On the Effective Dielectric Permittivity of Nanocomposite Structures

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During the investigation of multicomponent nanodispersed structures using magnetic, optical, and magneto-optical methods, it was discovered that they don't follow the principles of classical physics. Undoubtedly, any experimental or theoretical research performed in this field is greatly Interesting as numerous aspects still remain enigmatic. The article considers a multicomponent nanodispersed structure consisting of randomly oriented ellipsoidal nanoparticles in a matrix with a permittivity ε_m. Formulas are obtained for calculating the effective dielectric permittivity of such a structure. It is shown that the calculation of the average value of the polarization of particles will be brought to the introduction of the effective value of the depolarization coefficient. The dependence of the effective dielectric permittivity of a single-component nanostructure on its structural parameters has been studied.

Keywords: Nanocomposite Structures, dielectric permittivity, depolarization coefficient.

Introduction

Effective medium methods are widely used to describe the optical properties of nanocomposite structures [1-13]. Today, these methods are used to describe both the optical and magneto-optical properties of nanocomposite structures. However, it should be noted that experimental data and theoretical results do not always agree [7, 8]. Therefore, the existing theory is not universally applicable and requires further development in this area. To this end, this paper discusses a multicomponent nanodispersed structure consisting of randomly oriented ellipsoidal nanoparticles in a matrix of dielectric permittivity ε_m, and the average value of the polarization of particles is calculated by introducing the effective value of the depolarization factor. Accounting for these conditions in the effective medium approach model is a novelty of the work, which will lead to refinement and improvement of this model.

A nanodispersed structure can be considered as a new homogeneous medium with an effective permittivity ε_{ef} , which has the same optical properties as the given nanodispersed structure. Since the size of nanoparticles and the distance between them is less than the wavelength of light in the medium, it is sufficient to restrict ourselves to the electrostatic approximation to calculate the effective permittivity ε_{ef} of such a medium [14].

In order to determine the effective optical constants of a composite medium, we must have knowledge of the optical properties of each component, including their concentration and shape. This can be accomplished through the effective medium model. To solve this problem, we must first address the single-particle problem. Specifically, we need to calculate the polarization of a nanoparticle of a predetermined shape when placed in an external electrostatic field.

Dielectric core polarization coefficient

Let us consider the case when the nanoparticles have an ellipsoidal shape. Unlike spherical particles, ellipsoidal particles are characterized by shape anisotropy. The polarization of particles depends on the shape, which is determined by the ratio of the principal axes of the ellipsoid and their orientation in an external electrostatic field.

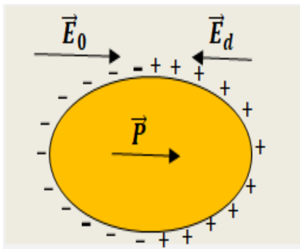

Fig. 1 Polarized ellipsoid

As theoretical calculations show [2, 12], uniform polarization of the ellipsoid occurs only if the external field E is oriented in the direction of one of the main axes of the ellipsoid $(i = a, b, c)$, and the depolarization field of the ellipsoid in any of these directions is expressed by the formula

$$\vec{E}_d = -4\pi f_i \vec{P} \qquad (1)$$

where P is the polarization vector and f is called the shape of the ellipsoid or the depolarization coefficient. It depends on the ratio of the principal axes of the ellipsoid and is calculated by the integral [2, 12]

$$f_i = \frac{abc}{2}\int_0^{\infty} \frac{ds}{(s+i^2)\left((s+a^2)(s+b^2)(s+c^2)\right)^{1/2}} \qquad (2)$$

The depolarization factors f_a, f_b and f_c satisfy the condition:

$$f_a + f_b + f_c = 1 \qquad (3)$$

Also, if $a < b < c$, then $f_a > f_b > f_c$.

Numerical values of the depolarization coefficients f_a, f_b and f_c for various ratios of a/b and b/c of the principal axes of the ellipsoid are displayed in Table 1.

