Frequency-Dependent Effective Material Parameters of Composites as a Function of Inclusion Shape

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1. Introduction

Electromagnetic composite materials have a number of promising applications in various radio-frequency (RF), microwave and high-speed digital electronic devices, and allow for solving problems related to electromagnetic compatibility (EMC) and electromagnetic immunity (EMI) [1]. For this reason, study and prediction of frequency-dependent radio-frequency RF and microwave properties of materials currently attract much attention. The problem of interest is the analytical description of wideband RF/microwave permittivity and permeability behavior of materials. This is necessary, in particular, to numerically optimize wideband electromagnetic performance of materials and devices at the design stage.

This chapter discusses frequency dependences of effective material parameters (permittivity and permeability) of different types of composites. The chapter consists of three sections. Section I presents a review of approaches for predicting effective material parameters of composites, such as mixing rules, the Bergman–Milton spectral theory, and the percolation theory. Section II suggests on how to select the most appropriate mixing rule for the analysis of properties of a particular composite. Section III considers the dielectric microwave properties of composites filled with fiber-shaped inclusions.

2. Approaches to describe effective material parameters of composites

2.1. Basic mixing rules

In most studies, two-component mixtures are considered, where identical inclusions are imbedded in a homogeneous host matrix. Effective properties of such a composite depend on the intrinsic properties of the inclusions and the host matrix, as well as on the

morphology of the composite. The morphology is a characterization of the manner, in which inclusions are distributed in the composite, including their concentration, shape, and correlations in the location. Therefore, the morphology determines how inclusions are shaped and distributed, whether they are mutually aligned/misaligned in the composite, and what concentrations of inclusion phases and a matrix material are.

A conventional approach to describe the properties of composites employs mixing rules, i.e., equations that relates the intrinsic properties of inclusions and the host matrix with the effective properties of composite based on a simple idealized model considering an ellipsoidal-shaped inclusion. Typically, the characterization of the concentration and the shape of inclusions are included explicitly in the mixing rules, and the account for other morphological characteristics is attempted by a proper selection of the mathematical form of mixing rules.

A number of mixing rules are found in the literature. The basic mixing rules are the Maxwell Garnet equation (MG) [2], Bruggeman's Effective Medium Theory (EMT) [3], and the Landau-Lifshitz-Looyenga mixing rule (LLL) [4, 5]. The MG mixing rule,

$$\frac{\chi_{\mathrm{eff}}}{1 + n\,\chi_{\mathrm{eff}}} = p \frac{\chi_{\mathrm{incl}}}{1 + n\,\chi_{\mathrm{incl}}}, \tag{1}$$

is equivalent to the Clausius–Mossotti approximation, and also complies with the Ewald-Oseen extinction theorem [6]. Bruggeman's EMT,

$$-(1-p)\frac{-\chi_{\mathrm{eff}}}{\chi_{\mathrm{eff}} + 1 - n\chi_{\mathrm{eff}}} = p \frac{\chi_{\mathrm{incl}} - \chi_{\mathrm{eff}}}{\chi_{\mathrm{eff}} + 1 + n\left(\chi_{\mathrm{incl}} - \chi_{\mathrm{eff}}\right)}, \tag{2}$$

is often referred to as the Polder-van Santen mixing rule in the theory of magnetic composites [7]. The Landau−Lifshitz−Looyenga mixing rule (LLL) is written as

$$\left(\chi_{\mathrm{eff}} + 1\right)^{1/3} - 1 = p\left(\left(\chi_{\mathrm{incl}} + 1\right)^{1/3} - 1\right). \tag{3}$$

Eqs. (1)–(3) are written for the generalized susceptibilities of inclusions, χ_{incl}, and the effective susceptibility, χ_{eff}, both normalized to the susceptibility of the host matrix, since all susceptibilities of a certain composite, including the effective permittivity and permeability, are governed by the same mixing rule [8], with a possible correction for the tensor nature of the susceptibilities. If permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ is under consideration, then $\chi_{\mathrm{incl}} = \varepsilon_{\mathrm{incl}}/\varepsilon_{\mathrm{host}} - 1$ and $\chi_{\mathrm{eff}} = \varepsilon_{\mathrm{eff}}/\varepsilon_{\mathrm{host}} - 1$. For the permeability $\mu = \mu' - i\mu''$, $\chi_{\mathrm{incl}} = \mu_{\mathrm{incl}} - 1$ and $\chi_{\mathrm{eff}} = \mu_{\mathrm{eff}} - 1$, because most magnetic composites are based on a non-magnetic host matrix. In Eqs. (1)–(3), n is the form factor, i.e., either depolarization or demagnetization factor, and p is the volume fraction of inclusions.

Starting from the basic mixing rules, simple empirical models of a composite may be suggested.

The MG mixing rule considers the total polarizability of inclusions represented by the right part of Eq.(1) and assumes that this polarizability is acquired to a homogeneous medium. As

a consequence, this mixing rule defines the weakest possible cooperative phenomena between neighboring inclusions that are feasible for the given volume fraction of inclusions. The MG mixing rule is an accurate result for the case, when excitation of inhomogeneous fields due to multiple scattering on inclusions and the effect of neighboring inclusions are negligible. Therefore, it coincides with the lower Hashin−Shtrikman limit [9] that provides the smallest possible material parameter in the case, when loss is negligible. The MG mixing rule is believed to be valid for regular composites, i.e., those comprising regularly arranged inclusions, and for the case of conducting inclusions covered with an isolating shell [10, 11].

The physical model for the EMT assumes that the host matrix consists of particles having the same shape that inclusions have, and both the inclusions and the host matrix particles, are embedded in an effective medium with the material constant equal to the effective material constant the composite. The sum of the polarizabilities of these two types of particles must be zero, which corresponds to a homogeneous medium. Though a practical realization of the EMT involves a very special morphology of a composite [12], this mixing rule is widely used, because it incorporates the percolation threshold when modeling a metal-dielectric mixture. The percolation threshold, p_c, is the lowest concentration, at which a macroscopic conductivity appears in the mixture. From the standpoint of the mathematics, the EMT is reduced to a quadratic equation for the effective permittivity. Below and above the percolation threshold, different solutions of the equation must be selected according to the physical selection rules. Equation (2) yields $p_c=n$. In the MG mixing rule (1), the percolation threshold is $p_c=1$.

The LLL mixing rule is built up by an iterative procedure starting from a homogeneous material of inclusions and replacing small amount of this material by the material of the host matrix. After that, the resulting "effective" material is regarded as the homogeneous component for the succeeding substitution step, and so on, which results in Eq. (3). The mixing rule obtained by the same iterative procedure starting with the homogeneous host matrix is referred to as the asymmetric Bruggeman approximation. The result of the LLL mixing rule is independent of the form factor of inclusions. For a metal-dielectric composite, the LLL mixing rule always provides a conductive mixture, so that $p_c=0$.

The LLL mixing rule is known to be an accurate result for the case when the material parameter of inclusions differs slightly from that of the host matrix. In particular, this mixing rule is valid for all material parameters of composites at very high frequencies, because any intrinsic susceptibility of any material approaches zero with the frequency tending to infinity. Agreement of both the MG and EMT mixing rules with the LLL mixing rule in the case of the susceptibility of inclusions slightly differing from zero is attained only if $n=1/3$.

