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Nanocomposite material with the unit refractive index

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Abstract. **Optical properties of a composite medium comprised of metallic nanospheres located at the sites of a three-dimensional lattice and embedded into a dielectric matrix are considered. It is shown that for a certain ratio of the dielectric constants, the refractive index of the composite medium may be equal to unity. A method taking into account the delay effects during interaction of nanospheres with radiation has been developed to describe the optical properties of the composite medium. It is shown that in the limit when the distances between nanospheres are negligibly small compared to the wavelength, the results coincide with the results of the Maxwell – Garnett theory.**

Keywords: *metal – dielectric composites, heterogeneous media, photonic crystals.*

1. Introduction

In recent years, one-, two- and three-dimensional artificial structures have been often investigated. Photonic crystals, various heterogeneous media and microstructurised fibres can be used as such structures. A typical system of this type is a structure formed by metal particles embedded into a dielectric matrix. Such structures are often analysed using numerical methods, including the finite difference technique [1], the method of finite elements or the method of moments [2, 3]. However, such methods do not lead to a physical understanding of the properties of such structures. An alternative approach for describing composite structures involves the use of effective permittivity and effective permeability. This is usually done with the help of Maxwell – Garnett theory [4, 5]. However, this theory is inapplicable for particles occupying more than 30% of the volume of the composite medium. Moreover, the Maxwell – Garnett theory cannot be used if the separation between particles forming the composite medium is comparable with the wavelength of the external radiation. In all these cases, one has to resort to special methods for calculating the optical properties of composite materials [6 – 8].

In this paper, we propose a method for calculating the effective permittivity of a composite medium on the basis of an in-depth consideration of the delay in radiative interaction between the particles constituting the medium. This method allows us to calculate the optical properties of composite media in which the distance between the particles is comparable with the wavelength of the external radiation.

'Left-handed media' characterised by a negative refractive index and, consequently, unusual electromagnetic properties of the medium have been the subject of intense studies in recent years [9, 10]. Materials with a zero refractive index [11] are also interesting objects for investigations. The possibility of using composite materials for obtaining a high refractive index has been studied theoretically [12, 13]. In this work, we consider the possibility of producing a composite medium with the unit refractive index. The unit refractive index may be obtained in resonance media due to saturation of the interaction of high-intensity optical radiation with the medium [14]. In contrast to this, a strong saturating field is not required in the present analysis for producing a composite medium with unit refractive index. Moreover, an appropriate choice of parameters can ensure that the refractive index will be equal to unity over a wide spectral range. In this case, the phase velocity as well as group velocity of propagation of optical pulses in the composite will be equal to the velocity of light in vacuum. A composite material with unit refractive index can be used, for example, for preparing low-reflectance coatings.

Let us assume that a layer of the material with a complex refractive index $\tilde{n} = n + \mathrm{i}\kappa$ ($n = 1$, $\kappa \ll 1$) has been deposited on a perfectly reflecting surface. Let light be incident on this layer from vacuum. In this case, the amplitude coefficient of reflection from the layer is described by the expression [15]

$$r = \frac{r_{\mathrm{inf}} - \exp(2\mathrm{i}\psi)}{1 - r_{\mathrm{inf}}\exp(2\mathrm{i}\psi)}, \tag{1}$$

where r_{inf} is the amplitude coefficient of reflection from a semi-infinite heterogeneous medium. In the case of normal incidence of light, we can write

$$r_{\mathrm{inf}} = \frac{-\mathrm{i}\kappa}{2 + \mathrm{i}\kappa}. \tag{2}$$

It follows from this equation that $|r_{\mathrm{inf}}| \sim \kappa \ll 1$. For normal incidence of light, the quantity ψ in (1) is defined as

$$\psi = k_0 h(1 + \mathrm{i}\kappa),$$

where k_0 is the wave number in vacuum and h is the layer thickness. If the condition $h \geqslant 1/(k_0\kappa)$ is satisfied, the

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exponent in expression (1) becomes negligibly small and $r \approx r_{\inf}$, $|r| \ll 1$. In this case, light is practically not reflected from the layer.

Consider the properties of the components for producing a composite material with the unit refractive index.

