Light & Engineering
Vol. 27, No. 1, pp. 4–14, 2019

EFFECTIVE ELECTRODYNAMIC PARAMETERS OF NANO-COMPOSITE MEDIA AND THE THEORY OF HOMOGENISATION

Leon A. Apresyan

Prokhorov General Physics Institute of the Russian Academy of Sciences
E-mail: leon_apresyan@mail.ru

ABSTRACT

When creating new lighting and optoelectronic devices, great attention in recent years is paid to use nano-composite materials, i.e. the media containing impregnations of nanometre size, such as nano-particles of metals, quantum points, carbon nanotubes, graphenes, etc. This allows obtaining media with new, formerly unattainable characteristics. An initial point when describing properties of such medias is usually evaluation of their effective parameters (dielectric permeability, conductivity, heat conduction and of other similar transport coefficients) in the model of macroscopically heterogeneous media, in other words, media containing macroscopic impregnations with known or determined from experiments characteristics. Main approaches used in such cases are known Maxwell Garnett and Bruggeman approximations. In this review, methodical questions connected with various approaches to obtain these approximations and of their generalisations are discussed. Also some new results are given, which connected with evaluations of percolation thresholds within generalised Bruggeman approximations in the event of multi-component media.

Keywords: nano-composite media, effective parameters, quasistatic approximation, Maxwell Garnett approximation, Bruggeman approximation, percolation threshold, multi-component composites

1. INTRODUCTION

A constant improvement of lighting devices connected with development of modern technology applications, such as photovoltaic [1, 2] and optoelectronics [3–6], brings to the forefront the problem of creating new optical materials with unattainable formerly properties. This problem is solved in particular by obtaining new composite materials. If it comes to the purely optical aspect of the problem abstracting from numerous applications of composites, such as power mechanical, heat-conducting, etc. structures, then first it is about nano-composites, i.e. about the composites with non-uniformity size of tens nanometres. Such inclusions are various carbon structures (nano-tubes, graphenes, fullerenes), quantum dots, as well as metal nano-particles, which are used long since from the historical point of view. Study of such objects has led to creation of a new science direction known as nano-photonics, or otherwise as nano-optics [5, 6] being a subsection of general photonics, which is a science about transformation and propogation of photons within the interval from IR to ultraviolet.

Nano-photonics studies behaviour of light "compressed" to nanometre sizes, as well as its interaction with the nanometre objects. Both of these directions are interconnected. The first part is focused on overcoming the Rayleigh limit (i.e. impossibility of photon localisation in normal conditions on scales smaller than the wavelength) due to plasmon effects in metal nano-particles, nano-sized apertures or spires used in the near-field scanning microscopy. The second encloses study both of purely

quantum features of light interaction with single nano-objects, and of properties of ensembles with large number of N >> 1 particles, which is typical for the case of composite media. The prospective nano-photonics application field is extremely wide and includes both already quoted applications in solar photovoltaic and optoelectronics, and many other fields: lighting engineering, electrical engineering, biophysics and biochemistry, medicine, etc. Large lists of references are available in monographs [2–6].

Nano-sized particles with a good approximation can be considered as purely classical macro-objects with their macro-characteristics (dielectric and magnetic permeability, conductivity, heat conduction, etc.). Besides, they can be "corrected" if necessary to account micro-effects (such as limitation of electron free path length by the particle size [7]). If such inclusions are distributed in a composite spatially uniformly, then as the first step, the composite can be characterised using some averaged "effective parameters", which are closely connected with specific measurements and are often sufficient for the composite description corresponding to practical applications. In doing so, it is considered that the composite volume under study can be replaced when calculating with the same volume of a homogeneous medium described using effective parameters. A creation of models and calculation of such parameters is called homogenisation. And in materials science, "mixing formulas" (mixing rules) name is widely used instead of this term [8, 9]).

This review considers methodical questions of creating the main models used during homogenisation, as well as some new results connected with evaluation of percolation thresholds. The review is first of all intended for students and graduate students who are interested, how to obtain effective parameters and to use practically homogenisation methods. The reference list is very limited and mainly contains references to the last monographs and reviews, as well as to some very instructive classical works, which became available in Internet. Useful discussions of similar questions in reviews should be also noticed [10, 11]. The problems connected with description of single diffusers with plasmonics and quantum effects, as well as with optics of meta-materials [12, 13] and meta-surfaces [14] obtained by artificial of ordering nano-particles are not considered here. We will refer in this regard to the recently appeared monographs [14–19] describing electrodynamics of nano-particles. These monographs are suitable for a deeper study of the specified problems.

Methodical questions connected with a possibility of introduction of effective parameters are discussed in Section 2 (where, when, why). Approaches used to obtain most widespread approximations of homogenisation, namely: Maxwell Garnett (MG) approximation and of Bruggeman effective medium (Effective Medium Approximation, EMA) in the simplest model of spherical "effective cells" are discussed in Section 3. Generalisations of these approximations for the case of elliptic cells are described in Sections 4 and 5. Expressions for percolation thresholds in the generalised Bruggeman approximations are considered in Section 6. Main conclusions are briefly formulated in Section 7.

2. GENERAL REASONS

On the face of it, the "optics of composites" concept usually is at once associated with the need of the attraction of the multiple scattering theory, as composites inherently contain many of statistically distributed scattering non-uniformities. This is really so in case of a complete wave description of the problem.

Fortunately, it turns out that for composites with small-scale non-uniformities relative to the wavelength, simple heuristic models suitable both for description of experiments and for creation of composites with required properties are often rather well usable. Good results can be obtained when using even very rough characteristics of real composites, such as volumetric relations of the components. However, as inner structure of various composites with a set volume of the components can differ essentially, one cannot recon to obtain "universal" dependences of effective parameters on limited number of the composite characteristics equally suitable for a wide range of problems. When changing inner parameters of a composite, which control is usually difficult, or when changing the measurement method, or the used radiation wavelengths, different models of effective parameters can be claimed.