Table 1. Numerical values of the depolarization coefficients f_a, f_b and f_c for various ratios of a/b and b/c of the principal axes of the ellipsoid

№	a/b	b/c	f_a	f_b	f_c
1	1/1	1/1	0,333	0,333	0,333
2	1/2	2/3	0,574	0,265	0,161
3	1/4	4/5	0,723	0,158	0,136
4	1/10	1/10	0,901	0,089	0,010
5	1/10	1/1	0,857	0,072	0,072
6	10/1	1/1	0,020	0,490	0,490

The calculations are much easier in the case of a spheroid (a rotating ellipsoid). The two principal equatorial axes of the spheroid are equal, $b = c \neq a$ and therefore $f_b = f_c \neq f_a$. In this case, the depolarization factor in the direction of the polar axis a will be reduced to an elementary integral of the following form:

$$f_a = \frac{ab^2}{2}\int_0^{\infty} \frac{ds}{(s+a^2)^{3/2}(s+b^2)} \quad (4)$$

In the case of a spheroid oblate concerning the polar axis a<b and an ellipsoid prolate with respect to the polar axis a>b, the solution of the integral (4) has the form

$$f_a = \begin{cases} \frac{1}{1-\vartheta^2}\left(1 - \frac{\vartheta}{\sqrt{1-\vartheta^2}} \cdot arcsin\left(\sqrt{1-\vartheta^2}\right)\right) & when\ a < b \\ \frac{1}{\vartheta^2-1}\left(\frac{\vartheta}{\sqrt{\vartheta^2-1}} \cdot ln\left(\vartheta + \sqrt{\vartheta^2-1}\right) - 1\right) & when\ a > b \end{cases} \quad (5)$$

Where $\boldsymbol{\vartheta} = \frac{\boldsymbol{a}}{\boldsymbol{b}}$.

Coefficient of depolarization relative to the equatorial axis is $f_b = f_c = \frac{1}{2}(1 - f_a)$.

Fig. 2 shows the dependence curves of the depolarization coefficients f_a and f_b on the parameter ϑ.

As can be seen from this graph, the shape factor of the spheroid changes both in the direction of the rotation axis (0; 1) and in the direction perpendicular to it (0; 0.5).

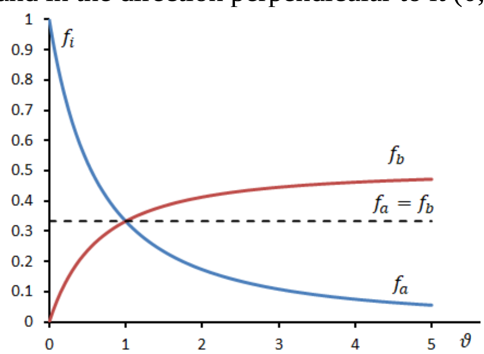

Fig. 2. The dependences of the depolarization coefficients f_a and f_b on the parameter ϑ for a spheroid

Let's take a look at the following cases:
1. $a = b = c$ - factor of nucleus depolarization is: $f_a = f_b = f_c$;
2. $a \gg b$ - a strongly elongated spheroid (needle) about the axis of rotation, form factor $f_a = 0$ along the axis of rotation and $f_b = \frac{1}{2}$ in its perpendicular direction;
3. $a \ll b$ - a spheroid that is highly flattened into a disk shape, $f_a = 1$ (direction perpendicular to the axis or plane of the disk) and $f_b = 0$ (directed perpendicular to the axis of the disk or along the plane).