2. Formulation of the problem

Consider a structure formed by identical spheres arranged at the sites of a regular periodic lattice. In order to determine the ratio of the optical constants of the components of the composite medium for obtaining the unit refractive index, we use the Maxwell–Garnett theory. According to this theory, the effective permittivity of a two-component heterogeneous medium is defined by the equation [4, 5]

$$\frac{\varepsilon_{\mathrm{mix}} - \varepsilon_{\mathrm{m}}}{\varepsilon_{\mathrm{mix}} + 2\varepsilon_{\mathrm{m}}} = \eta \frac{\varepsilon_{\mathrm{b}} - \varepsilon_{\mathrm{m}}}{\varepsilon_{\mathrm{b}} + 2\varepsilon_{\mathrm{m}}}, \tag{3}$$

where $\varepsilon_{\mathrm{mix}}$, ε_{m} and ε_{b} are the permittivities of the heterogeneous medium, matrix and the material of the spheres, respectively; and η is the relative volume occupied by the spheres. Since η can assume values only in the interval (0, 1), we obtain from Eqn (3)

$$\varepsilon_{\mathrm{b}} \in (-2\varepsilon_{\mathrm{m}}, 1). \tag{4}$$

If a dielectric with permittivity $\varepsilon_{\mathrm{m}} > 1$ is used as the material of the matrix, it follows from (4) that the permittivity of the material of the spheres must be negative in the spectral range in which we are interested. In the spectral range 200–2000 nm, only metals possess this property. In this paper, we consider the possibility of using silver as a material for the composite particles. This is due to the fact that unlike other metals, the permittivity of silver has a comparatively small imaginary part.

For the scattering at composite particles to be of the Rayleigh type and the composite to be treated as a homogeneous medium, the particle size must be much smaller than the wavelength. For a wavelength λ, the maximum radius of the nanosphere $r_{\mathrm{b}}^{\max}$ is determined by the expression [16]

$$r_{\mathrm{b}}^{\max} = \frac{\lambda}{2\pi|\varepsilon_{\mathrm{b}}|^{1/2}}. \tag{5}$$

For silver nanospheres, $r_{\mathrm{b}}^{\max} = 20$ and 30 nm for $\lambda = 800$ and 400 nm, respectively. For a relative volume $\eta = 0.1$ and radius $r_{\mathrm{b}} = 20$ nm of the nanospheres, the distance R_{b} between the centres of nanospheres is ~ 70 nm. The product kR_{b} ($k = 2\pi/\lambda$), which determines the magnitude of the delay, is much larger than zero in this case ($kR_{\mathrm{b}} \approx 0.8$ for $\lambda = 500$ nm). This means that the delay effects must play a significant role. Hence it is expedient to generalise Eqn (3) to the case when the separation between nanospheres cannot be treated as negligibly small compared to the wavelength.

3. Influence of delay effects on the optical properties of composite media

Consider a unit sphere with the permittivity ε_{b} placed in a medium with the permittivity ε_{m} at a considerable distance from the interfaces. It is well known [15] that a sphere placed in an external electric field $\boldsymbol{E}_1$ produces in its surrounding medium a field determined by a dipole with a moment

$$\boldsymbol{d}_{\mathrm{b}} = \alpha_{\mathrm{b}}\boldsymbol{E}_1 = r_{\mathrm{b}}^3 \frac{\varepsilon_{\mathrm{b}} - \varepsilon_{\mathrm{m}}}{\varepsilon_{\mathrm{b}} + 2\varepsilon_{\mathrm{m}}}\boldsymbol{E}_1. \tag{6}$$

where α_{b} is the polarisability of the nanospheres. If an electromagnetic wave of intensity $\boldsymbol{E}_1$ falls on the sphere, expression (6) remains valid under the condition that the size r_{b} of the sphere is small compared to the wavelength and the surrounding medium is not an amplifying one. Indeed, the field intensity inside the sphere can be treated as constant over the entire volume. If we take into account the effect of the medium on the polarisation of the sphere, we can confine the analysis just to the nearest zone, i.e., take into account only the electrostatic part of the scattered field.

Let us now assume that we have a set of nanospheres arranged at the sites of a regular periodic lattice. In analogy with the case of dipoles in vacuum [17], we define the field at the position of a nanosphere through the expression

$$\boldsymbol{E}(\boldsymbol{r}_i) = \boldsymbol{E}_1(\boldsymbol{r}_i) + \sum_j \nabla \times \nabla \times \boldsymbol{d}_{\mathrm{b}} G(R) + \mathrm{i}\frac{2}{3} k_{\mathrm{m}}^3 \boldsymbol{d}_{\mathrm{b}}, \tag{7}$$