When the volume fraction of inclusions is small, $p \ll p_c$, and the interaction between the inclusions is negligible, all three theories are reduced to the small perturbation limit,

$$\chi_{\text{eff}} = \frac{p\,\chi_{\text{incl}}}{1 + n\,\chi_{\text{incl}}} \,. \tag{4}$$

Strictly speaking, Eqs. (1), (2), and (4) are valid for the case of inclusions of perfectly spherical shape, which have the shape factor equal to 1/3. Otherwise, the equations are not consistent with the LLL mixing rule in the limiting case of high frequencies. For non-spherical particles, the polarizability of inclusions must be averaged over all three principal axes of the inclusion [13]. Two particular cases of non-spherical inclusions are of practical interest - nearly spherical inclusions and highly elongated inclusions (long fibers or platelets). For nearly spherical inclusions, the composites are conventionally described by Eqs. (1), (2), (4) with averaged form factor involved, which is found empirically and may differ from 1/3. For elongated inclusions, the form factor along the shorter axis (in the platelet case), or the sum of two form factors along the shorter axes (in the fiber case) is close to unity, and the polarization of inclusion is these directions can be neglected. In this case, the above equations are valid again, with a randomization factor, κ, included in the right-hand part of the equations to account for an alignment of non-spherical inclusions. For a fiber-filled composite, $\kappa=1/3$, when the fibers are randomly oriented in space, and $\kappa=1/2$, when the fibers are randomly oriented in plane and the wave vector in perpendicular to the plane. For composites filled with platelet-shaped inclusions, $\kappa=2/3$ for the 3D isotropic orientation. For the permeability of composites filled with non-spherical particles, possible anisotropy of magnetic moment, associated with crystallographic anisotropy of particle material, should be also taken into account, see, e.g., [14].

2.2. The Bergman-Milton theory

A generalization of mixing rules may be made with the use of the Bergman-Milton spectral theory (BM) [8]. The theory expresses the effective material parameter of a composite as

$$\chi_{\text{eff}} = p \int_0^1 \frac{\chi_{\text{incl}} b(n) dn}{1 + n \chi_{\text{incl}}}, \qquad (5)$$

where the spectral function, $b(n)$, is introduced as a quantitative characterization of the composite morphology. As is seen from Eq. (5), the BM theory accounts for a distribution in effective form factors of inclusions in a composite. This distribution may be associated with the following statistical parameters and processes within the composite: a spread in shapes of individual inclusions comprising the composite; possible agglomeration of inclusions to clusters; and the effects of multiple scattering and inhomogeneous fields excited by neighboring inclusions. Again, the spectral function is the same for all susceptibilities of a particular composite.

The sum rules,

$$\int_0^1 b(n) dn = 1 \quad \text{and} \quad \int_0^1 n b(n) dn = \frac{(1-p)}{D}, \qquad (6)$$

relate the spectral function $b(n)$ to the volume fraction of inclusions p for a macroscopically isotropic composite in D dimensions. The practically important cases are $D=3$ (an isotropic 3D composite with non-aligned randomly distributed inclusions, the shape of which is arbitrary in the general case) and $D=2$ (an assembly of infinitely long cylinders). The sum rules provide an agreement of the spectral theory with the LLL mixing rule at $\chi_{\text{incl}} \to 0$.

The spectral theory provides a complete characterization of the frequency dependence of the effective material parameters. The concentration dependence of effective material parameters is implicit in the spectral theory, with the volume fraction involved in the spectral function as a parameter. The analysis of concentration dependences is a powerful tool for understanding properties of composites. However, application of the spectral function approach is not convenient for such analysis.

Another reason that prevents the BM theory from the wide use for the analysis of measured data is that the theory exploits an unknown function, which is difficult to find from the experiment. There are just a few published examples of how to apply the BM theory to the measured data analysis and predicting frequency characteristics of composites [15]. A conventional approach is to accept a functional dependence $b(n)$ as a function of some parameters and to search for these parameters from the measured data [16–18].

Figure 1 shows the calculated spectral functions $b(n)$ for some mixing rules. The spectral function for the MG mixing rule is a delta-function, as is shown in Fig. 1a. The spectral function for the EMT mixing rule presented in Fig. 1b is a semi-circle when plotted as $nb(n)$ against n. Plots d, e, and f show the spectral functions for the McLachlan, Sheng, and Musal–Hahn mixing rules, correspondingly, which are discussed in Subsection 1.4. The latter two plots are composed of several distinct peaks of spectral function even at $n=1/3$. Other examples of calculated spectral functions for mixing rules are found in [19]. In case of elongated inclusions, or if a composite is composed of inclusions with significantly different aspect ratios, the spectral function may consist of two or larger number of separated peaks. Also, several distinct peaks of the spectral function are found to appear due to the interaction between inclusions in periodical composite structures [8].

2.3. The percolation theory

A different approach is provided by the percolation theory, see, e.g., [17]. The percolation theory considers the quasi-static permittivity of a metal-dielectric mixture at concentrations close to the percolation threshold. The main assumption of the theory is that the properties of the material are due to statistical properties of large conductive clusters in this case, rather than due to individual properties of inclusions. The theory predicts a power dependence of static permittivity of the mixture on the difference between the concentration, p, and the percolation threshold, p_c:

$$\begin{aligned}
\varepsilon'_{\text{eff}} &\propto \left(p_c - p\right)^{-s}, \quad p < p_c, \quad s \approx 0.7 \\
\varepsilon''_{\text{eff}} &\propto \left(p - p_c\right)^{t}, \quad p > p_c, \quad t \approx 1.8
\end{aligned} \tag{7}$$

The values of critical indices, s and t, are believed to be universal, i.e., independent of detailed structure of composite.

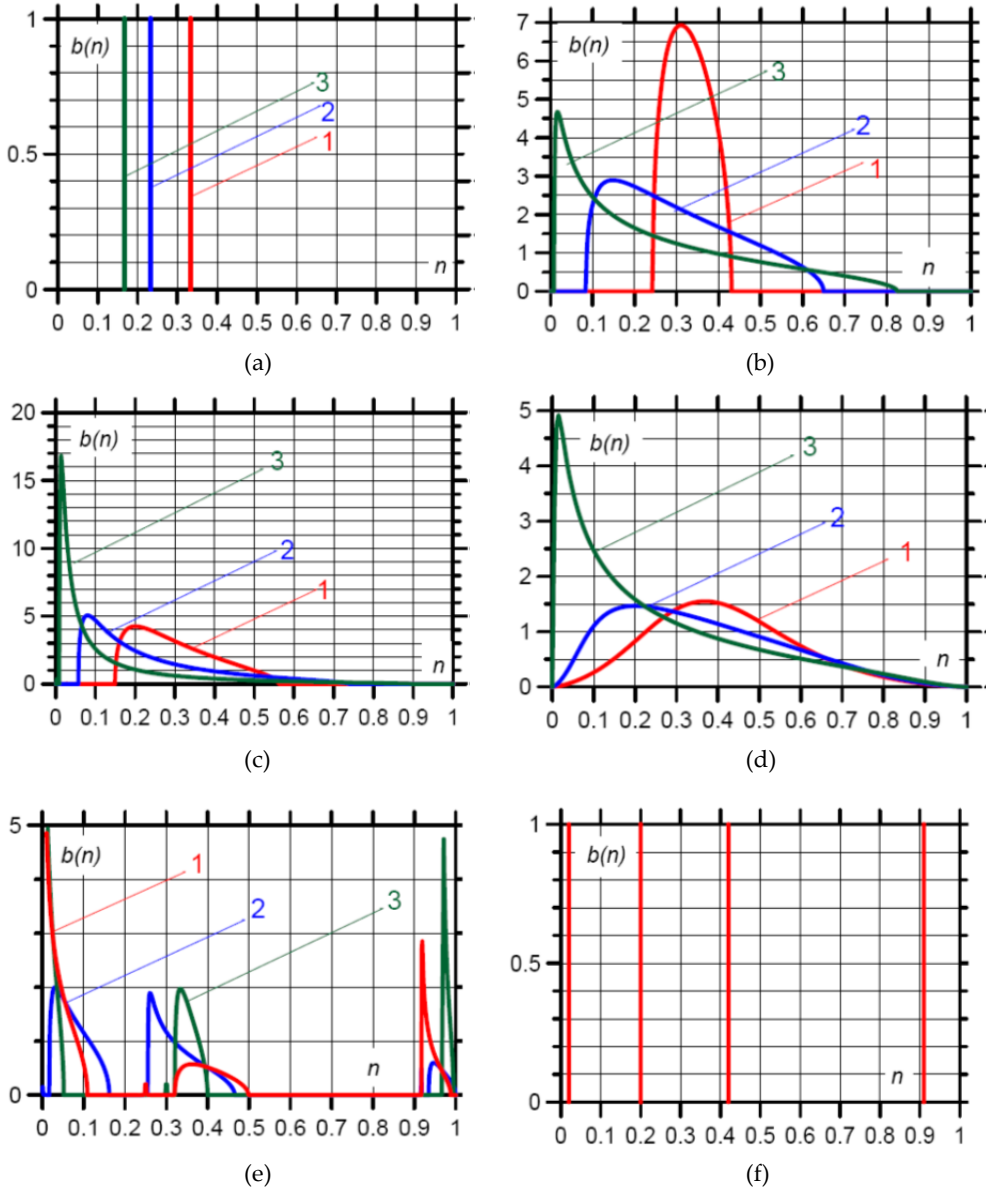A consequence of Eqs. (7) is a power dependence of the real and imaginary permittivity on frequency f:

Figure 1. The spectral function, $b(x)$, calculated for various mixing rules: (a) MG, $n=1/3$: 1 − p=0.1, 2 − p= 0.2, 3 − p=0.5; (b) EMT, $n=1/3$: p=0.01, 2 − p= 0.1, 3 − p=0.25; (c) Asymmetric Bruggemann's mixing rule: 1 − p=0.1, 2 − p= 0.3, 3 − p=0.6, (d) McLachlan's theory, $n=1/3$, s=1.8, t=0.7: p=0.01, 2 − p= 0.1, 3 − p=0.25; (e) Sheng theory, $n=1/3$: 1 − p=0.25, F=0.25,, 2 − p=0.1, F=0.25, 3 − p=0.25, F=0.75; (f) Musal–Hahn theory: $n=1/3$, p=0.4, F =0.2.

$$\varepsilon'_{\text{eff}} - \varepsilon'_{\text{host}} \propto f^{-Y}, \quad \varepsilon''_{\text{eff}} \propto f^{-Y} \tag{8}$$

The equality of critical indices for the real and imaginary permittivity established by Eq. (8) follows from the Kramers–Krönig relations, if the frequency dependence of permittivity is governed by law (8) within the whole frequency range. In this case, the dielectric loss tangent, $\varepsilon''/\varepsilon'$, is independent of frequency and equal to $\tan(\pi Y/2)$. It follows from the percolation theory that $Y=s/(s+t)\approx0.28$. In practice, observed values of Y are typically closer to zero [20].

The physical reason for the powder dependence of the permeability on frequency may be understood as follows. Assume that the frequency response of an individual inclusion in the composite is governed by the Debye frequency dispersion law,

$$\varepsilon(f) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + if\tau}, \tag{9}$$

where ε_0 is the static permittivity, ε_∞ is the optical permittivity, and τ is the characteristic relaxation time, which is reciprocal to the linear relaxation frequency f_{rel}: $\tau=1/f_{\text{rel}}$. The Debye dispersion law governs the frequency dependence of composites filled with conducting inclusions in most cases. When individual inclusions form large clusters of various sizes, a spread of the characteristic relaxation times τ appears. In this case, the total permittivity is written as:

$$\varepsilon(\omega) = \varepsilon_\infty + \int_0^\infty \frac{B(y)\,dy}{1 + i\omega y}, \tag{10}$$

where $B(y)$ is the distribution function of the relaxation times, and

$$y = \tau/\tau_0 \quad \text{and} \quad \int_0^\infty B(y)\,dy = 1. \tag{11}$$

The cumulative dispersion curve becomes more gently sloping. With a special form of the distribution,

$$B(y) = \frac{y}{2\pi} \frac{\sin\beta\pi}{\cosh(1-\beta)y - \cos\beta\pi}, \tag{12}$$

the Cole-Davidson frequency dispersion, see, e.g., [21], is obtained,

$$\varepsilon(f) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (if\tau)^{1-\alpha}}. \tag{13}$$

Dispersion law (13) involves a frequency region governed by a power frequency dependence of the permittivity. The form of the distribution does not significantly affect the result provided that the distribution is wide, which can be a kind of justification for the percolation theory.

When the property under consideration is the permeability, the percolation behavior is not readily observed [22].

2.4. Complex mixing rules

There are many practical scenarios when none of the simple mixing laws agree with the measured data on a practical composite. A classical example is related to carbonyl iron composites. Despite almost perfect spherical shape of carbonyl iron particles, the form factor restored from the volume fraction dependence of the permittivity or permeability frequently differs greatly from 1/3 [18, 23]. The reason is an agglomeration of the inclusions.

Another example is the percolation threshold study in composites composed of the same carbon black and different polymer host matrices [24]. Depending on a polymer, the percolation threshold may vary from 5 to 50%. Polymerization with different polymers results in different morphology of the composites. The reason is agglomeration or de-agglomeration of inclusions, which depends on the properties of the interface between inclusions and the host matrix. The importance of spatial distribution of inclusions in a composite for validity of mixing rules is discussed in [25].

Practically, in describing properties of composites, many other factors must be accounted for. Among these factors, there are the distribution of inclusions in shape [26−28] and size [29]; the presence of an oxide layer on the surface of conducting particles, statistical spread of intrinsic material parameters of inclusions, e.g., their conductivities [30], as well as possible cones of orientations, if elongated particles are aligned or randomly oriented [31]. For these reasons, fitting parameters are typically unavoidable in accurate description of material properties of composites.

Therefore, taking into account peculiarities of a composite morphology may be crucial for accurate description of composite performance, especially in the case of permittivity of metal-dielectric mixtures, where the intrinsic permittivity of inclusions is infinity in the quasi-static case, and the effective permittivity of composite is determined solely by the shape of inclusions.

Conventionally, a composite morphology is accounted for using more complex mixing rules, which involve some fitting parameters. Three examples of such mixing rules are discussed below. These theories combine the above mentioned basic approaches, and allow for introducing appropriate fitting parameters.

A well known example of such combination is the Lichtenecker mixing rule [32], which is written for the case of the effective permittivity as

$$\varepsilon_{\mathrm{eff}}^{k} = p\,\varepsilon_{\mathrm{incl}}^{k} + \left(1-p\right)\varepsilon_{\mathrm{host}}^{k}\,. \tag{14}$$

In Eq. (14), k has a physical meaning of a critical exponent, which is conventionally treated as a fitting parameter to obtain an agreement with measurements. Equation (14) may be considered as an empirical combination of the LLL mixing rule and the percolation theory.

A combination of the EMT mixing rule and the percolation theory is MsLachlan's Generalized Effective Medium Theory [33]:

$$p\frac{\varepsilon_{\mathrm{incl}}^{1/t} - \varepsilon_{\mathrm{eff}}^{1/t}}{\varepsilon_{\mathrm{eff}}^{1/t} + n\left(\varepsilon_{\mathrm{incl}}^{1/t} - \varepsilon_{\mathrm{eff}}^{1/t}\right)} + (1-p)\frac{\varepsilon_{\mathrm{host}}^{1/s} - \varepsilon_{\mathrm{eff}}^{1/s}}{\varepsilon_{\mathrm{eff}}^{1/s} + n\left(\varepsilon_{\mathrm{host}}^{1/s} - \varepsilon_{\mathrm{eff}}^{1/s}\right)} = 0 .$$ (15)

In this equation, which is also written for the case of permittivity, the EMT equation (2) is supplemented with percolation indices s and t. These indices, together with the effective depolarization factor of inclusions n, are also treated as the fitting parameters.