Let us return to the problem of a dielectric ellipsoid and calculate the polarization of a nucleus with volume V and permittivity ε placed in an external electrostatic field $\vec{E}_0$. Let us assume that the medium around the nucleus is a vacuum. In this case, the local field strength acting on the particle, which is equal to the sum of the external $\vec{E}_0$ and depolarization $\vec{E}_d$ fields, is expressed by the formula:

$$\vec{E}_L = \vec{E}_0 - 4\pi f_i \vec{P} \tag{6}$$

For the dielectric susceptibility χ

$$\varepsilon = 1 + 4\pi\chi \tag{7}$$

and

$$\vec{P} = \chi \vec{E}_L \tag{8}$$

From formulas (6-8) we obtain the polarization vector:

$$\vec{P} = \frac{1}{4\pi} \cdot \frac{\varepsilon - 1}{1 + f(\varepsilon - 1)} \vec{E}_0. \tag{9}$$

The dipole moment acquired by a particle in an external field $\vec{E}_0$ is expressed by the formula

$$\vec{P}_0 = \vec{P} \cdot V = \frac{V}{4\pi} \cdot \frac{\varepsilon - 1}{1 + f(\varepsilon - 1)} \vec{E}_0 \tag{10}$$

Therefore, the polarization of a sphere with volume V and the permittivity ε in a vacuum will be equal to

$$\beta_i = \frac{\vec{P}_0}{\vec{E}_0} = \frac{V}{4\pi} \frac{\varepsilon - 1}{1 + f_i(\varepsilon - 1)} \tag{11}$$

and the polarization coefficient

$$\alpha_i = \frac{\vec{P}}{\vec{E}_0} = \frac{1}{4\pi} \frac{\varepsilon - 1}{1 + f_i(\varepsilon - 1)} \tag{12}$$

Suppose a particle whose permittivity is equal to ε is placed in a dielectric with permittivity ε_m. In this case, the problem will be reduced to determining the polarization coefficient of a particle of relative permittivity $\xi = \frac{\varepsilon}{\varepsilon_m}$ placed in a vacuum [14].

If we replace ε in formula (12) with relative permittivity $\xi = \varepsilon/\varepsilon_m$, we get for an ellipsoid, with permittivity ε and volume V, placed in the permittivity matrix $\boldsymbol{\varepsilon}_m$, the following formula for calculating the polarization coefficient:

$$\boldsymbol{\alpha}_i = \frac{1}{4\pi} \frac{\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_m}{\boldsymbol{\varepsilon}_m + \boldsymbol{f}_i(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_m)}. \tag{13}$$

Effective dielectric permittivity of a nanocomposite structure

Let us consider a multicomponent nanocomposite structure consisting of anisotropic nanoparticles (inserts) randomly distributed in a dielectric (matrix) with permittivity ε_m. To sort the particles according to the permittivity $\boldsymbol{\varepsilon}_i$ (i=1,2,3,· ··,n). In this case, the problem will also be reduced to determining the effective permittivity $\boldsymbol{\xi}_{ef} = \boldsymbol{\varepsilon}_{ef}/\boldsymbol{\varepsilon}_m$ of the same ensemble of particles with relative permittivity $\boldsymbol{\xi_i = \varepsilon_i/\varepsilon_m}$ placed in a vacuum. Suppose the particles have identical ellipsoid shapes and are oriented in the same direction, and the external field $\vec{E}_0$ acting on the environment is directed towards one of the main axes of the ellipsoids. Then there will be equal polarization of particles (Fig. 3).

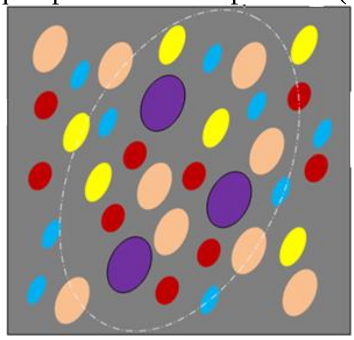

Fig.3. A model of a multicomponent nanocomposite.

