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1991 J. Phys.: Condens. Matter 3 8149

(http://iopscience.iop.org/0953-8984/3/41/013)

J. Phys.: Condens. Matter 3 (1991) 8149–8157. Printed in the UK

Optical properties of thin discontinuous metal films

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Received 27 February 1991, in final form 10 June 1991

Abstract. We present numerical calculations of the absorbance of light by a plane of metallic spheres. The absorbance is calculated as a function of frequency for s- and p-polarized light, for different angles of incidence and for different coverages. We demonstrate the importance of l-pole terms beyond the dipole ($l = 1$) term in interparticle scattering. We examine the effect of disorder and consider the influence of a dielectric substrate on the absorbance of the system consisting of a substrate plus adsorbed spheres.

1. Introduction

The optical properties of a thin discontinuous metal film which consists of a two-dimensional array of non-overlapping metallic particles are of considerable interest for technological reasons. In recent years a number of workers have presented results relating to the transmittance and absorbance of light by a variety of systems (see, e.g., [1, 2] and references therein) and calculations have been presented to account for the observed phenomena (see, e.g., [3, 4] and references therein). In most of these calculations the metal particles are replaced by interacting dipoles with a polarizability given by the Drude formula. The dielectric constant of the composite medium is then calculated using the Clausius–Mossotti equation or a variation of it to obtain the effective field on a given particle due to the presence of the other particles and the surrounding medium. These methods cannot be used when the size of the particles and/or the interparticle distance is of the order of the wavelength of the incident light or when the volume occupied by the spheres is about half or more of the total volume.

In our theoretical paper [5] (to be referred to as I) we presented a method for the calculation of the scattering (and absorbance) of light by a periodic two-dimensional array of spherical particles adsorbed on a uniform dielectric slab. By this method, multiple scattering of light between the particles of the overlayer and between the overlayer and the substrate is fully taken into account. In the present paper we present the results of numerical calculations made with the formulae in I and which aim to answer some important questions relating to the optical properties of the system under consideration. The system that we consider consists of a two-dimensional (plane) array of non-overlapping metallic spheres with radii of the order of 100 Å. We assume, to begin with, that the spheres are arrayed periodically on a square lattice; we use this system to test the convergence of our multiple series expansion of the wavefield (see I). We find that keeping only the dipole term ($l = 1$) is sufficient only for spheres with small radii and for a small concentration of spheres, and we demonstrate the importance of higher-order terms ($l > 1$) when the above conditions are not satisfied.

In real systems the particles are not arrayed periodically. We examine the effect of disorder by assuming a two-dimensional lattice with a fraction of its sites (chosen randomly) unoccupied. We calculate the absorbance of light by this system using an average **T**-matrix approximation as described earlier [6] and compare the result with the absorbance of a periodic structure with the same concentration of spheres.

Finally, we demonstrate the dependence of the optical properties of the discontinuous film on coverage (concentration of spheres), on the angle of incidence and on the polarization of the incident light.

It has been suggested by Yamaguchi *et al* [7] that the interplay between the discontinuous metal film and the substrate (a transparent dielectric slab) may have a significant effect on the optical properties of the system. They calculated that, in the case of a silver film on a poly(vinyl alcohol) (PVA) substrate, this leads to a shift of the absorption peak to longer wavelengths. We calculated, using the formulae in I, the absorbance of light by a plane of Ag spheres on a sheet of PVA taking into account the effect of the substrate. We did not find the shift of the absorption peak expected by Yamaguchi *et al*.

In all our calculations we assumed that the optical response of the individual metallic sphere is adequately described by the Drude dielectric function

$$\varepsilon(\omega) = 1 - \omega_p^2/\omega(\omega + i/\tau). \tag{1}$$

Following Persson and Liebsch [4] we have taken $\hbar\omega_p = 6.93$ eV and $\hbar\tau^{-1} = 0.158$ eV, which, it is assumed, are appropriate for silver particles.

We note that, in applying the formulae in I, only the term corresponding to $g = 0$ needs to be retained in all the cases examined.