Another approach for developing complex mixing rules is to divide inclusions in composite into two groups (e.g., a part of inclusions are considered as isolated and the other part are assumed to compose dense clusters [34], or any other way of subdivision into groups), and then to mix these groups with different mixing rules. The value of F, $0 < F < 1$, a fraction of inclusions attributed to one of the groups, provides a fitting parameter. An example of this approach is Sheng's theory [35]:

$$FP_1 + (1-F)P_2 = 0 ,$$ (16)

where P_1 and P_2 are the effective polarizabilities of the two groups of particles; for the case of spherical inclusions, P_1 and P_2 are found in Sheng's theory as

$$P_1 = \frac{\left(\varepsilon_{\mathrm{eff}} - \varepsilon_{\mathrm{host}}\right)\left(\varepsilon_{\mathrm{incl}} + 2\varepsilon_{\mathrm{host}}\right) + \left(\varepsilon_{\mathrm{host}} - \varepsilon_{\mathrm{incl}}\right)\left(\varepsilon_{\mathrm{eff}} + 2\varepsilon_{\mathrm{host}}\right)p}{\left(2\varepsilon_{\mathrm{eff}} + \varepsilon_{\mathrm{host}}\right)\left(\varepsilon_{\mathrm{incl}} + 2\varepsilon_{\mathrm{host}}\right) + 2\left(\varepsilon_{\mathrm{eff}} - \varepsilon_{\mathrm{host}}\right)\left(\varepsilon_{\mathrm{host}} - \varepsilon_{\mathrm{incl}}\right)p} ,$$ (17)

$$P_2 = \frac{\left(\varepsilon_{\mathrm{eff}} - \varepsilon_{\mathrm{incl}}\right)\left(2\varepsilon_{\mathrm{incl}} + \varepsilon_{\mathrm{host}}\right) + \left(\varepsilon_{\mathrm{incl}} - \varepsilon_{\mathrm{host}}\right)\left(\varepsilon_{\mathrm{eff}} + 2\varepsilon_{\mathrm{host}}\right)\left(1-p\right)}{\left(2\varepsilon_{\mathrm{eff}} + \varepsilon_{\mathrm{incl}}\right)\left(2\varepsilon_{\mathrm{incl}} + \varepsilon_{\mathrm{host}}\right) + 2\left(\varepsilon_{\mathrm{eff}} - \varepsilon_{\mathrm{incl}}\right)\left(\varepsilon_{\mathrm{incl}} - \varepsilon_{\mathrm{host}}\right)\left(1-p\right)} .$$ (18)

Equation (17) describes the polarizability of a spherical particle consisting of an inclusion material and then coated by a shell of the host matrix material. Equation (18) represents the inverse structure, with the shell made of the inclusion material and the core made of the host matrix material. Both Eqs. (17) and (18) are consistent with the MG formalism. The effective structures are mixed with each other according to the EMT equation (16). An analogous approach is suggested by Musal and Hahn [36], with the only difference that the EMT equation (16) describing a mixture of the two groups is substituted in the MG equation (1). Doyle and Jacobs [34, 37] suggested the model, where the two groups of inclusions comprise isolated inclusions and clusters of closely packed inclusions.

The complex mixing rules are suggested and provide rather good/reasonable agreement with measured data mostly for the concentration dependences of the permittivity in metal-dielectric mixtures. However, these theories may fail when describing frequency dependences of material parameters. The reason is that the complex mixing rules have the spectral function consisting of several isolated peaks even in the case of nearly-spherical inclusions, as is seen in Fig. 1 *e* and *f*. A physical meaning can hardly be attributed to these

peaks in case of a random composite filled with spherical inclusions, because, as is shown below, the appearance of isolated peaks of spectral function generally results in the appearance of several isolated regions of frequency dispersion of material parameters.

Another approach to the problem of the permittivity dependence on concentration for metal-dielectric mixtures has been suggested by Odelevskiy [38]. He was the first who noticed the analogy between the MG and EMT equations, in which the concentration dependence of the permittivity for conducting inclusions are written as

$$\varepsilon_{\text{eff}} = 1 + \frac{1}{n}\frac{p}{1-p} \tag{19}$$

and

$$\varepsilon_{\text{eff}} = 1 + \frac{1}{n}\frac{p}{1-p/n}, \tag{20}$$

respectively. Odelevskiy suggested an equation that generalizes these two theories in the case of a metal-dielectric mixture:

$$\varepsilon_{\text{eff}} = 1 + \frac{1}{n}\frac{p}{1-p/p_c}. \tag{21}$$

In Eq. (21), the form factor n and percolation threshold p_c are the two fitting parameters. With these fitting parameters, the equation demonstrates an excellent agreement with measured data for a variety of different metal-dielectric mixtures [39], if the concentration of inclusions is not very close to the percolation threshold. Equation (21) cannot be considered as an independent mixing rule, because it does not leave a room for the permittivity of inclusions different from infinity.

3. Frequency-dependent behavior of composites and validity of mixing rules

Effective properties of composites in the majority of mixing rules and theories are considered in the quasi-static approximation. Because of this, the frequency dependence of effective material parameter appears due to the difference in frequency dependences of material parameters of constituents.

Frequency dispersion of permittivity in a composite frequently appears due to the different frequency behavior of its dielectric host matrix and of conducting inclusions. Host matrices are typically considered as non-dispersive over a frequency range of interest, while the permittivity of metallic inclusions is imaginary and reciprocal to frequency. There are other dielectric materials possessing dielectric dispersion at microwaves, e.g., water, some ferroelectrics [40], some lossy polymers, but necessity of accounting for this dispersion is a fairly rare.

In contrast, a multitude of magnetic materials exhibit frequency dispersion of permeability at microwaves. The reason is that all magnets lose their magnetic properties at frequencies below several gigahertz, as is shown in Subsection 2.2. These are the microwaves, or even lower frequencies, where the permeability changes from large static permeability to unity. Notice that the intrinsic permeability of magnetic powders is generally unknown. It depends not only on the composition of the material, but also on manufacturing and treatment technology, and the latter dependence may be essential.

In the first-order approximation, the frequency dependence of material parameters may be considered as an assembly of loss peaks accompanied by corresponding frequency dispersion of the real part, according to the Kramers-Kronig relations. In many cases, the Lorentzian (resonance) dispersion law,

$$\chi(f) = \sum_{i=1}^{m} \frac{\chi_{\mathrm{st},i}}{1 + \mathrm{i}\, f \big/ f_{\mathrm{rel},i} - \left(f \big/ f_{\mathrm{res},i}\right)^2} \, , \tag{22}$$

provides a good fitting of measured dependences of susceptibility χ on frequency f. In Eq. (22), m is the number of the resonance terms involved in the dispersion law, and $\chi_{\mathrm{st},i}$, $f_{\mathrm{rel},i}$, and $f_{\mathrm{res},i}$ are the static susceptibility, relaxation frequency, and resonance frequency attributed to i-th resonance term, respectively.

3.1. Frequency-dependent behavior of composites

Almost all mixing rules deduce the effective material parameters from the polarizability,

$$P = \frac{\chi_{\mathrm{incl}}}{1 + n\,\chi_{\mathrm{incl}}}, \tag{23}$$

embedded in either a host matrix or the effective medium. From Eq. (23), two limiting cases are clearly seen, $n\chi_{\mathrm{incl}} \ll 1$ and $n\chi_{\mathrm{incl}} \gg 1$.

In the case of $n\chi_{\mathrm{incl}} \ll 1$, the LLL mixing rule (3) is a rigorous result. For majority of practical cases, Eq. (3) may be rewritten just as the perturbation limit given by Eq. (4). In this case, the effective material parameter is just the intrinsic material parameter multiplied by the volume fraction of inclusions. This means that the effect of interaction between inclusions is negligible. The morphology of the composite, including the shape of inclusions, does not affect the effective material parameter. This case is typical for the microwave permeability of composites filled with either fibrous or platelet inclusions, as well as for all effective susceptibilities at very high frequencies.

In the other limiting case, $n\chi_{\mathrm{incl}} \gg 1$, the effective material parameter depends on the morphology only. Here, the effective static susceptibility increases non-linearly with the concentration of inclusions, according to the percolation behavior and Odelevskiy equation (21). It is the case, for which most of the complex mixing rules have been developed. The case is related to the permittivity of metal-dielectric mixtures, since the imaginary part of the

permittivity of metal inclusions is so high that the absolute value of the microwave permittivity can be considered as infinite. As to the permeability, this case may be observed in some composites filled with ferromagnetic inclusions of spherical shape, or for low-frequency magnetic materials, whose permeability may be very high.