This explains a wide use in applications of various homogenisation models. So, the model choice to a large extent depends on intuition of the experi-

menter and on quality of the results obtained when customising free parameters.

A possibility of introduction of effective parameters is not obvious; it can be implemented not in all cases and depends not only on structure of the composite but also on the measurement method (see, e.g., an old review [20], where former and often unsuccessful attempts to replace insular films with equivalent uniform layers are discussed). A wide class of the problems, for which effective parameters are especially useful, is enclosed by the quasistatic approximation, when wavelength of the used radiation is big in comparison with the composite non-uniformities, and not precise characteristics of the field are measured but only averaged by space size, which is much more than the non-uniformity size. One can say that in doing so neither the wave, nor the observer "notice" small-scale fluctuations, which always take place, when the space size is of the medium non-uniformities size order. A strict description of such fluctuations is outside the effective parameters theory.

For small-scale composites, a close analogy of homogenisation with the classical fundamental problem of statistical substantiation of macroscopic electrodynamics exists. This analogy concerns the transition from micro- to macro-description of the observed values. Really, this transition means a possibility to use macroscopic, i.e. averaged by physically infinitely small environment volume characteristics to create electrodynamics of macroscopic bodies of any configuration. The difference is that if in statistical physics, atoms and molecules appear as primary micro-objects, which differ from each other not too essentially (except for the case of macromolecules), then in the event of composites they are replaced with macroscopic non-uniformities, which configuration can change in a random way within rather wide limits. In other words, a variety of inner structures for composites is much wider than for macroscopically uniform bodies usually considered in statistical physics. Therefore if to distract from quantum effects and from difference in freedom degree number, in some specified sense, a strict calculation of effective parameters gives much more many-sided problem than calculation of macro-characteristics of molecular objects.

The simplest composite version is a two-component mixture with volume component parts f_0 and f_1 (so that $f_0 + f_1 = 1$). For a more distinctness, we primarily consider a mixture of two dielectrics with dielectric permeability ε_0 and ε_1, though similar reasoning are also applicable for many other kinetic coefficients: electrical conductivity, heat conduction, diffusion coefficient, etc. [8]. Inherently, in each point of a composite, induction $\mathbf{D}(\mathbf{r})$ is expressed using dielectric permeability $\varepsilon(\mathrm{r})$ and electric field strength $\mathbf{E(r)}$ as $\mathbf{D}\ (\mathrm{r}) = \varepsilon(\mathrm{r})\mathbf{E(r)}$. In this connection, effective permeability ε^* is determined by the following relation:

$$\left\langle \mathbf{D}(\mathbf{r}) \right\rangle_v = \varepsilon^* \left\langle \mathbf{E}(\mathbf{r}) \right\rangle_v, \tag{1}$$

where angular brackets mean averaging over volume V,

$$\left\langle \ \right\rangle_v = \frac{1}{V}\int_V \ldots dr, \tag{2}$$

and instead of points there can be an arbitrary function $\mathbf{r}$. As V, "physically infinitely small volume" is selected. This volume contains many ($N >> 1$) non-uniformities, but it is small in comparison with the composite size. And it is supposed that statistical uniformity of a composite, as well as choice of the electromagnetic field source, allow considering averaged values of $\left\langle \mathbf{D}(\mathbf{r}) \right\rangle_v$ and $\left\langle \mathbf{E}(\mathbf{r}) \right\rangle_v$ to be constant, i.e. not dependent on the choice of point $\mathbf{r}$.

Effective dielectric permeability of a composite as function of volume parts should meet obvious "boundary conditions" (for clearness, it is written down as $\varepsilon^*(f_0, f_1)$):

$$\varepsilon^*(1,0) = \varepsilon_0, \ \ \varepsilon^*(0,1) = \varepsilon_1. \tag{3}$$

These conditions correspond to the full filling environment of one component. As a matter of fact, strictly speaking, condition (3) is not necessary for practical applicability of ε^* various models as suitability of most of them even for composite narrow classes is usually limited to some field of values of f_0 and f_1 only. Nevertheless, conditions (3) are performed in many empirical and simulation approximations for ε^* mentioned in the publications. But this fact should not mislead concerning their applicability with any relations of f_0 and f_1. Generally accomplishment of conditions (3) can be only considered as a courageous extrapolation of the considered model for the whole interval of f_0 and f_1 concentrations. The perturbation theory by concentration of one of the components, such as f_1, requires a smallness of this concentration in compa-

rison with 1 and naturally is unsuitable with $f_1 \sim 1$, though effective value ε^* calculated according to this theory sometimes can be also applied with f_1 concentration being not too small.

To obtain an expression for effective permittivity ε^* automatically meeting conditions (3), they often use a formal trick already going from classical works of Maxwell [21]: they empirically select function $F(\varepsilon(\mathbf{r}))$ so that ε^* is determined from equation:

$$F(\varepsilon^*) = \left\langle F(\varepsilon(r)) \right\rangle_v = f_0 F(\varepsilon_0) + f_1 F(\varepsilon_1).$$

In [22] this property is called additivity of $F(\varepsilon(\mathbf{r}))$. In this case, at uniform filling of a composite using dielectric with ε_0 or ε_1, fluctuations disappear and, averaging symbol can be omitted, which at once gives $\varepsilon^* = \varepsilon$, provided that F- is an unambiguously reversible function. In the referenced publications, for different problems, most different choices of the $F(x)$ function were used and are widely used up to now, namely: $F = x$, $1/x$, $x^{1/3}$, $\log x$, $\frac{1}{2}(x+1/x)$, etc. (see, e.g. the report of various approximations in [23]). It should be noticed that the MG approximation considered below can also be referred to this class, if to consider F to be depended on the dielectric permeability matrix.