2. Numerical results

2.1. Absorption of light by a single sphere

The number of partial waves $l = 1, 2, \ldots, l_{max}$ that need to be retained in the multiple-series expansion of the wave field to obtain convergence increases with increasing radius of the sphere. This is demonstrated in figure 1, which shows the calculated absorbance as a function of the photon energy for four different values of the radius S of the sphere. We see that for small spheres ($S \leqslant 100$ Å) the dipole approximation suffices in the treatment of the single sphere. The dotted curve in figure 1(a) is obtained in the electrostatic approximation (see I). The physical origin of the $l = 1$ resonance is well known; it corresponds to the excitation of a dipole plasma mode, relating to oscillations of induced charge on the surface of the sphere. For larger spheres, additional absorption peaks appear at higher frequencies which derive from l-pole resonances of corresponding plasma oscillations [8].

2.2. Multiple effects in interparticle scattering

We consider an array of spheres centred on the sites of a square lattice. The ratio S/a, where S and a, respectively, denote the radius of the spheres and the lattice constant,

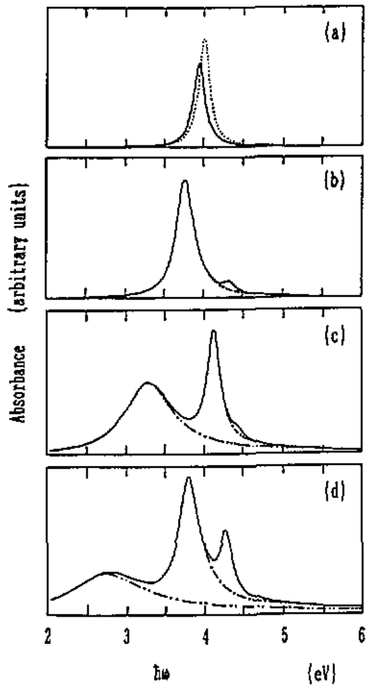

Figure 1. Absorbance of light of angular frequency ω by a single silver sphere of radius (*a*) $S = 100$ Å, (*b*) $S = 200$ Å, (*c*) $S = 400$ Å and (*d*) $S = 600$ Å: ———, $l_{max} = 4$; – – –, $l_{max} = 3$; – · –, $l_{max} = 2$; – · · · –, $l_{max} = 1$. The dotted curve in (*a*) is obtained in the electrostatic approximation.

determines the convergence of the multiple-series expansion of the wave field (l-convergence). We found that, provided that $S/a \leqslant 0.4$, good convergence is obtained if we keep l-pole terms up to and including $l_{max} = 4$. This is true for the entire range of optical wavelengths and for lattice constants ranging from 100 to 1000 Å. This is demonstrated in figure 2, which shows the absorbance by a square array of silver spheres, of light incident normally on the plane of the spheres. We note that the absorbance of a single sphere of radius 80 Å is determined entirely by the dipole ($l = 1$) term (see figure 1). Therefore, the l-pole ($l > 1$) contribution to the absorbance of the array of spheres comes through interparticle scattering of light which determines the total wave field incident on a given sphere in the manner described in I. We see that inclusion of higher l-pole terms is necessary for the correct description of interparticle scattering of light and that it leads to qualitatively new features in the absorbance curve. In the present case it leads to the appearance of a second absorption peak approximately 1 eV above the dipole peak.

2.3. *The effect of disorder*

We consider a two-dimensional (square) lattice and assume that a fraction, denoted by c, of its sites are occupied at random by identical spheres and that the remaining sites are empty. In the average **T**-matrix approximation (ATA) the partly empty lattice is replaced by a fully occupied lattice and the matrix **T** which describes the scattering of light by a single sphere (see I) is replaced by an average matrix given by $c\mathbf{T}$ [6]. We obtain a measure of the effect of disorder by comparing the absorbance of light by the disordered, partly empty lattice with lattice constant a, with that calculated for an

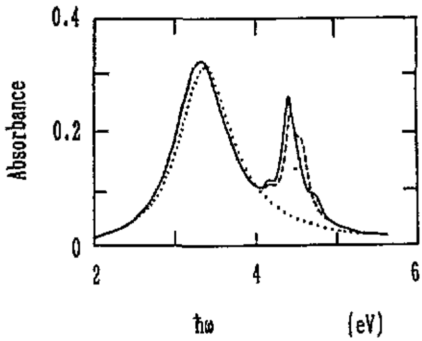

Figure 2. Absorbance of light of angular frequency ω, incident normally on a square array of silver spheres of radius $S = 80$ Å with lattice constant $a = 200$ Å: ———, $l_{max} = 6$; – – –, $l_{max} = 4$; · · · · , $l_{max} = 1$.