Let the effective material parameter be considered in a wide frequency range. Assume that the host matrix of the composite is lossless and non-dispersive. Then, the frequency dispersion in the composite is due to the frequency dispersion of inclusions. It is well known that a material parameter of any medium approaches unity with the frequency tending to infinity. Because of that, the case of $n\chi_{incl} \ll 1$ is always observed at very high frequencies, where the LLL mixing rule (3) describes material parameters of composites.

If the intrinsic susceptibility of inclusions is low, the LLL mixing rule is valid for low frequencies as well. In this case, the frequency dependence of any effective material parameter is just proportional to the dependence for the intrinsic material parameter, and the volume fraction of inclusions is the coefficient of proportionality. The loss peak in the composite and the loss peak of inclusions are located at the same frequency. The concentration dependence of the effective parameter is linear over the entire frequency range.

Another possibility is when the inequality $n\chi_{incl} \gg 1$ holds at low frequencies. In this case, the frequency dispersion in the composite appears, when the absolute value of $n\chi_{incl}$ is about unity. The loss peak in the composite is shifted towards higher frequencies as compared to the loss peak of inclusions. As the concentration of inclusions increases, the loss peak is shifted to the lower frequencies. At frequencies above the peak, the effective susceptibility is again proportional to the intrinsic susceptibility. At frequencies below the peak, the effective permeability depends mostly on the composite morphology and is independent of the intrinsic susceptibility. The concentration dependence of the effective susceptibility is non-linear.

This case is typical for metal-dielectric mixtures. However, the conductivity of metals is usually too high to provide a loss peak of permittivity at microwaves. The microwave permittivity for most metal-dielectric composites may be considered as non-dispersive and low-loss. An exception is the percolation behavior, which will be discussed in Section 3.

If the frequency dependence of the intrinsic material parameter is Lorentzian (22) with $m=1$, and the mixing rule describing the composite is the MG, then the frequency dependence of the effective material parameter is Lorentzian as well. The parameters of the dispersion law for the effective material parameters are given by the simple equations [41]

$$\chi_{st,eff} = \frac{\chi_{st,incl} p}{\chi_{st,incl} n(1-p)+1}, \tag{24}$$

$$f_{rel,eff} = f_{rel,incl}\left(\chi_{st,incl} n(1-p)+1\right), \tag{25}$$
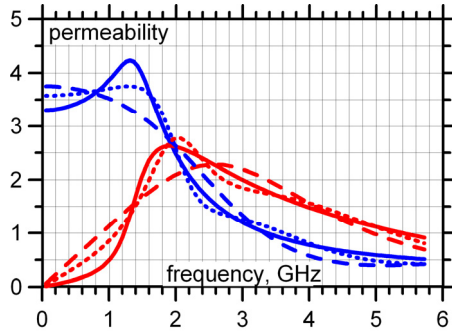
Figure 2. The frequency dependence of effective permeability of a composite calculated by the EMT (2) with p=0.25 and n=1/3 (solid curves, blue curve for real permeability and red curve for imaginary permeability). Inclusions in the composite exhibit the Lorentzian frequency dispersion (22) with m=1, χ_{st}=100, f_{res}=1 GHz, and f_{rel}=2 GHz. The dashed curves are the best fit of the solid line with the Lorentzian dispersion law with m=1, the dotted curves − with a sum of two Lorentzian terms, m=2.

and

$$f_{res,eff} = f_{res,incl} \sqrt{\chi_{st,incl}\, n(1-p)+1}\,, \tag{26}$$

where subscript "incl" indicates the Lorentzian parameters of the intrinsic permeability of inclusions and subscript "eff" is related to the Lorentzian parameters of the effective susceptibility of composite. It is clearly seen from the equations that the non-linear concentration dependence of static susceptibility is accompanied by a low-frequency shift of both the characteristic frequencies. A general validation of this fact is given in the next subsection.

As is seen from Eqs. (25) and (26), the MG mixing rule retains the shape of effective susceptibility loss peak characteristic for the intrinsic susceptibility of inclusions. From the standpoint of the BM spectral theory, the reason is that additional loss due to mixing may arise over the entire range of effective form factors, where the spectral function has non-zero values. The spectral function for the MG mixing law is a delta-function, therefore, additional loss, which may distort the loss peak, does not appear.

Other mixing rules are characterized by a spectral function of a finite width and may therefore result in distorted shape of the loss peak. Figure 2 shows the frequency dependence of effective permeability of a composite calculated by the EMT (2). Inclusions in the composite are assumed to exhibit the Lorentzian frequency dispersion (22) with m=1. In the figure, the dashed curves are the best fit of the calculated permeability with the Lorentzian dispersion law with m=1, the dotted curves are obtained for the sum of two Lorentzian terms, m=2. It is seen that the EMT produces a large distortion of the Lorentzian dispersion curve, when the concentration is close to the percolation threshold. The distortion has a form of the increased loss at the high-frequency slope of the loss peak, because the spectral function peak for the EMT is extended to the region of large arguments, see Fig. 1*b*.

3.2. Integral relations for the frequency dependences in composites

The low-frequency shift of the loss peak appearing with increasing volume fraction and accompanied by non-linear concentration dependence of static susceptibility is a general rule. Let us consider two integrals,

$$I_1 = \frac{2}{\pi} \int_0^\infty \chi'' f \, df \quad \text{and} \quad I_2 = \frac{2}{\pi} \int_0^\infty \chi' \, df \, , \tag{27}$$

which are analogous to the well-known sum rule for the Kramers-Kronig relations,

$$\chi'_{st} = \frac{2}{\pi} \int_0^\infty \frac{\chi'' df}{f} \, . \tag{28}$$

The difference between (28) and (27) is that the values of I_1 and I_2 are determined by the high-frequency asymptote of the susceptibility, rather than by the low-frequency asymptote, which defines the value of integral (28). In composites, this asymptotic behavior is governed by the LLL mixing law. Therefore, integrals I_1 and I_2 for any composite are equal to the corresponding values for the bulk material of inclusions multiplied by the volume fraction of inclusions [42,43]

$$I_{i,composite} = p I_{i,inclusions}. \tag{29}$$

Consideration of Eq. (29) makes sense if the integrals are convergent and have a non-zero value. For I_1, this is true for the Lorentzian dispersion law (22) that has the high-frequency asymptote given by:

$$\chi(f) \approx -\chi_{st} \left(\frac{f_{res}}{f} \right)^2 + i\chi_{st} \left(\frac{f_{res}}{f} \right)^3 \frac{f_{res}}{f_{rel}} \, . \tag{30}$$

For I_2, the convergence is provided by the Debye dispersion law (9), which is the limiting case of (22) at $f_{res} \rightarrow \infty$ and has the high-frequency asymptote represented as:

$$\chi(f) \approx i\chi_{st} \left(\frac{f_{rel}}{f} \right) + \chi_{st} \left(\frac{f_{rel}}{f} \right)^2 \, . \tag{31}$$

In the theory of magnetic material, these integrals are employed to validate ultimate values of high-frequency permeability. The corresponding constants for magnetic materials depend on the saturation magnetization of the material, M_s. If the frequency dependence of effective permeability is either single-term Lorentzian or Debye, then the values of the integrals are related to the static magnetic susceptibility and the resonance frequency

$$I_1 = p\kappa(\gamma M_s)^2 \approx \chi_{st,eff} f_{res,eff}^2 \, , \tag{32}$$

$$I_2 = p\kappa(\gamma M_s) \approx \chi_{\text{st,eff}} f_{\text{rel,eff}}. \tag{33}$$
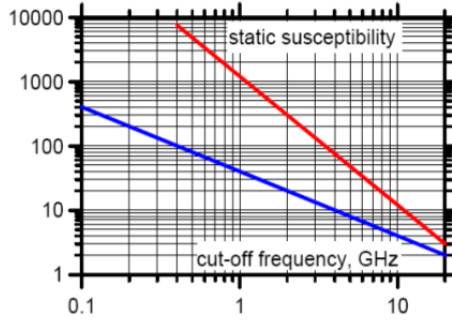

Figure 3. The static susceptibility as a function of cut-off frequency calculated with Acher's law (32) (red line, κ=1/3) and Snoek's law (33) (blue line, κ=2/3). In both the cases, M_s=2.15 T, p=1.