In order to determine the average depolarization field $\vec{\boldsymbol{E}}_{\boldsymbol{d}}$ created by polarized particles, we make the assumption that these particles are situated within an ellipsoidal void that corresponds to their shape and orientation. In this case [13]:

$$\vec{E}_d = 4\pi f \vec{P} \tag{14}$$

Where $\boldsymbol{f}$ is the coefficient of depolarization of the ellipsoid in the direction of the field. The average value of the local field $\vec{\boldsymbol{E}}_{\boldsymbol{L}}$ acting on particles is equal to the sum of the average values of the fields $\vec{\boldsymbol{E}}_0$ and $\vec{\boldsymbol{E}}_{\boldsymbol{d}}$ directed in the direction of the main axis of the ellipsoids, and is expressed by the formula:

$$\vec{E}_L = \vec{E}_0 + 4\pi f \vec{P} \tag{15}$$

If the dielectric susceptibilities of a given medium are equal to $\boldsymbol{\chi_{ef}}$, then

$$\vec{P} = \chi_{ef} \vec{E}_L \tag{16}$$

and

$$\xi_{ef} = 1 + 4\pi\chi_{ef} \tag{17}$$

The polarization coefficient of ellipsoidal particles of permittivity $\boldsymbol{\xi_i}$ is determined by the formula (13):

$$\alpha_i = \frac{1}{4\pi}\frac{\xi_i - 1}{1 + f(\xi_i - 1)} \tag{18}$$

where $\boldsymbol{f}$ is the shape factor of the ellipsoid in the direction of the field. If the concentrations of particles with permittivities $\boldsymbol{\varepsilon_i}$ (i=1,2,3,· ··,n) are equal to n_i, and the volumes are V_i, then under the action of the field $\vec{\boldsymbol{E}}_{\boldsymbol{L}}$ the dipole moment of particles with permittivities $\boldsymbol{\xi_i}$ is equal to $\vec{p}_i = V_i \alpha_i \vec{E}_L$, and the polarization vector (the sum of the dipole moments of particles placed in a unit volume) will be equal to:

$$\vec{P} = \sum n_i V_i \alpha_i \cdot \vec{E}_L \tag{19}$$

By simple transformations from formulas (15), (16), (17), (18) and (19) we obtain:

$$\frac{\xi_{ef}-1}{1+f(\xi_{ef}-1)} = \sum q_i \cdot \frac{\xi_i-1}{1+f(\xi_i-1)} \quad (20)$$

where $q_i = n_i V_i$ is the volume fraction of particles of component i, i.e., volume fill factor. Note that the same result is obtained when considering different volumes of particles with permittivity ξ_i. In (20), when replacing $\xi_i = \varepsilon_i/\varepsilon_m$ and $\xi_{ef} = \varepsilon_{ef}/\varepsilon_m$, the formula for calculating the effective permittivity of the medium will be written as

$$\frac{\varepsilon_{ef}-\varepsilon_m}{\varepsilon_d+f(\varepsilon_{ef}-\varepsilon_m)} = \sum q_i \cdot \frac{\varepsilon_i-\varepsilon_m}{\varepsilon_d+f(\varepsilon_i-\varepsilon_m)} \quad (21)$$

(21) is a generalized formula for the Maxwell-Garnett effective medium model for a multicomponent nanodispersed medium with anisotropic constituent particles.

For a one-component nanocomposite medium $\varepsilon_i = \varepsilon$, $q_i = q$, from formula (6.8) we obtain the following formula for calculating the effective permittivity:

$$\varepsilon_{ef} = \varepsilon_m \left(1 + \frac{q(\varepsilon-\varepsilon_m)}{\varepsilon_m+f(1-q)(\varepsilon-\varepsilon_m)}\right) \quad (22)$$

Effective depolarization factor

In the case of randomly oriented particles of an elliptical shape, the average value of the ellipsoid polarization in the direction of the principal axes should be used:

$$\bar{\alpha_\iota} = \frac{1}{3}\sum \alpha_i = \frac{1}{3}\sum \frac{1}{4\pi} \cdot \frac{\varepsilon-\varepsilon_m}{\varepsilon_m+f_i(\varepsilon-\varepsilon_m)} = \frac{1}{12\pi}\sum \frac{\xi-1}{1+f_i(\xi-1)} \quad (23)$$