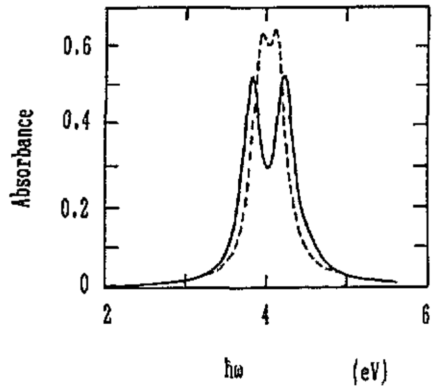

Figure 3. Absorbance of p-polarized light of angular frequency ω incident at an angle $\theta = \pi/4$ on a disordered array of silver spheres of radius $S = 80$ Å occupying randomly 25% of the sites of a square lattice of lattice constant $a = 200$ Å (———) and on an ordered square array of silver spheres of radius $S = 80$ Å with lattice constant $a = 400$ Å (– – –).

ordered fully occupied lattice with a lattice constant $a' = a/\sqrt{c}$, so that the coverage (number of spheres per unit area) is the same in both cases.

The result shown in figure 3 is obtained with p-polarized light incident at an angle (with the normal to the plane of spheres) $\theta = \pi/4$. The component of the wavevector parallel to the plane of spheres $k_{\parallel} = (k_x, k_y) = (k_{\parallel}, 0)$ and the electric field lies in the plane of incidence. The broken curve shows the absorbance of the ordered array ($a =$ 400 Å; $c = 1$; $S = 80$ Å). The low-energy peak at $\hbar\omega = 3.94$ eV corresponds to a parallel mode resonance, i.e. charge oscillating parallel to the plane of the spheres, excited by the component of the electric field parallel to this plane. The high-energy peak at $\hbar\omega =$ 4.10 eV corresponds to a normal mode resonance, i.e. charge oscillating normal to the plane of the spheres, excited by the component of the electric field normal to this plane. We note that the two peaks are shifted from the resonance peak of the single sphere (at $\hbar\omega = 4$ eV), the parallel mode towards lower frequencies and the normal mode towards higher frequencies. The full curve shows the absorbance of the disordered array ($a =$ 200 Å; $c = 0.25$; $S = 80$ Å). We see that disorder pushes the normal mode further up to higher frequencies and the parallel mode further down to lower frequencies.

The effect of disorder on the absorbance curve of a two-dimensional array of spheres has also been considered by Persson and Liebsch [4] in the dipole approximation using an approximate version of the coherent-potential approximation (CPA). In table 1 we compare the results of their calculation with those obtained by our method (ATA) with $l_{max} = 1$. In both cases, the disordered structure consists of a square array of lattice constant $a = 100$ Å, with a randomly occupied fraction of lattice sites $c = 0.3$, by spheres of radius $S = 50$ Å. The corresponding ordered array has a lattice constant $a' =$ 182.57 Å. We confirmed that in this case inclusion of higher l-poles does not change significantly the results shown in table 1. The table gives the shift of the parallel and normal mode absorbance peaks relative to the corresponding peaks of the corresponding ordered structure. These are denoted by $\Delta\Omega_{\parallel}$ and $\Delta\Omega_{\perp}$, respectively. We see from this

Table 1. Shift of absorbance peaks due to disorder.