By nature (or more precisely, by topology) of the spatial structure, composites can be usually separated into aggregates (statistically symmetric, like powder mixtures), and cermets (asymmetric), in which spatial distribution statistics of a matrix is other than statistics of fillers as it is in the event of environments with random impregnations (Fig. 1, [24]). In the first case, if consider topological aspects only, i.e. connectivity of a composite component, it is impossible to divide formally the matrix and the inclusions. Below we will mainly describe the cermet case, or otherwise media with random impregnations, when statistical properties of the components are various, and matrix can be separated from them (for definiteness, it will be the first component, i.e. f_0) and impregnations (it will be the second component, i.e. f_1).

Fig. 1. Topology of composites: (a) cermets: discrete impregnations into a matrix (b); aggregates: symmetric filling of a composite without selected matrix [23]

Most widespread approximations meeting these two topologies are Maxwell Garnett approximations [25][1], which in an elementary form are often written as the equation:

$$\frac{\varepsilon^* - \varepsilon_0}{\varepsilon^* + 2\varepsilon_0} = f_1 \frac{\varepsilon_1 - \varepsilon_0}{\varepsilon_1 + 2\varepsilon_0}, \qquad (4)$$

and symmetrical Bruggeman approximation of an effective medium [27].

$$f_0 \frac{\varepsilon_0 - \varepsilon^*}{\varepsilon_0 + 2\varepsilon^*} + f_1 \frac{\varepsilon_1 - \varepsilon^*}{\varepsilon_1 + 2\varepsilon^*} = 0, \qquad (5)$$

Another asymmetric Bruggeman approximation is also known but we don't consider it here.

Approximations (4) and (5) are based on use of the spherical particle model. When generalising these relations for the case of non-spherical particles, ellipsoid model is usually initial. It also is widely used in the referenced publications. In the elementary case of identical and equally oriented (mono-directed) ellipsoids, the medium becomes anisotropic, and relation (5) is transformed to the following:

$$f_0 \frac{\varepsilon_0 - \varepsilon^*}{\varepsilon^* + L_i(\varepsilon_0 - \varepsilon^*)} + f_1 \frac{\varepsilon_1 - \varepsilon^*}{\varepsilon^* + L_i(\varepsilon_1 - \varepsilon^*)} = 0, \qquad (6)$$

where L_i is depolarisation factor along the axis under consideration (see below). Relation (6) is correct for three orthogonal axes $i = x, y, z$ coinciding with main axes of the ellipsoid. If as L_i, normal depolarisation factors are used, which are determined for an isotropic medium, then (6) gives three independent equations for each of axes. This approximation is known as "traditional" [28, 29], and has

[1] Relation (4) is often called "Maxwell Garnett formula" connecting it by that with J. C. M Garnett [25], (one of his names was Maxwell). A more correct is "Maxwell-Garnett formula", which takes into consideration thereby the fundamental contribution of Maxwell who had obtained an equivalent result for conductivity long before Garnett [21]. An addition here of Rayleigh name who obtained this formula also before Garnett together with correction terms [26], would make it somewhat awkward, though more informative.

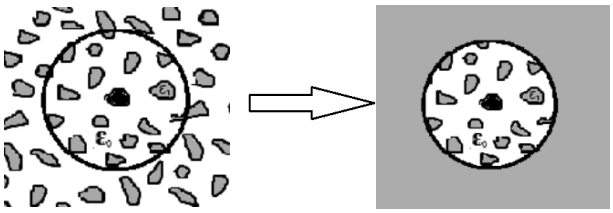

Fig. 2. Lorentz's sphere

been widely used in applications. In case of a more sequential approach [30], depolarisation factors as L_i in anisotropic medium differ from normal depolarisation factors [31]. And then (6) appears to be a more complex system of three connected equations (a comparison of these approaches is available in [29]). A successful use of equation (6) with "incorrect" depolarisation factors in some applications should not be surprising, if to take into account that all considered models are a consequence of use of a less exact approximation using L_i as adjustable parameters. It should be noticed that in the model of chaotically oriented ellipsoids, medium again becomes statistically isotropic, so even formal necessity to use depolarisation factors in anisotropic medium in this case is eliminated.

Any macroscopic composite is a particular case of non-uniform dielectrics with dielectric permeability $\varepsilon(\mathbf{r})$, which is a complex function of spatial co-ordinate **r**. As in practical situations, $\varepsilon(\mathbf{r})$ distribution in each point is not measured and some external parameter values are only recorded (like components relation) and $\varepsilon(\mathbf{r})$. As a result, ***E(r)*** can be considered as some random fields [32]. In case when their spatial correlations quickly decrease (a spatial ergodicity takes place), averaging with respect to volume can be replaced by statistical averaging [32]. Such replacement of volumetric averaging by averaging over a statistical ensemble will be used below.

Equations (4) – (6) can be solved easily, if explicit dependences $\varepsilon^*(f_0, f_1, \varepsilon_1, \varepsilon_2)$, are obtained. However, generally accepted configurations of equations (4) – (6) are convenient first to compare with other versions of these theories, and secondly as observance of boundary conditions (3) follows from them with evidence. Though formally approximation (4) is derived for the case of cermet topology, and (5) and (6) are for aggregates, both these approximations are often used independently from the composite expected topology. Let's consider the main approaches to obtain these approximations.

3. HOMOGENISATION METHODS

In the referenced publications, many various approaches to obtain approximations (4) – (6) and their generalisations are described. We give briefly most widespread of them. As these approaches are multiply repeated in the publications, we don't give numerous references to the sources (see, e.g., [8–11]).