In Eqs. (32) and (33), $\gamma \approx 3$ GHz/kOe is the gyromagnetic ratio, and κ is the randomization factor. For I_2, typically κ=2/3; for I_1, different possibilities are discussed in [14]. Equations (32) and (33) represent the well known Acher's law [44] and Snoek's law [45], respectively. Then I_1 has a meaning of Acher's constant, and I_2 is Snoek's constant. For most materials, Snoek's law is valid, which involved Debye frequency dependence and integral I_2. For some materials, such as hexagonal ferrites and thin ferromagnetic films, Acher's law is valid, so that integral I_1 is calculated as Eq. (32), and much larger high-frequency permeability values can be obtained. The laws (32) and (33) are used for estimating high-frequency magnetic behavior of materials. A magnetic material may have high permeability value at frequencies below the cut-off frequency, which is the least of f_{res} and f_{rel}, where the permittivity falls to values close to unity. As the saturation magnetization of magnetic materials is typically below approximately 2 T, it follows from (32) and (33) that magnetic materials with high static permeability are permeable at frequencies of microwave range or lower.

Figure 3 shows the ultimate values of the static magnetic susceptibility as a function of the cut-off frequency calculated with Acher's law (32), red line, and Snoek's law (33), blue line. In both cases, M_s=2.15 T and p=1, which corresponds to a homogeneous sample of pure iron. For Snoek's law, κ=2/3; for Acher's law, κ=1/3 is accepted, which corresponds to random distribution of thin platelets. It is seen from the figure that with low values of the cut-off frequency, below 1 GHz, Acher's law enables a large advantage over Snoek's law in feasible values of the static permeability. At higher frequencies, this advantage eliminates, and both the laws permits rather small ultimate values of static permeability with cut-off frequencies of several dozen gigahertz.

For the permittivity of a metal-dielectric mixture, the frequency dependence is of Debye type, and an analogue of Snoek's law may be introduced. As $\varepsilon''_{\text{ind}}=2\sigma/f$, where σ is the conductivity of inclusions, the analogue of Snoek's constant for permittivity would be just the doubled conductivity of inclusions,
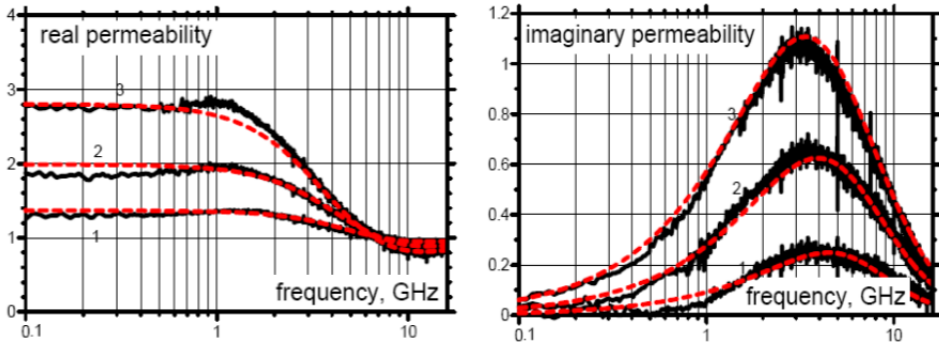
$$I_2 = 2p\sigma. \tag{34}$$

Figure 4. The measured frequency dependence of permeability of hexagonal ferrite composites (black curves, left: the real part, right: the imaginary part) for the Co_2Z composites. The volume fractions of ferrite are: 1, $p=0.1$; 2, $p=0.3$; and 3, $p=0.5$. The red curves show the results of fitting the measured data with the Lorentzian dispersion law (22) with $m=1$ [41].
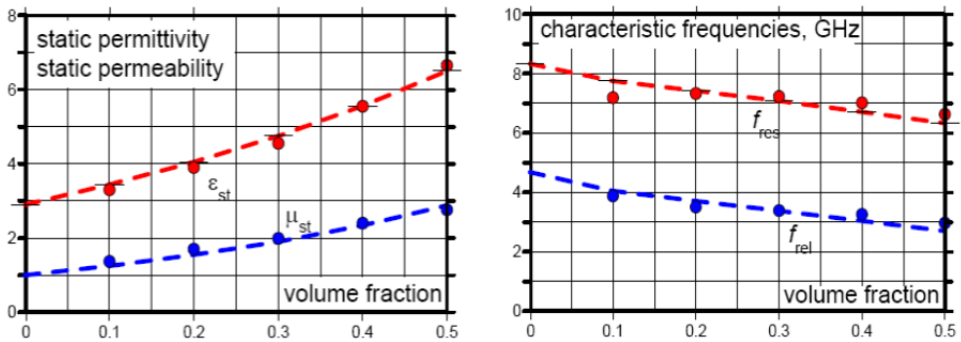

Figure 5. Left: the static permittivity (red dots) and static permeability (blue dots); right: the resonance frequency (red dots) and relaxation frequency (blue dots). The data are obtained for hexagonal ferrite composites by fitting the measured frequency dependences of permeability with the Lorentzian dispersion law (22) with $m=1$. The curves are the best fit of corresponding dots with Eqs. (24–26) [41].

3.3. Applicability of the MG mixing rule

The MG mixing rule usually agrees closely with the measured data, when $n\chi_{incl} \sim 1$. This is a frequent occasion for the microwave permeability of magnetic composites. The intrinsic permeability of magnetic materials does not exceed several units at microwaves due to the fast decrease with frequency, according to Snoek's and Acher's laws. With these relatively low intrinsic permeability values, the dependence of the effective material parameters on the shape of inclusions appears. In particular, a low-frequency shift of the loss peak is observed as p increases. However, the dependence is still weak and may therefore be characterized by an averaged demagnetization factor n.
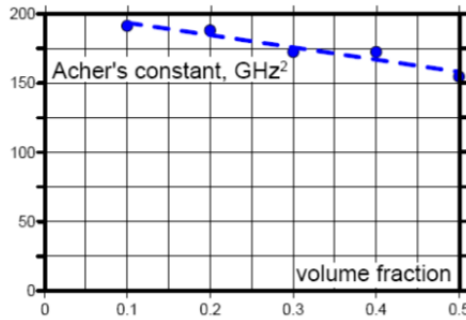
Figure 6. The measured ratio of Acher's constant to the volume fraction plotted against the volume fraction (dots). The line show the linear fit of the measured data [41].

An example of measured data having a good agreement with the MG mixing rule is taken from [41], where composites filled with powders of hexagonal ferrite have been studied. Figure 4 shows the measured microwave permeability for three of the samples. Application of the single-term Lorentzian dispersion law (22) provides a good agreement with the measured data for all volume fractions. This is seen from Fig. 5, where the static permittivity and the Lorentzian characteristic frequencies, obtained by the best fits of the measured magnetic dispersion curves, are plotted as functions of volume fraction. The curves in the figure are obtained by fitting the experimental points (dots) with Eqs. (24–26). For the bulk hexagonal ferrite, the retrieved static values are $\varepsilon_{st,incl}$=16 and $\mu_{st,incl}$=11, and $n\approx$0.33, which indicates that the ferrite particles are of nearly spherical shape. Therefore, $n\chi_{st,incl}$ is the range from 3 to 5, and is reasonably close to unity. The measured data on the microwave material parameters of the composites under study agree with the MG mixing rule calculations, which is evidenced by close agreement of the dots and the fitting curves in Fig. 5.

However, an accurate analysis of the data reveals some disagreement. Acher's constant of the composites, calculated from the data for different volume fractions does not agree with Eq. (32). As Fig. 6 shows, Acher's constant depends on the volume fraction of inclusions, which should not be the case. The reason could be a distribution of shapes of individual inclusions that may result in deviation of the morphology from that postulated in the MG approach. This problem is discussed in more details in the next Subsection.