	$\hbar\,\Delta\Omega_{\parallel}$ eV	$\hbar\,\Delta\Omega_{\perp}$ (eV)
ATA	−0.17	0.25
CPA	−0.60	0.40

table that the shifts predicted by the ATA calculation are in the same direction as but smaller than, especially in the case of the parallel mode, those of the CPA calculation. A reliable comparison with experimental data cannot be made at this stage because of other factors which enter into the determination of experimental spectra (see also next paragraph). We should point out that the ATA and CPA methods of treating disorder (both methods replace the disordered structure by an effective ordered structure) are the simplest possible. While appropriate for systems with weak or moderate disorder, at least for semiquantitative estimations, they are not appropriate in the case of strong disorder and in particular in those cases when such disorder may lead to localization of the wave field [9].

2.4. Variation in absorbance with coverage, angle of incidence and polarization of the incident light

We consider a square lattice ($a = 200$ Å) with a fraction c of its sites occupied randomly by spheres of radius $S = 80$ Å. We calculate the absorbance of light by such an array using the ATA formulla. In figure 4 we show the absorbance as a function of the photon energy for different coverages corresponding to $c = 0.25$, 0.75 and 1.00, respectively, for light incident normally on the plane of the spheres. In the limit $c = 0$ the absorbance curve (not shown in the figure) is given by a Lorentzian peak centred at $\hbar\omega = 4$ eV and corresponds to absorption by isolated spheres. The dotted curves are obtained in the dipole approximation ($l_{max} = 1$), and the full curves are obtained with higher l-pole terms included until convergence is obtained with $l_{max} = 4$. We have already noted in relation to figure 2 that the second peak owes its origin to the interparticle scattering of light which determines the total wave field incident on a given sphere. We see that the magnitude of this peak, which is not obtainable in the dipole approximation, increases with coverage.

In figure 5 we show the absorbance of s-polarized light as a function of the photon energy, for a given coverage ($c = 0.75$), for different angles of incidence corresponding to $\theta = 0, \pi/6, \pi/4$ and $\pi/3$. We see that the second absorbance peak is more pronounced at the larger angles of incidence. There is no experimental confirmation of the existence of this peak as far as we know. It may be that deviation from the spherical shape, which is not taken into account in our calculation, destroys this peak.

In figure 6 we show the absorbance as a function of the photon energy for different coverages corresponding to $c = 0.25$, 0.50 and 1.00 of p-polarized light incident at an angle $\theta = \pi/4$ ($k_{\parallel} = (k_{\parallel}, 0)$ and the electric field lies in the plane of incidence). The dotted curves are obtained in the dipole approximation. The lower-frequency absorbance peak corresponds to excitation of a parallel mode and the higher-frequency peak to excitation of a normal mode resonance by the corresponding components of the incident electric field. We see that with increasing coverage the parallel mode resonance is shifted towards

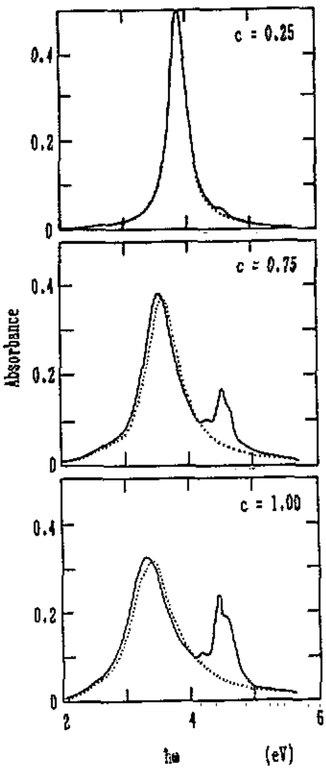

Figure 4. Absorbance of light of angular frequency ω, incident normally on a square lattice of lattice constant $a = 200$ Å with a fraction c of its sites occupied randomly by spheres of radius $S = 80$ Å: ———, $l_{max} = 4$; . . . , $l_{max} = 1$.