Lorentz sphere method is most widespread when obtaining the considered approximations. Each diffuser is mentally surrounded with a big sphere (Fig. 2), and it is considered that effective field E_L near it is composed from averaged $\langle E \rangle$ plus Lorentz field $\langle P \rangle / 3\varepsilon_0$ (in the CGS system $4\pi \langle P \rangle / 3$) from diffusers out of the sphere, which are considered as point dipoles with polarizability α_1 "smeared out" into continuous environment $E_L = \langle E \rangle + \langle P \rangle / 3\varepsilon_0$, where $\langle P \rangle$is average polarization. And field of particles inside the sphere is considered on average to be equal to zero in the centre of the sphere, which is correct not in all cases (see, e.g., discussion in the classical textbook [33]. Supposing that average polarization $\langle P \rangle = n\alpha_1 E_L$, where $n = N/V$ is average number of particles in the volume unit, it is easy to obtain the known Clausius-Mossotti formula (it is also named Lorentz-Lorentz formula, if it is written down for particles in vacuum refraction index $\sqrt{\varepsilon^*}$).

$$\frac{\varepsilon^* - \varepsilon_0}{\varepsilon^* + 2\varepsilon_0} = \frac{n\alpha_1}{3\varepsilon_0}. \qquad (7)$$

Replacement of polarizability of dot dipoles $\alpha_1$with the well-known polarizability of volume v_1 sphere with dielectric constant ε_1 (see, e.g., [9])[2],

$$\alpha_1 = 3v_1 \frac{\varepsilon_1 - \varepsilon_0}{\varepsilon_1 + 2\varepsilon_0}\varepsilon_0, \qquad (8)$$

[2] It should be noticed that different authors determine polarizability of a particle in dielectric medium with ε_0 differently: either as in (6): $\alpha = P/E$ [9], or as $P/(\varepsilon_0 E)$ [7], where P is particle dipolar moment, which should not lead to misunderstanding.

transforms (7) into MG formula (4). The same relation (7) is often used to generalise MG approximation to more complex particle sets, for which it is enough to substitute the sum of the correspondent polarizabilities in (7) instead of $n\,\alpha_1$. So for example, for a set of n_i spherical particles with different dielectric permeability ε_i, i = 1.2,…, we have from (7):

$$\frac{\varepsilon^* - \varepsilon_0}{\varepsilon^* + 2\varepsilon_0} = \sum_{i\geq 1} \frac{n_i \alpha_i}{3\varepsilon_0}. \qquad (9)$$

Equivalent scatterer method originates from classical studies of Maxwell [21]. Spherical volume V of a composite is selected with non-uniformities interpreted as spherical impregnations of dielectric permeability ε_i in matrix ε_m, where ε_m is a heuristically selected free parameter (Fig. 3). Effective permittivity ε^* is selected from the requirement that scattered field far from V coincides with a scattered field with uniform filling of volume V by medium with dielectric permeability ε^* provided that the particles are sufficiently rarefied and that they scatter independently from each other. For this purpose, it is enough to equate polarizability of a uniform sphere to the sum of the polarizabilities of the particles of the composite sphere, which gives as follows:

$$\mathrm{V}\frac{\varepsilon^* - \varepsilon_\mathrm{m}}{\varepsilon^* + 2\varepsilon_\mathrm{m1}} = \mathrm{v}_0 \frac{\varepsilon_0 - \varepsilon_\mathrm{m}}{\varepsilon_0 + 2\varepsilon_\mathrm{m}} + \mathrm{v}_1 \frac{\varepsilon_1 - \varepsilon_\mathrm{m}}{\varepsilon_1 + 2\varepsilon_\mathrm{m}},$$

or as $f_i = v_i/V$,

$$\frac{\varepsilon^* - \varepsilon_m}{\varepsilon^* + 2\varepsilon_m} = f_0 \frac{\varepsilon_0 - \varepsilon_m}{\varepsilon_0 + 2\varepsilon_m} + f_1 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}. \qquad (10)$$

Believing here $\varepsilon_m = \varepsilon_0$, we obtain MG approximation (4), and with $\varepsilon_m = \varepsilon^*$ it is Bruggeman approximation (5). It should be noticed that in work [34], the considered condition was extended to the general case as a requirement of absence of scattering towards "forward" in the effective medium. Having replaced spherical objects with ellipsoids everywhere, it is easy to obtain by the same generalisation method these approximations for the case of anisotropic particles, as well as for the case of anisotropic composites (if such particles are fractionally or completely ordered).

Macroscopic averaging method uses a direct averaging **D**(**r**) and **E(r)** over volume with the ε^* determination (1). An advantage of this approach

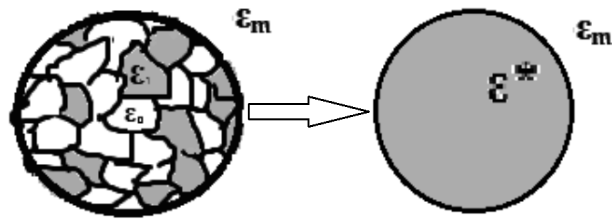

Fig. 3. Equivalent scatterer method

is more obvious description of the accepted approximations, which allows estimating at least qualitatively, conditions of applicability of final results. Let's turn our attention to it in more detail based on our work [35].

Let's consider the general case of medium with random (generally non-uniform) impregnations (cermet), divide the whole considered volume V into two parts, $V = V_0 + V_1$ so that V_0 corresponds to points of matrix **r**, and that $V_1 = \sum_{i=1}^{N} v_i$ corresponds to points of particles with volumes v_i.