Let us explore whether it is possible to determine the average value of the polarization of the ellipsoid by introducing the effective form factor f_{ef}. If it is possible, then the value of f_{ef} will be in the interval [0;1] and fulfill the relation:

$$\bar{\alpha_\iota} = \frac{1}{4\pi} \frac{\varepsilon-\varepsilon_m}{\varepsilon_m+f_{ef}(\varepsilon-\varepsilon_m)} = \frac{1}{4\pi} \frac{\xi-1}{1+f_{ef}(\xi-1)} \quad (24)$$

From formulas (21) and (22) we can derive the following formula for the spheroid ($f_b = f_c \neq f_a$)

$$f_{ef} = \frac{1}{\xi-1} \cdot \left(\frac{3\cdot(1+(\xi-1)f_a)(1+(\xi-1)f_b)}{3+(\xi-1)(2f_a+f_b)} - 1\right) \quad (25)$$

Therefore, the effective shape factor is determined by the relative permittivity of the particle and the medium around the particle $\xi = \boldsymbol{\varepsilon/\varepsilon_m}$ and depends on the ratio of the principal axes of the spheroid $\boldsymbol{\vartheta = \frac{a}{b}}$.

Fig. 4 shows the dependence of f_{ef} on the relative permittivity ξ, considering the parameters ϑ=a/b with values of a>b, a=b, and a<b.

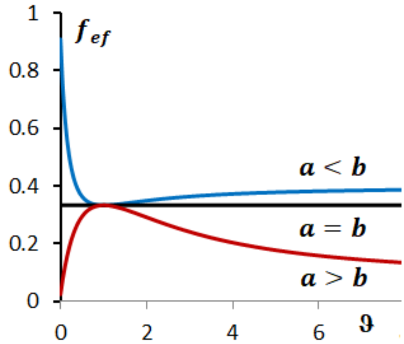

Fig. 4. Dependencies of the $\boldsymbol{f_{ef}}$ on the ξ with different $\boldsymbol{\vartheta}$

As shown in Fig. 4 the value of the effective depolarization factor is always in the range 0-1. This makes it possible to prove that an ensemble of anisotropic nanoparticles can be replaced by an ensemble of nanoparticles with a depolarization coefficient f_{ef} uniformly oriented with respect to the external electric field.

Taking into account the effective depolarization factor, formula (22) is written in the following form:

$$\varepsilon_{ef} = \varepsilon_m \left(1 + \frac{q(\varepsilon - \varepsilon_m)}{\varepsilon_m + f_{ef}(1-q)(\varepsilon - \varepsilon_m)}\right) \quad (26)$$

From formula (26) for given values of the parameters q, ε and ε_m, when f_{ef}=0, we obtain

$$\varepsilon_{ef} = q\varepsilon + (1-q)\varepsilon_m, \quad (27)$$

And when $f_{ef} = 1$ we get

$$\frac{1}{\varepsilon_{ef}} = \frac{q}{\varepsilon} + \frac{1-q}{\varepsilon_m} \quad (28)$$

For any configuration of nanocomposite structures, formulas (27) and (28) determine the minimum and maximum values of the effective dielectric permittivity.

Conclusions

The article considers a multicomponent nanodispersed structure consisting of randomly oriented ellipsoidal nanoparticles. Formulas are obtained for calculating the effective dielectric permittivity of such a structure. It has been demonstrated that if particles are randomly oriented, calculating the average value of the system's polarization vector can be simplified by introducing the effective form factor f_{ef}. Formulas are derived to calculate the upper and lower limits of effective permittivity for any configuration of a nanocomposite structure.

The article discusses nanoparticles with dielectric properties. When nanoparticles are conductors, the polarization coefficient, effective form factor, and effective permittivity are complex quantities and require additional research.

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