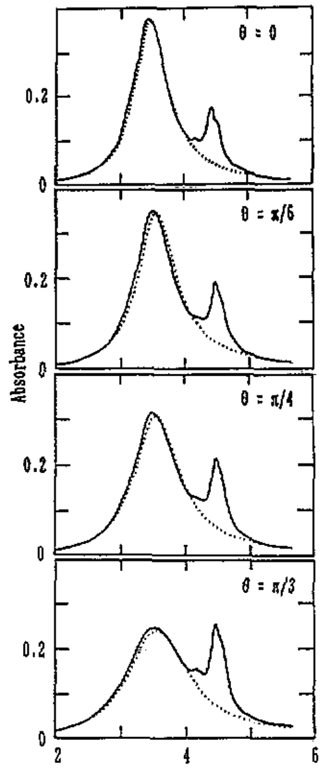

Figure 5. Absorbance of s-polarized light of angular frequency ω by an array of silver spheres of radius $S = 80$ Å occupying randomly 75% of a square lattice of lattice constant $a = 200$ Å, for various angles of incidence θ: ———, $l_{max} = 4$; . . . , $l_{max} = 1$.

lower frequencies and the normal mode resonance to higher frequencies in agreement with available experimental data (see figure 5 of Yamaguchi *et al* [7]). Inclusion of l-pole terms above the dipolar (convergence is obtained with $l_{max} = 4$) leads to additional structure as shown by the full curves in figure 6. This additional structure has not been observed experimentally, probably because of the deviation from spherical shape of the metal particles, as mentioned above.

In figure 7 we show the absorbance of a p-polarized light as a function of the photon energy, for a given coverage ($c = 0.75$) for different angles of incidence corresponding to $\theta = \pi/12, \pi/6$ and $\pi/3$. The dotted curves are obtained in the dipole approximation. We see that the intensity of the normal mode absorbance peak (higher in frequency) goes from zero (at $\theta = 0$) through a maximum, at about $\theta \simeq \pi/6$ or so, as the angle of incidence increases, whereas the intensity of the parallel mode resonance increases gradually with the angle of incidence. Inclusion of higher l-pole terms (convergence is obtained with $l_{max} = 4$) leads to additional structure in the absorbance curve as shown by the full curves in figure 7. Again it remains to be seen whether this structure survives when the deviation from the spherical shape of the metallic particles is introduced into the calculation.

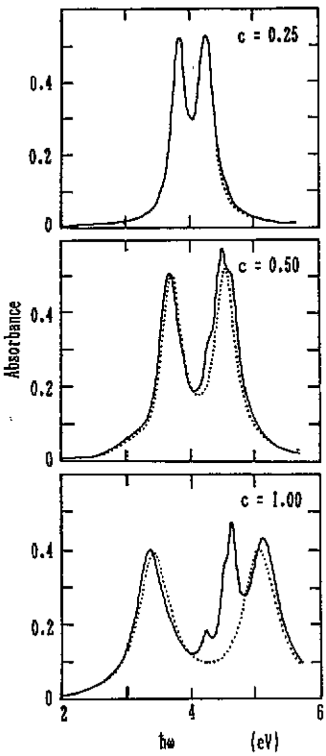

Figure 6. Absorbance of p-polarized light of angular frequency ω incident at an angle $\theta = \pi/4$ on an array of silver spheres of radius $S = 80$ Å occupying randomly a fraction c of the sites of a square lattice of lattice constant $a = 200$ Å: ———, $l_{max} = 4$; . . . , $l_{max} = 1$.

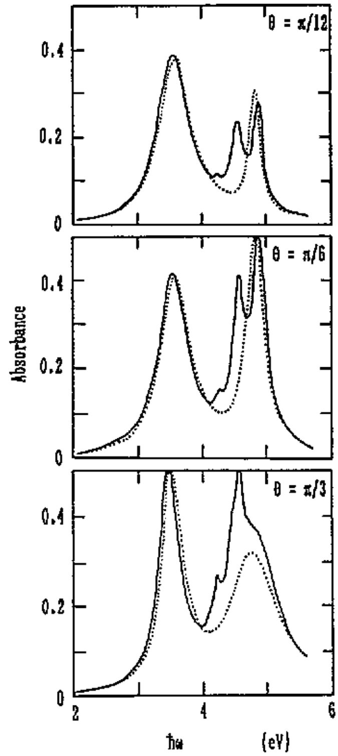

Figure 7. Absorbance of p-polarized light of angular frequency ω by an array of silver spheres of radius $S = 80$ Å occupying randomly 75% of the sites of a square lattice of lattice constant $a = 200$ Å, for various angles of incidence θ: ———, $l_{max} = 4$; . . . , $l_{max} = 1$.