Dividing the full integral when averaging over volume V into sum of integrals by partial volumes, it is easy to obtain in accordance with (1):

$$\varepsilon^* = \frac{\langle \mathbf{D}(\mathbf{r}) \rangle_v}{\langle \mathbf{E}(\mathbf{r}) \rangle_v} = \frac{f_0 \langle \varepsilon(\mathbf{r})\mathbf{E}(\mathbf{r}) \rangle_{v_0} + f_1 \langle \varepsilon(\mathbf{r})\mathbf{E}(\mathbf{r}) \rangle_p}{f_0 \langle \mathbf{E}(\mathbf{r}) \rangle_{v_0} + f_1 \langle \mathbf{E}(\mathbf{r}) \rangle_p}. \qquad (11)$$

Here $f_i = V_i/V$ is the matrix material volume fraction (i = 0), or particles fraction (i = 1), $f_0 + f_1 = 1$, (substantiation of formal operation of division by vector (9) can be found in [35]). Brackets with index p mean averaging with respect to particle ensemble of the following type:

$$\langle \ldots \rangle_p \equiv \sum_{i=1}^{N} P_i \langle \ldots \rangle_{v_i}, \qquad (12)$$

and $P_i = v_i/V_1$ is ratio of i particle within volume of all particles, which can be interpreted as a conventional probability "to meet" this particle among all particles, so $\sum_{i=1}^{N} P_i = 1$.

Relation (11) is exact formally, if to consider distributions of ε(**r**) and of E(**r**) field in the composite as known. Though at present, computing abilities allow carrying out computer simulations with

simultaneous estimation of **E(r)** and of applicability of different models [36], in most of practical situations, these distributions can be considered as stochastic functions, which exact values are not recorded in experiments. But to obtain approximations (4) – (6), as well as their generalizations, it is enough to use simple statistical hypotheses about particle typical configuration and on "typical values" of the field inside and out of them. Thereby averaging with respect to volumes of medium and particles is heuristically replaced with a statistical averaging over volumes of some "effective cells". Selecting such cells of different structures and setting field distribution **E(r)** out and inside them, one can obtain different approximations for ε^*.

4. MAXWELL-GARNETT APPROXIMATION

The main assumption necessary to obtain MG approximation from (11) is that particles on average can be considered as being in the uniform external field. To obtain MG approximation (4) from (11), it is enough to consider that all particles are uniform, have identical dielectric permeability ε_1, as well as identical spherical shape, and the field out of the particles is accepted to be equal to the uniform field E_0 without particles. Instead we will at once consider generalisation (4) for a case of chaotically oriented elliptic particles with random distribution of depolarisation factors L_i. The field within such a particle in the uniform external field $\mathbf{E_0}$ is also uniform and expressed using the known relation:

$$\mathbf{E}_{in} = \Lambda \mathbf{E}_0, \tag{13}$$

where tensor Λ is expressed by means of a depolarisation tensor being diagonal in the ellipsoid main axes $L = \mathrm{diag}(L_1, L_2, L_3)$ as

$$\Lambda = \frac{1}{1 + L\left(\frac{\varepsilon_1}{\varepsilon_0} - 1\right)}. \tag{14}$$

Here and below we don't add special designations for tensor values considering that their nature is clear from the context. The division in (14) is understood as a matrix inversion, and explicit expressions for depolarisation factors Li are well-known[3] and are not written here (see e.g. Section 4 [22]; (1 in (14) is the symbol of unit matrix). With due regard to (13), formula (11) can be written as

$$\frac{\varepsilon^*}{\varepsilon_0} = 1 + \frac{f_1 \langle \alpha \rangle}{1 - f_1 \langle L\alpha \rangle}, \tag{15}$$

where

$$\alpha = \frac{\alpha_1}{\varepsilon_0 v_1} = (\varepsilon_1 - \varepsilon_0)\Lambda \tag{16}$$

is the tensor of specific polarizability of the ellipsoid, and symbol of full statistical averaging $\langle \ldots \rangle$ includes both averaging with respect to orientation, which is limited to calculating 1/3 of tensor trace, and averaging with respect to random distribution of depolarization factors connected with the particle configuration. So

$$\langle \ldots \rangle = \frac{1}{3} \mathrm{Sp}\Lambda \langle \ldots \rangle_L, \tag{17}$$

where $\mathrm{Sp}\Lambda = \Lambda_1 + \Lambda_2 + \Lambda_3$, $\Lambda_i = (1 + L_i (\frac{\varepsilon_1}{\varepsilon_0} - 1))^{-1}$.

To implement averaging over L, one should set a model of random distribution for depolarization factors L_i. For particles of identical configuration with prescribed L_i, averaging with respect to L in (17) can be omitted. We will not fix on it here in more detail (see, e.g., [7], section 12.2.5). A similar expression (15) can be also obtained in the event of partially ordered orientations of ellipsoids, when the composite becomes anisotropic, and ε^* becomes tensor.

If particles have a different nature, besides with random dielectric permeability ε_i, then averaging over L in (17) should be added with a statistical averaging over ε_i, which expands the class of the permissible composites with multi-component fillers.

The considered method to obtain MG allows at least a qualitative estimating applicability condi-

[3] Nevertheless, there are various readings in the referenced publications: so for example, in known monograph [7] when determining ellipsoid depolarization factors, polarizability relative to vacuum but not to medium is considered, which forces to add new depolarization factors depending on dielectric permeability of the medium and on the ellipsoid besides normal depolarization factors named in [7] as geometrical factors.

tions for this approximation. Indeed, each particle is considered on average as distant enough from its neighbours, and this requires a smallness of the effects connected with fields scattered by particles, as well as with "adhesion" of particles. This places upper limit for particle relative volume f_1 (so as such limitation, condition $f_1 < 0.4$ is considered in [37]).

Applications of MG approximation are extremely broad. It should be noticed as examples only, interesting evaluations of composites with refractive indices both high [38], and close to zero [39], as well as antiglare optical composite coatings [40].

As in the event of dielectric matrices in MG approximation, each particle is considered to be surrounded with non-conducting dielectric, for metal (well conducting) particles, this approximation allows describing the so-called conductivity resonance connected with electron movement limitation by particle volume [41]. One can find a more detailed discussion of this question for example in [37]. From the other side, for the same reason MG approximation does not describe emergence of percolation threshold (or otherwise, percolation phenomenon [42]), because it excludes a possibility of particle contact. This phenomenon consists in emergence a dielectric-metal junction in the specified composite with increase of the conducting phase concentration f_1 not beginning from $f_1 = 0$ but after some threshold value f_{1c} is only achieved [42]. This disadvantage can be eliminated in the self-coordinated Bruggeman approximation, which even in the elementary form (5) allows qualitative describing emergence of percolation threshold.

