 \ \text{Å}, \epsilon_c = 2.37, \ D = 50 \ \text{Å}, \ h\omega_p = 9.2 \ \text{eV}, \ \tau = \infty)\) in gelatine \((\epsilon = 2.37)\), with \(f = 0.3\). (b): The corresponding transmittance curve for light incident normally on a (001) slab, 16-layers thick, of the above crystal. (c): Absorbance of light incident normally on a 129-layers thick slab of the above crystal, except that \(h\tau^{-1} = 0.2 \ \text{eV}\).

Finally, we consider a 3D array of non-overlapping coated spheres centred on the sites of an fcc lattice. The radius of a coated sphere is denoted by \(S\); its core of radius \(S_c\) consists of dielectric material \((\epsilon_c = 2.37)\) and its outer shell of thickness \(D = S - S_c\) is assumed to be silver. There are two (dipolar) plasma resonances of an isolated coated sphere in a surrounding medium with a dielectric constant \(\epsilon\) given by (Bohren and Huffman, 1983)

\[
\omega_{pcs} = \frac{\omega_p}{(1 + K/2 + \frac{1}{2}(K^2 - 4\epsilon\epsilon_c)^{1/2})^{1/2}}
\]

where \(K = [\epsilon_c(1/2 + \beta) + \epsilon(2 + \beta)]/(1 - \beta)\) and \(\beta = (S_c/S)^3\). The frequencies \(\omega_{pcs}\), given by Eq. (3), are to be compared with the (dipolar) plasma resonance of a homogeneous silver sphere in the same host medium, \(\omega_{ps} = \omega_p/\sqrt{1 + 2\epsilon}\). We expect dipolar absorption by the crystal of coated spheres to occur in the region of \(\omega_{pcs}\) in the same way that absorption by a crystal of silver spheres occurs in the region of \(\omega_{ps}\). We note that the value of \(\omega_{pcs}\) corresponding to the plus sign of Eq. (3), when \(\beta\) is close to unity, is much smaller than \(\omega_{ps}\), and, as we have already noted, at these frequencies \((h\omega < 1.5 \ \text{eV})\), the plasmonic approximation is very good. The value of \(\omega_{pcs}\) corresponding to the minus sign of Eq. (3) is close to the plasma frequency of bulk silver \(\omega_p\), and we shall not deal with it, as it lies well above the optical region.

The scattering properties of the individual sphere enters the calculation through the \(T\)-matrix for the sphere. Using the \(T\)-matrix for the coated
sphere (Bohren and Huffman, 1983) in our formalism we calculated the band structure, shown in Fig. 4a, of an fcc crystal of non-absorbing silver-coated spheres with \( f = 0.3 \). This is to be compared with that of Fig. 1a for the crystal of homogeneous spheres. As expected, we find that the frequency gap associated with the dipolar plasma resonances of the spheres opens up at lower frequencies, in the vicinity of \( \hbar \omega_{pcs} \simeq 0.99 \) eV. The flat bands in Fig. 4a are multipolar bands as in Fig. 1a. Next to the frequency band structure, in Fig. 4b, we show the transmission coefficient of light incident normally on a slab of 16 layers. In Fig. 4c we show the absorption coefficient of light incident normally on a thicker slab of the same crystal, allowing for absorption by putting \( \hbar \tau^{-1} = 0.2 \) eV in Eq. (1). We see that the crystal of silver-coated spheres absorbs over a frequency range much lower than that of the crystal of homogeneous silver spheres. Which shows that by an appropriate choice of parameters we can vary the range of frequencies over which absorption of light takes place.

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