3.4. Account for the distribution in shapes of inclusions

A case, which may require a sophisticated mixing rule, is a composite filled with conducting ferromagnetic inclusions, whose both permittivity and permeability must be predicted, for example, to describe electromagnetic performance of the composite. In this case, two products of the form factor and the static susceptibility are involved, for the dielectric and magnetic susceptibility, which enlarges the range of variation of this value with a result of necessity for a more sophisticated theory to obtain better agreement between the measured data and theory.
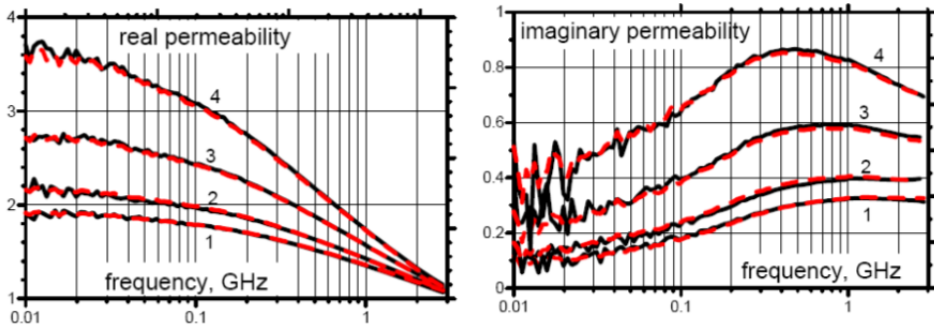
Figure 7. Black curves: the measured frequency dependencies of permeability of composites filled with milled iron powder (black lines), left – real permeability, right – imaginary permeability. Red curves – fitting of the measured data with theory (35). Volume fractions of inclusions are 15.0% (1), 17.7% (2), 23.6% (3), 30.3% (4) [39].

Recently, a new theory, which unites the MG and EMT approaches, has been proposed [46]. This theory allows for introducing the percolation threshold through a general quadratic equation, the same as the EMT, postulating two requirements to the solution. The On the one hand, the solution must be consistent with the LLL mixing rule (3) for the case of low intrinsic material parameter; on the other hand, it should satisfy the Odelevskiy equation (21) for the case of intrinsic material parameter tending to infinity. This produces a unique solution for the equation, which can be considered as a new mixing rule, which generalizes the EMT and MG mixing rules,

$$p\,\frac{\chi_{\text{eff}}}{\chi_{\text{incl}}} + \frac{1-p}{Dpn}\,\frac{1}{1/p - 1/p_c - 1/n/\chi_{\text{eff}}} = 1\,, \tag{35}$$

where D is the dimensionality of composite. Mixing rule (35) involves two fitting parameters: the effective form factor of inclusions, n, and the percolation threshold, p_c, that can be found from the concentration dependence of the effective permittivity. In fact, these parameters are related to peculiarities of morphology of composites, such as the distribution of inclusions in shape.

The derivation of Eq. (35) is based on the assumption that the spectral function has a single wide peak. It is shown [46] that Eq. (35) allows for a variation of these parameters over the ranges,

$$\sqrt{4/D} - 1 < n < 1/D\,,$$
$$\frac{1}{2}\left(Dn(1+n) - n\sqrt{D}\,\sqrt{D(1+n)^2 - 4}\right) < p_c < 1. \tag{36}$$

These conditions correspond to the case of nearly-spherical inclusions. Derivation of similar approach for composites filled with highly-elongated inclusions, such as thin platelets or fibers, must incorporate a spectral function comprising two separated peaks, which would require more sophisticated mathematical approaches. However, to develop such approach is

not a challenging problem. As is shown above, the dilute limit approximation is sufficient for the analysis of microwave magnetic performance of such composites.

With the fitting parameters retrieved from the concentration dependence of permittivity, the intrinsic permeability of inclusions may be found from the measured effective permeability at each volume fraction of inclusions in the composite, as is described in [39]. An agreement of the data on the intrinsic permeability of inclusions found from different concentrations of inclusions provides an additional test for the validity of the mixing rule. It is found that the theoretical predictions agree closely with the measured microwave permittivity and permeability of composites filled with milled Fe powders [39], see Fig. 7. In the figure, the intrinsic permeability of inclusions was calculated for each concentration of inclusions, after which the average value was used to calculate the theoretical curve for each concentration. This is the reason for the noise observed in the theoretical curves in Fig. 7.

4. Composites with fibrous inclusions

4.1. Measured microwave permittivity of fiber-filled composites

Frequency dispersion of permittivity typically is not observed in composites over the microwave range. One of the rare examples of microwave dielectric dispersion is provided by composites filled with carbonized organic fibers. The conductivity of such fibers is much lower that that of metals. The thickness of the fibers is about a few microns, and their length can be on the order of several millimeters. The form factor of the fiber is very low, and the region of frequency dispersion may be at microwaves, as is seen in Fig. 8 [47].

Figure 8 shows the measured frequency dependence of permittivity for a composite filled with carbon fibers with length l=1.5 mm, thickness d=8 μm, and resistivity of 10 000 Ohm×cm. The volume fraction of the fibers in the composite is p=0.01%. The sample is a sheet polymer-based composite of thickness of less than 1 mm. Fibers are parallel to the sheet material plane, and they are distributed and oriented randomly in this plane. Experimental details are given in [47]. The frequency dependence of permittivity is of the Debye type. The low-frequency permittivity varies linearly with the volume fraction. The measured frequency and concentration dependences of permittivity agree well with the dilute limit approximation (4), written for the case under consideration as

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{host}} \left(1 + p\kappa \frac{2\mathrm{i}\,\sigma/f - \varepsilon_{\text{host}}}{\varepsilon_{\text{host}} + n\left(2\mathrm{i}\,\sigma/f - \varepsilon_{\text{host}}\right)} \right), \tag{37}$$

where σ is the conductivity of the fibers, κ is a factor describing the averaged polarizability of inclusions, and n is the depolarization factor of the fibers,
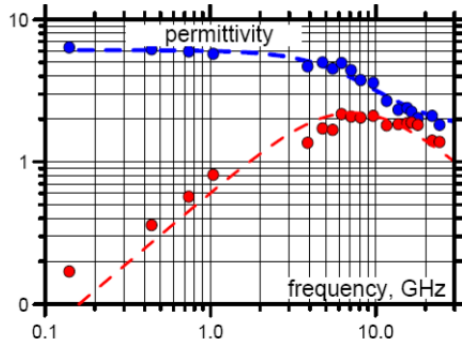
$$n = \frac{d^2}{l^2} \ln \frac{l}{d}. \tag{38}$$

Figure 8. The measured frequency dependence of real (blue dots) and imaginary (red dots) permeability of a composite filled with carbon fibers of 1.5 mm in length with the resistivity of 10 000 Ohm×cm. The volume fraction of the fibers is 0.01% [47]. Curves are the result of fitting of measured data with the Debye dispersion law.

The value of κ =1/3 in Eq. (37) for the case under consideration, that is a product of the value of ½, which accounts for the isotropic in-plane orientations of the fibers in a sheet sample, and the value of 2/3, which accounts for cylindrical shape of fibers instead of ellipsoidal shape considered by the theories.

The type of the frequency dependence observed in fiber-filled composites is determined by the conductivity of fibers. In the general case, the dielectric dispersion curve is of the Lorentzian type with the parameters written as [48]

$$\chi_{st} = \frac{1}{3}\frac{\varepsilon_{host}p}{\ln l/d}\left(\frac{l}{d}\right)^2 , \ f_{rel} \approx \frac{2\sigma}{\varepsilon_{host}}\left(\frac{d}{l}\right)^2 \ln l/d , \ f_{res} \approx \frac{c}{2l\sqrt{\varepsilon_{host}}} \tag{39}$$

The resonance of the permittivity arises from the half-wavelength resonance excited within the fibers.

Figure 9 shows the measured frequency dependence of permittivity for a composite filled with aluminum-coated fibers of 10 mm long [47]. The volume fraction the fibers is 0.01%. Due to high conductivity of the fibers, the frequency dependence of permittivity is of pronounced resonance (Lorentzian) type.