5. BRUGGEMAN APPROXIMATION IN MODELS OF ELLIPTIC CELLS

To obtain this approximation from (11), it is enough to accept the following "effective cells" model: effective cells are ellipsoids filled with the correspondent material (with ε_0 for environment points and with ε_1 for particles). The self-coordination condition consists in that each such cell is considered to be placed into an "effective medium" with dielectric permeability ε^*, in which field is regarded as uniform and equal to an average field $\langle \mathbf{E} \rangle$ (Fig. 4).

In an elementary model leading to (5), instead of ellipsoids a sphere is used, for which $L_1 = L_2 = L_3 = 1/3$.

Now let's consider a more general model of chaotically oriented ellipsoids, for which medium is statistically isotropic with scalar effective dielectric permeability ε^*. In this approximation, the field both in medium points, and in particles is expressed using relation (13), where an average field $\langle \mathbf{E} \rangle$ appears as an external field $\mathbf{E}_0$, and tensor corresponding to ellipsoids Λ is presented as expression (14) with different depolarization tensors $L^{(0)}$ for medium points and $L^{(1)}$ for particles (we will further designate these tensors as $\Lambda^{(i)}$). In this model of "effective cells", configuration of ellipsoids for particle and medium points can be various and generally this configuration is random.

Taking into account this difference allows first introducing additional free parameters into the model and secondly, corresponds to physical intuition. Indeed, "particle cell" structure is determined by choice of their typical configuration, whereas "medium cell" configuration is connected with particle relative positions. Taking into consideration the all said and using (11), after simple transformations we obtain the following:

$$f_0 \left\langle \left(\frac{\varepsilon_0}{\varepsilon^*} - 1\right) \frac{1 - L^{(0)}}{1 + L^{(0)}\left(\frac{\varepsilon_0}{\varepsilon^*} - 1\right)} \right\rangle + f_1 \left\langle \left(\frac{\varepsilon_1}{\varepsilon^*} - 1\right) \times \right.$$

$$\left. \times \frac{1 - L^{(1)}}{1 + L^{(1)}\left(\frac{\varepsilon_1}{\varepsilon^*} - 1\right)} \right\rangle = 0 . \qquad (18)$$

Here statistical averaging is still understood as (17), and if necessary it can be added with averaging over random dielectric permeability ensuring description of multi-component fillers.

If as an initial approximation, expression (6) is accepted, then after setting different depolarization factors for environment and for particles, after averaging we have:

$$f_0 \left\langle \left(\frac{\varepsilon_0}{\varepsilon^*} - 1\right) \frac{1}{1 + L^{(0)}\left(\frac{\varepsilon_0}{\varepsilon^*} - 1\right)} \right\rangle + f_1 \left\langle \left(\frac{\varepsilon_1}{\varepsilon^*} - 1\right) \times \right.$$

$$\left. \times \frac{1}{1 + L^{(1)}\left(\frac{\varepsilon_1}{\varepsilon^*} - 1\right)} \right\rangle = 0. \qquad (19)$$

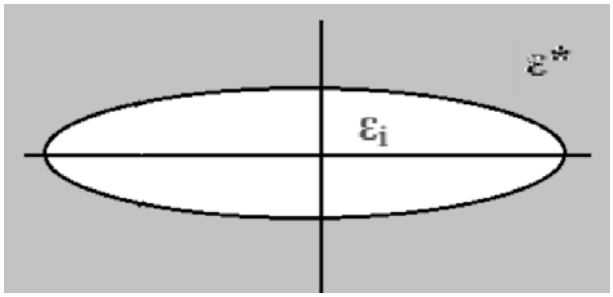

Fig. 4. Effective cell in approximation of the self-consisted Bruggeman field: ellipsoid in effective medium with ε^*

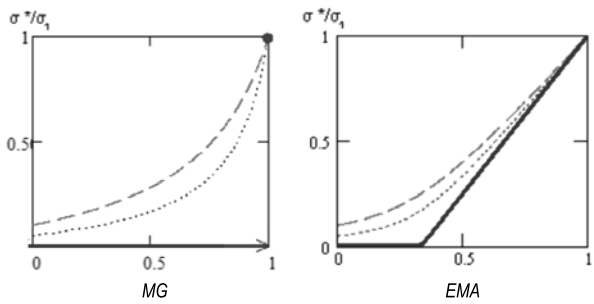

Fig. 5. Dependences of effective conductivity on filling factor f_1 in approximations MG (4) and EMA (5); – – –σ_2/σ_1= 0,1; – - -σ_2/σ_1 = 0,05; —— $\sigma_2/\sigma_1 \to 0$

Such configuration of EMA (Effective medium approximation) was widely used in different works (see, e.g., [43, 44])

Equation (18) differs from (19) by presence of multiplier factors $1\text{-}L^{(i)}$ in each summand numerator. For identical and mono-directed ellipsoids, these common multiplier factors can be omitted, so (18) and (19) are transformed into (6), however generally such simplification does not happen. Thus (18) and (19) correspond to different models of effective medium.