For completeness we have also calculated for a specific case, besides the absorbance A, the transmittance T and the reflectance R as functions of frequency. These are shown in figure 8. We note that $T + R + A = 1$.

2.5. *Influence of the substrate*

Finally, we examine what the effect might be of the substrate, which supports the two-dimensional array of metallic spheres, on the absorbance of the system. This can be done in a straightforward manner without approximation using the formulae in I. We consider a square lattice with a fraction $c = 0.75$ of its sites randomly occupied on a substrate of PVA which has a dielectric constant $\varepsilon_s = 2.25$ [7]. The absorbance of the system (metal particles and substrate) varies periodically with the thickness of the substrate. We calculate an average absorbance (the average taken over a period of variation) assuming that the uncertainty in the thickness of the substrate exceeds optical wavelengths. The result of the calculation for light incident normally on the plane of the spheres is shown in figure 9. The broken curve shows the absorbance of the array of metal particles on its own, and the full curve shows the average absorbance of the

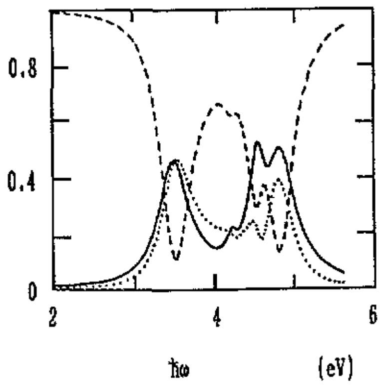

Figure 8. Absorbance (———), reflectance (. . .) and transmittance (– – –) of p-polarized light of angular frequency ω incident at an angle $\theta = \pi/4$ on an array of silver spheres of radius $S = 80$ Å occupying randomly 75% of the sites of a square lattice of lattice constant $a = 200$ Å.

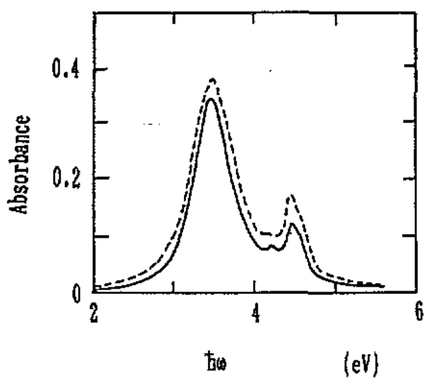

Figure 9. Absorbance of normally incident light of angular frequency ω on an array of silver spheres of radius $S = 80$ Å occupying randomly 75% of the sites of a square lattice of lattice constant $a = 200$ Å on a PVA substrate (———): – – –, absorbance by the coating layer of silver spheres alone.

complete system (metal particles on the PVA sheet) with multiple scattering of light between metal spheres and substrate taken into account. We see that there is no significant effect to be had from the interaction with the substrate, in contrast with the conclusion reached by Yamaguchi *et al* [7] whose approximate treatment of this interaction (the induced dipoles in the metal particles interact electrostatically with their mirror images in the substrate) predicts a shift of the absorption peaks to longer wavelengths.

3. Conclusion

We presented numerical calculations of the absorbance of light by a plane of silver spheres. We have shown that l-pole terms above the dipole ($l = 1$) term become important as the radius of the spheres increases, and/or as the concentration of spheres increases. Higher l-pole terms introduce new structure (peaks) in the absorbance curve through interparticle multiple scattering.

We have examined the effect of disorder in the ATA and shown that this leads to shifts in the absorption peaks comparable with but not so pronounced as those predicted in the dipole approximation by a CPA method.

We calculated the absorbance as a function of frequency for s- and p-polarized light, for different angles of incidence and different coverages.

Finally, we have examined the effect of the substrate (a dielectric slab) on the absorbance of the system: substrate plus adsorbed spheres. Our calculations do not justify earlier claims that interaction with the substrate leads to considerable shifts of the absorption peaks.

Acknowledgment

We thank V Karathanos for his assistance in the computation of the absorbance of single spheres.

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