where $G(R) = R^{-1}\exp(\mathrm{i}k_{\mathrm{m}}R)$ is the Green function for a dielectric medium with the permittivity ε_{m}; k_{m} is the wave number in the material of the matrix; and $R = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ is the distance between ith and jth nanospheres. Summation in Eqn (7) is carried out over all nanospheres except the ith one. Differentiation is performed with respect to the coordinates of the point of observation. Expression (7) differs from the analogous expression in [17] in the last term on the right hand side. This term takes into account the self-action of the dipole $\boldsymbol{d}_{\mathrm{b}}$ in terms of the scattered electromagnetic field and is responsible for the observance of the energy conservation law. It acquires a special significance in rarefied media [18]. According to the microscopic approach to the interaction of radiation with condensed media, the external wave is quenched at the interface between the media [17]. Let us assume that the field in the composite is a plane electromagnetic wave with a wave vector $\boldsymbol{k}_{\mathrm{mix}}$. This assumption is valid only for the points of observation at the centres of nanospheres. The polarising effect of the matrix on such points is taken into account in expression (6). In the case of points of observation lying in the dielectric matrix, one must also take into account the inhomogeneities of the field between nanospheres and seek the solution in a more complex form, e.g., as an expansion in plane waves.

By extending the summation in (7) to an infinite volume, we can assume that the external wave is quenched at infinity and omit $\boldsymbol{E}_1$ in (7). Multiplying both sides of Eqn (7) by the unit vector $\boldsymbol{e}$ directed along the polarisation vector of the external wave and dividing them by the amplitude of this wave, we obtain an equation for determining the effective refractive index of nanocomposite material n_{mix} taking into account the delay effects:

$$1 = \alpha_{\mathrm{b}}\boldsymbol{e}\sum \nabla \times \nabla \times \boldsymbol{e}\exp(\mathrm{i}k_{\mathrm{m}}R)\exp(\mathrm{i}\boldsymbol{k}_{\mathrm{mix}}\boldsymbol{R}) + \mathrm{i}\frac{2}{3}k_{\mathrm{m}}^3\alpha_{\mathrm{b}}, \tag{8}$$

where $k_{\mathrm{mix}} = n_{\mathrm{mix}}k_0$.

If the distance between nanospheres is negligibly small compared to wavelength, the sum in (8) can be replaced by an integral. Using the standard technique for obtaining an expression for the refractive index [17], it can be shown that expression (8) is transformed into (3).

It was mentioned above that the distance between nanoparticles for the composite under consideration cannot be treated as small in comparison with the wavelength. In this case, we use the Lorentz sphere method for calculating the lattice sums [18, 19]. In this method, it is assumed that nanospheres are distributed discretely inside a sphere of volume L_0, while the distribution of nanospheres can be treated as continuous outside this sphere. Moreover, when summation is replaced by integration for rarefied media outside the Lorentz sphere, additional correction terms must be taken into account [18]. Thus, Eqn (7) can be written in the form

$$\boldsymbol{E} = \boldsymbol{E}_1 + \boldsymbol{E}_\sigma + \boldsymbol{E}_\mathrm{b} + \int_\sigma \nabla \times \nabla \times N_\mathrm{b} \boldsymbol{d}_\mathrm{b} G(R) \mathrm{d}^3 \boldsymbol{r}', \qquad (9)$$

where $\boldsymbol{E}_\sigma$ describes the contribution from atoms inside a Lorentz sphere of volume σ, and N_b is the concentration of nanospheres in the dielectric matrix. Integration in (9) is carried out over the entire volume of the medium except the Lorentz sphere surrounding the point of observation. The term $\boldsymbol{E}_\mathrm{b}$ emerges upon a transition from summation to integration outside the Lorentz sphere due to the finiteness of the product $k_\mathrm{m} R_\mathrm{b}$. According to [18],

$$\boldsymbol{E}_\mathrm{b} = N_\mathrm{b} (k_\mathrm{m} R_\mathrm{b})^2 \hat{\gamma}_{\mathrm{b}0} \boldsymbol{d}_\mathrm{b} + N_\mathrm{b} R_\mathrm{b}^2 \hat{\gamma}_{\mathrm{b}2} \vdots (\nabla \nabla \boldsymbol{d}_\mathrm{b}).$$

We assume that the nanospheres are arranged at the sites of a simple cubic lattice. In this case, we can write [18]

$$\hat{\gamma}_{\mathrm{b}0} \boldsymbol{d}_\mathrm{b} = -\frac{\pi}{9} \boldsymbol{d}_\mathrm{b}, \quad \hat{\gamma}_{\mathrm{b}2} \vdots (\nabla \nabla \boldsymbol{d}_\mathrm{b}) = \frac{\pi}{30} \left(\frac{1}{3} \Delta \boldsymbol{d}_\mathrm{b} - \mathrm{grad}\, \mathrm{div}\, \boldsymbol{d}_\mathrm{b} \right).$$