6. GENERALIZED BRUGGEMAN APPROXIMATION AND PERCOLATION THRESHOLD

Equations (18) and (19) are generally rather complex and can be solved numerically. In this regard, the known problem of choice of a "correct" branch of the EMA equation solution, which generally is many-valued, should be noticed [45]). However, without solving these equations, one can at once find expressions from them for correspondent percolation thresholds. With that end in view, we will pass from consideration of dielectric permeability ε to conductivity σ, for which all relations are retained in quasistatic approximation as it was specified above. To find percolation threshold, we will consider the case of dielectric matrix $\sigma_0 = 0$ with conducting particles $\sigma_1 \neq 0$. Having replaced ε with σ everywhere and considering in (18) and (19) first $\sigma_0 = 0$, and then $\sigma^* = 0$ (order of these substitutions is important!), it is easy to obtain the following expressions for threshold value of volume particles part. In case of (18):

$$f_{1c} = 1 \Big/ \left\langle \frac{1}{L^{(1)}} \right\rangle, \qquad (18)$$

and in case of (19):

$$f_{1c}^* = \frac{1}{1 + \dfrac{\left\langle 1/L^{(1)} \right\rangle}{\left\langle 1/(1-L^{(0)}) \right\rangle}}. \qquad (19)$$

We will not further discuss these expressions, which for the model of spherical cells are both reduced to the well-known evaluation for the Bruggeman approximations $f_{1c} = 1/3$ (5). For an illustration, we are limited to comparison of MG and EMA approximations in simplest models (4) and (5). Fig. 5 shows effective dependences of conductivity σ^* in these models on volume part of conducting component for different relations σ_0/σ_1. One can see from these figures that MG approximation (4) gives dependence σ^* converging in limit $\sigma_0/\sigma_1 \to 0$ to a discontinuous function $\sigma^* = 0$ at $0 \leq f_1 < 1$ and $\sigma^* = 1$ at $f_1 = 1$, which corresponds to absence of the percolation threshold, whereas for EMA in this limit there are two sections of right lines with threshold value $f_{1c} = 1/3$ (Fig. 5).

7. CONCLUSIONS

In this review, we have briefly considered various methodical approaches to obtain MGA and EMA as most widespread homogenisation approximations, i.e. to replace a strongly non-uniform composite with a homogeneous medium so that to save invariable the measured averaged electro-dynamic characteristics of the composite. Such a procedure even for composites with non-uniformities being small in comparison with the wavelength, is feasible not always and practically leads to neglect of possible strong small-scale field fluctuations in the composite. Due to a big variety of

composite inner structures, one cannot expect a creation of formulas for effective medium parameters suitable in all cases, and this explains presence of many various models in the publications. Nevertheless, MGA, EMA and their generalisations remain basic approximations when describing many nano-composite media. In this review, we have not touched on many questions connected with taking into account in MGA and EMA various complicating factors, which description can be found in the quoted references.

At present, a rapid development of nano-photonics continues, and homogenisation theory occupies a useful niche in this development, which often allows obtaining uncommon results using simple facilities.

REFERENCES

1. Milichko V. A., Shalin A.S., Mukhin I.S., Kovrov A.E., Krasilin A.A., Vinogradov A.V., Belov P.A., Simovsky K.R. Solar photovoltaics: current state and trends of development //Achievements of physical sciences, 2016, V.186, pp. 801–852. DOI:10.3367/UFNr.2016.02.037703

2. Valenta J., Mirabella S. (Eds.) Nanotechnology and Photovoltaic Devices: Light Energy Harvesting with Group IV Nanostructures.Taylor & Francis Group, 2015, 441p.

3. Lourtioz J.-M. et al., eds. Nanosciences and Nanotechnology: Evolution or Revolution? – Springer, 2016, 438 p. DOI:10.1007/978–3–319–19360–1

4. Di Bartolo B., Collins J., Silvestri L. (eds.) Nano-Structures for Optics and Photonics: Optical Strategies for Enhancing Sensing, Imaging, Communication and Energy Conversion. Springer, 2015, 586p.

5. Novotny L., Hekht B. foundations of nanooptics, Moscow: Fizmatlit, 2009, 484 p.

6. Quinten M. Optical properties of nanoparticle systems: Mie and beyond. Weinheim: Wiley-VCH, 2011, 488p. DOI:10.1016/j.jqsrt.2011.10.001

7. Boren K., Hafman D. Absorption and scattering of light by small particles. Moscow: Mir, 1986, 660 p.

8. Milton G.W. The Theory of Composites. Cambridge Univ. Press, 2004, 749 p.

9. Sihvola A. Electromagnetic Mixing Formulas and Applications, Electromagnetic Wave Series 47, London: IEE Publishing, 1999, 284p.

10. Markel V.A. Introduction to the Maxwell Garnett approximation: tutorial// J. Opt. Soc. Amer. 2016, A 33, No.7, pp.1244–1256. DOI:1084–7529/16/071244–13

11. Markel V.A. Maxwell Garnett approximation (advanced topics): tutorial // J. Opt.Soc.Amer.-2016, A 33, № . 11, pp.2237–2255. DOI:1084–7529/16/112237–19

12. Sarychev A. K., Shalaev V.M. Electrodynamics of metamaterials. Moscow: Naychny Mir, 2011, 224 p.

13. Cai W., Shalaev V. Optical Metamaterials. Springer, 2009, 200 p. DOI: 10.1007/978–1–4419–1151–3

14. Remnev M. A., Klimov V.V. Metasurfaces: a new view on Maxwell's equations and new methods of light control // Achievements of physically sciences. 2018, V.188, pp. 169–205.

15. Andrianov E. S., et al. Quantum nanoplasmonics. Dolgoprudny: Intellect Publiching house, 2015, 368 p.

16. Pal R. Electromagnetic, Mechanical, and Transport Properties of Composite Materials, 2015, CRC Press, 400p.

17. Aliofkhazraei M., ed., Handbook of Nanoparticles. Springer, 2015, 1439 p. DOI 10.1007/978–3–319–15338–4

18. Kong E. S.W. K., ed. Nanomaterials, polymers, and devices. Wiley, 2015, 584p.

19. Stenzel O. The physics of thin films. Optical spectra. An Introduction. 2nd Edition. Springer, 2016, 352 p. DOI: 10.1007/978–3–319–21602–7

20. Rosenberg G.V. Current state of the theory of optical properties of translucent metal coatings // Achievements of physically sciences, 1956, V.58, pp. 487–518. DOI:10.3367/UFNr.0058.195603d.0487

21. Maxwell J.C. Treatise on electricity and magnetism. V.1. Moscow: Nauka, 1989, 415 p.

22. Landau L. D., Lifshits E.M. Electrodynamics of solid environments. The 4th, stereotypic edition. Moscow: Fizmatlit, 2003, 656 p.

23. Taherian R. Experimental and analytical model for the electrical conductivity of polymer-based nanocomposites // Composites Science and Technology.2015. DOI: 10.1016/j.compscitech.2015.11.029

24. Lamb W., Wood D.M. and Ashcroft N.W. Long-wavelength electromagnetic propagation in heterogeneous media // Phys. Rev.1980, B21, № 6, pp.2248–2266. DOI: 10.1103/PhysRevB.21.2248

25. Maxwell Garnet J.C. Colours in metal glasses and in metallic films // Phil. Trans.R.Soc.London. 1904, A203, pp.385–420; Colours in metal glasses, in metallic films, and in metallic solutions, II., ibid. 1906, A 205, pp.237–288.

26. Strutt J. (Lord Rayleigh). On the influence of obstacles arranged in rectangular order upon the properties of a medium// Phil. Mag.1892, V. 34, 481p. DOI:10.1080/14786449208620364

27. Bruggeman D.A.G. Calculation of various physics constants in heterogeneous substances. I. Dielectric constants and conductivity of mixed bodies from isotropic substances //Ann. Phys. 1935, V.23, pp.636–664. DOI:10.1002/andp.19354160705

28. Smith G.B. Effective medium theory and angular dispersion of optical constants in films with oblique columnar structure// Opt. Commun. 1989, V.71, № 5, pp.279–284. DOI:10.1016/0030–4018(89)90008–4

29. Schmidt D., Schubert M. Anisotropic Bruggeman effective medium approaches for slanted columnar thin films //J. of Applied Physics. 2013, V.114, № 8, 083510. DOI: 10.1063/1.4819240

30. Mackay T.G., and A. Lakhtakia A. Bruggeman formalism versus "Bruggeman formalism": particulate composite materials comprising oriented ellipsoidal particles // J.of Nanophotonics. 2012, V.6, № 1, 0695012. DOI:10.1117/1.JNP.6.069501

31. Apresyan L. A., Vlasov D.V. On factors of depolarisation of anisotropic ellipsoids // Journal of technical physics. 2014, V. 84, #12, pp. 23–28.

32. Rytov S. M., Kravtsov Yu. A., Tatarsky V.I. Introduction in statistical radiophysics. V.1.2. Moscow: Nauka, 1978.

33. Tamm I.E. Fundamentals of theory of electricity: Textbook for high education institutions. Revised 11th edition, Moscow: Fizmatlit, 2003, 616 p, ISBN5–9221–0313-X.

34. Stroud D., Pan F.P. Self-consistent approach to electromagnetic wave propagation in composite media: Application to model granular metals// Phys.Rev. 1988, B37, № 15, pp.8719–8724.

35. L. A. Apresyan, D.V. Vlasov, D.A. Zadorin, V.I. Krasovsky. On a model of effective environment for particles with complex structure // Journal of technical physics. 2017, V.87, № 1, pp. 10–17. DOI: 10.21883/JTF.2017.01.44011.1841

36. Brosseau C. Modelling and simulation of dielectric heterostructures: a physical survey from an historical perspective // J. Phys. D: Appl. Phys.– 2006. – V. 39. – P. 1277–1294. DOI:10.1088/0022–3727/39/7/S02

37. Petrov Yu.I. Physics of small particles. Moscow: Nauka, 1982, 359 p.

38. Orayevsky A.N., Protsenko I.E. A high refraction factor and other features of optical properties of heterogeneous environments // Letters to JETP. 2000, V.72, pp. 641–646.

39. Liznev E. O., Dorofeenko A.V., Vinogradov A.P. Creation of environments with dielectric permeability close to zero in a wide frequency interval // Optical journal. 2010, V.77, pp. 11–12.

40. Moiseev S.G. Composite medium with silver nanoparticles as an anti-reflection optical coating//Applied Physics A. 2011, V.103, pp. 619–622.

41. Marton J.P., Lemon J.R. Optical properties of aggregated metal systems. 1.Theory // Phys.Rev.– 1971, V.B4, № 2, pp.271–280.

42. Bergman D.J., Stroud D. Physical properties of macroscopically inhomogeneous media // Solid State Physics Phys, 1992, V. 46, pp.148–269.

43. Wang Y. and Weng G.J. Electrical conductivity of carbon nanotube and graphen -based nanocomposites, Ch. 4 in: S.A. Meguid, G.J. Weng (eds.), Micromechanics and Nanomechanics of Composite Solids, Springer International Publishing AG 2018. DOI 10.1007/978–3–319–52794–9_4123

44. Liang D., Schmid D., Wang H. et al. Generalized ellipsometry effective medium approximation analysis approach for porous slanted columnar thin films infiltrated with polymer // Applied Physics Letters, 2013, V. 103, № 11, 111906 (1). DOI: 10.1063/1.4821159

45. Vinogradov A. P., Dorofeenko A.V., Zukhdi S. Concerning the question of effective parameters of metamaterials // Achievements of physical sciences. 2008, V. 178, #5, pp. 511–518.

Leon A. Apresyan,
Ph.D. (Phys.-math. sciences, 1978), graduated from Moscow Physical-Technical Institute (MPhTI) in 1972. At present, he is the Senior Researcher in Prokhorov General Physics Institute of the Russian Academy of Sciences. His fields of interest are statistical radio-physics and electrodynamics of randomly inhomogeneous media