The field $\boldsymbol{E}_\sigma$ can be determined by direct numerical calculation. Because the field $\boldsymbol{E}$ fluctuates about a certain value due to partial mismatching of the summation and integration regions upon a variation of the radius of Lorentz sphere, the radius of the Lorentz sphere in numerical computations varies from $2R_\mathrm{b}$ to several tens of R_b. For the final value, we averaged the values of $\boldsymbol{E}$ calculated for several values of L_0. The integral in (9) was evaluated analytically. Integration was carried out in the spherical system of coordinates over the entire space with the exception of the Lorentz sphere. The contribution from infinity was disregarded in this case. The final expression for the integral in (8) is cumbersome and will not be presented here.

4. Results of numerical calculations

By extending integration in (9) to infinite volume and omitting $\boldsymbol{E}_1$, we obtain an equation analogous to (8) for calculating the permittivity ε_m for the matrix of the material under the condition that the refractive index of the nanocomposite is equal to unity. During calculations, one must not overlook the fact that the optical properties of metallic nanospheres depend on their size. The quantum approach was used in [20] to determine the change in the optical properties a metallic sphere of a nanometre size. It was assumed that conduction electrons are contained in a potential well with infinitely high walls. In the present report, the variation of ε_b is estimated by using the classical model taking into account the limited mean free path of the electrons [21]. This model makes it possible to obtain an expression for ε_b in analytic form. According to this model, the finite size of metallic spheres leads to a variation of the relaxation rate of conduction band electrons. Accordingly, the electron relaxation rate γ in nanospheres is connected with the electron relaxation rate γ_0 in the bulk of the metal through the relation

$$\gamma = \gamma_0 + \upsilon_\mathrm{F} r_\mathrm{b}^{-1},$$

where υ_F is the mean velocity of electrons at the Fermi surface ($\upsilon_\mathrm{F} = 1.4 \times 10^6$ m s^{-1} for silver). The expression for the permittivity of the nanosphere has the form [22]

$$\varepsilon_\mathrm{b}(\omega) = \varepsilon_\mathrm{exp}(\omega) + \frac{\omega_\mathrm{p}^2}{\omega(\omega + \mathrm{i}\gamma_0)} - \frac{\omega_\mathrm{p}^2}{\omega(\omega + \mathrm{i}\gamma)}, \qquad (10)$$

where $\varepsilon_\mathrm{exp}(\omega)$ is the experimentally determined permittivity of the bulk sample; ω_p is the plasma frequency; and ω is the frequency of the external radiation. For silver, $\hbar\gamma_0 = 0.02$ eV and $\hbar\omega_\mathrm{p} = 9.2$ eV [22]. The value of the permittivity $\varepsilon_\mathrm{exp}(\omega)$ was borrowed from [23].

Figure 1 shows the results of numerical calculations of the refractive index n_m of the composite material matrix with the unit refractive index for the case of silver nanospheres. The same figure also shows the dependence of the refractive index of the matrix on the wavelength, obtained by using the Maxwell–Garnett formula (3). One can see that delay effects do not make any significant contribution to the variation of n_m for separations $R_\mathrm{b} \approx 30$ nm between nanospheres. However, the difference between the refractive indices n_m calculated by taking into account the delay effect and by disregarding them may attain several tens of percents even for $R_\mathrm{b} \approx 50$ nm.

One can see that the refractive index n_m of the dielectric matrix must be quite large for ensuring the condition $n_\mathrm{mix} = 1$. A decrease in the volume fraction η of nano-

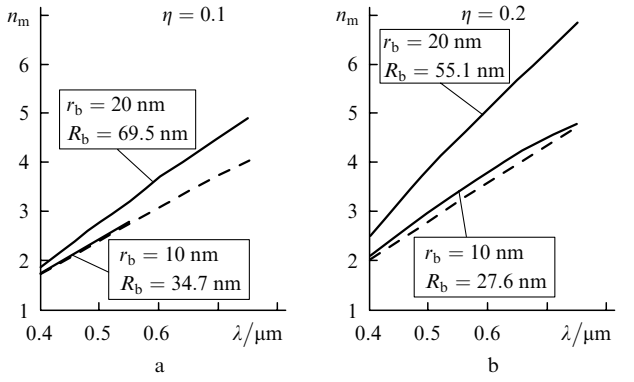

Figure 1. Dependences of the refractive index n_m of a matrix of a composite material with the unit refractive index on the wavelength λ of the external radiation for a relative volume of nanospheres $\eta = 0.1$ (a) and 0.2 (b), nanosphere radius $r_\mathrm{b} = 10$ and 20 nm and separation R_b between nanospheres equal to 34.7, 69.5 (a) and 27.6, 55.1 nm (b). The dashed curves show the dependence of n_m calculated by using the Maxwell–Garnett formula by neglecting the optical properties of nanospheres.

particles leads to a lower value of n_m. In this case, however, one can expect that the obtained composite will have a considerable dispersion on account of the fact that the lattice sum may be different for different directions of the vector $\boldsymbol{k}_{mix}$.

While carrying out calculations using formula (8) in this work, we assumed that the vector $\boldsymbol{k}_{mix}$ in the lattice of nanoparticles has a direction [0, 0, 1]. To reduce the spatial dispersion to a minimum, the Wigner–Seitz lattice cell of the nanospheres must assume a form closely resembling a sphere [19]. This happens, for example, for a body-centred cubic lattice or a lattice characteristic of diamond. Our calculations show that a decrease in the volume fraction of nanoparticles may also lead to a situation when the condition $\mathrm{Re}\, n_{mix} = 1$ may not be satisfied for any value of n_m. It follows from Fig. 1a that for $\eta = 0.1$ and $r_b = 10$ nm, the condition $\mathrm{Re}\, n_{mix} = 1$ cannot be satisfied for $\lambda > 550$ nm. For volume fractions $\eta < 0.05$ of nanoparticles, the refractive index of the composite medium does not become equal to unity in the entire optical range.

Figure 2 shows that the delay in interaction between nanospheres leads to an increase in the absorption coefficient of the composite material. Upon a decrease in the size of the nanospheres, the imaginary part of their permittivity increases. Nevertheless, the absorption of the composite can be decreased on the whole due to a weakening of delay effects upon a decrease in size and for a constant concentration of the nanospheres. It should be remarked that the technique used in this work for calculating the lattice sums does not permit a precise evaluation of the sum for $\mathrm{Im}(k_{mix} R_b) > 1$. For this reason, Fig. 2 shows the dependence of the absorption coefficients κ_{mix} on λ only for $r_b = 10$ nm and $\eta = 0.2$.

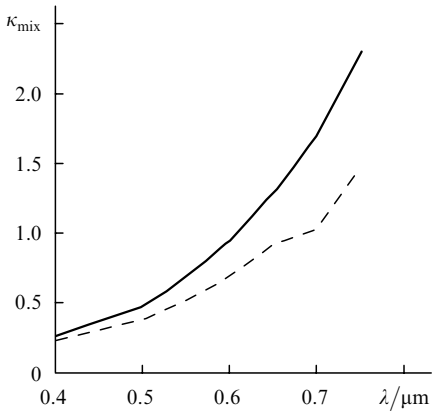

Figure 2. Absorption coefficient $\kappa_{mix} = \mathrm{Im}\, n_{mix}$ of a composite material with the unit refractive index for $\eta = 0.2$ and $r_b = 10$ nm. The solid curve is calculated by expression (8), and the dashed curve show is calculated by the Maxwell–Garnett formula.

One can see from Figs 1 and 2 that the conditions for obtaining the unit refractive index of a metal-insulator composite are most favourable in the blue spectral region. In this region, the required refractive index n_m of the medium is not too high and the absorption of the composite material is not expected to be too strong. For a wavelength 400 nm of the external radiation, we obtain $\kappa_{mix} = 0.25$. The coefficient of reflection from the semi-infinite nanocomposite medium is about 1 %.

One can try to reduce the absorption of the composite by selecting a metal with a lower imaginary part of the permittivity as a material for nanospheres. The absorption of the composite material can also be reduced if an active medium is used for the matrix [12, 13]. However, in view of the constraints applied during the derivation of Eqn (8), it can be expected that this equation (and hence the Maxwell–Garnett equation) is not applicable for active media. Indeed, the derivation of expression (6) and an analysis of the polarising influence of the surrounding medium on a nanosphere were carried out using the electrostatic approximation and considering the effect of only the part of the medium that occupies the near-field region. In the case of an amplifying medium, one cannot confine the analysis to the electrostatic approximation since the eliminated parts of the matrix will exert a very strong influence on the scattering nanosphere. Therefore, the extension of the model proposed here to the case of an active medium requires a separate analysis.

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