It is seen from Fig. 9 that the quality factor of the dielectric resonance is much lower than that predicted by Eq. (39). This is because Eq. (39) does not account for the radiation resistance of the fibers. The radiation resistance of a half-wavelength dipole is approximately 75 Ohm in the free space, which is much larger than the ohmic resistance of the fiber, and contributes dominantly to the quality factor of the resonance.

In fact, such composites behave as a kind of a metamaterial over the frequency range near the resonance, because they contain inhomogeneities, whose characteristic dimensions are close to the wavelength, and the principal features of their dielectric dispersion depend on the resonance scattering on the fibers. This is also evidenced by the facts that the measured

permittivity is less than that produced by the MG mixing law, and that the radiation resistance makes a dominant contribution into the quality factor of the dielectric resonance. Rigorously, metamaterials cannot be described in terms of effective material parameters. However, an experimental observation of deviation of microwave performance of the composites from Fresnel law has required special measurement conditions, see [49] for details.
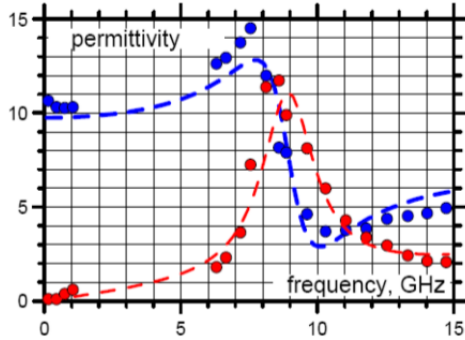

Figure 9. The measured frequency dependence of real (blue dots) and imaginary (red dots) permeability of a composite filled with aluminum-coated fibers 20 mm long. The volume fraction of the fibers is 0.01% [47]. Curves are the result of fitting of measured data with the Lorentzian dispersion law.

4.2. Theories for the effective properties of fiber-filled composites

A typical feature of fiber-filled composites is a low value of the percolation threshold: $p_c \propto d/l$, see [47] for the measured data. Although the percolation threshold is conventionally considered as a structure-dependent parameter, the dependence has been validated with composites based on a random mixture of conducting and non-conducting fibers, so that the dependence on agglomeration would be minimized. The standard EMT produces even lower values, $p_c \propto (d/l)^2$, and a large disagreement with the measured permittivity values at concentrations close to the percolation threshold can be observed. Mixing rules for the fiber-filled composites were primarily aimed at obtaining proper dependence of the percolation threshold on the aspect ratio of fibers.

Historically, the first theories describing the effective properties of fiber-filled composites have been suggested in [37] and [50]. However, the theory [37] describes the case of infinite conductivity of inclusions and is not suitable for describing of frequency dependences in metal-dielectric composites. Theory [50] is a modification of the EMT. It is based on the assumption of strong anisotropy of the effective medium in the vicinity of a particular fiber, which results in the equations

$$\frac{p}{3}\left(\frac{\varepsilon_{\text{eff},||}}{\varepsilon_{\text{eff},||}+n\left(\varepsilon_{\text{incl}}-\varepsilon_{\text{eff},||}\right)} + \frac{2\varepsilon_{\text{eff},\perp}}{\varepsilon_\perp + n_\perp \varepsilon_{\text{incl}}\left(\varepsilon_m - \varepsilon_{\text{eff},\perp}\right)} \right) + \frac{\left(1-p\right)\varepsilon_{\text{eff},\perp}}{\varepsilon_\perp + n\left(\varepsilon_{\text{host}}-\varepsilon_{\text{eff},\perp}\right)} = 1 , \qquad (40)$$

$$\frac{p}{3}\left(\frac{\left(\varepsilon_{\text{eff},||}-\varepsilon_{\text{incl}}\right)}{\varepsilon_{\text{eff},||}+n\left(\varepsilon_{\text{incl}}-\varepsilon_{\text{eff},||}\right)}+\frac{2\left(\varepsilon_{\text{eff},\perp}-\varepsilon_{\text{incl}}\right)}{\varepsilon_{\perp}+n_{\perp}\left(\varepsilon_{\text{incl}}-\varepsilon_{\text{eff},\perp}\right)}\right)+\frac{\left(1-p\right)\left(\varepsilon_{\text{eff},\perp}-\varepsilon_{\text{host}}\right)}{\varepsilon_{\perp}+n\left(\varepsilon_{\text{host}}-\varepsilon_{\text{eff},\perp}\right)}=0. \qquad (41)$$
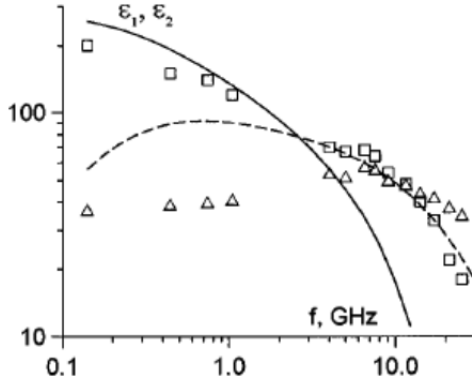

Figure 10. Dots: the measured dielectric dispersion curves for a composite filled with carbon fibers 1.8 mm long with the resistivity of 1400 Ohm×cm. The volume concentration of the fibers is 0.52%. Curves: calculation by Eq. (42) [47].

The two equations (40) and (41) are used for the search of two values of the effective permittivity, $\varepsilon_{\text{eff},||}$ and $\varepsilon_{\text{eff},\perp}$, in the directions parallel and perpendicular to a fiber, respectively; n is given by Eq. (38), $n_{\perp}=(1-n)/2$, and the observed effective permittivity of the composite is found by averaging of $\varepsilon_{\text{eff},||}$ and $\varepsilon_{\text{eff},\perp}$. The value of the randomization factor κ, defined in the Subsection 2.1, equals to 1/3, and is substituted in Eqs. (40) and (41). The theory [50] predicts correctly the dependence of the percolation threshold on the aspect ratio of fibers, but disagrees with the dilute limit approximation, and, therefore, with the measured permittivity of composites at low concentrations of fibers.

Theory [51] allows for a better quantitative agreement over a wide range of volume fractions below the percolation threshold. The theory is based on the assumption that, in the vicinity of a particular fiber, the permittivity of effective medium ε^* is a function of the distance from to fiber z:

$$\begin{aligned}\varepsilon^*\left(z\right)&=\varepsilon_{\text{host}}+\left(\varepsilon_{\text{eff}}-\varepsilon_{\text{host}}\right)\left(z/ax\right) \quad \text{at} \quad z<ax\\ \varepsilon^*\left(z\right)&=\varepsilon_{\text{host}} \quad \text{at} \quad z\geq ax\end{aligned} \qquad (42)$$

where x is a parameter of the theory. This assumption results in the EMT equation written as

$$\frac{\varepsilon_{\text{incl}}}{3\varepsilon_{\text{eff}}}\frac{p}{1+\left(d^2\varepsilon_{\text{incl}}/l^2\varepsilon_{\text{host}}\right)\ln\left(1+\left(lx\varepsilon_{\text{host}}\right)/\left(d\varepsilon_{\text{eff}}\right)\right)}+3\frac{\varepsilon_{\text{host}}-\varepsilon_{\text{eff}}}{\varepsilon_{\text{host}}+2\varepsilon_{\text{eff}}}=0, \qquad (43)$$

which is conventionally used in microwave studies of fiber-filled composites, see, e.g., [52].

There is lack of measured data on the frequency-dependent dielectric performance of fiber-filled composites near the percolation threshold in the literature; one of examples of the data is given in Fig. 10 [45]. It is seen from the figure that the EMT predicts a gradual shift of the loss peak. The measured dielectric loss peak differs from that predicted by the theory. In contrast, the measured variation of the loss peak appearing as approaching the percolation threshold looks like a rise of the low-frequency loss level, with a well-defined trace of the loss peak associated with individual fibers.

This difference between the theory and measurements may be associated not with the geometrical distribution of shapes of conducting clusters, as the percolation theory suggests, but with other low-frequency loss mechanisms near the percolation threshold. For example, imperfect electric contacts between fibers comprising a conductive cluster may contribute to the low-frequency loss [20]. The conductivity of such contacts must be much lower than the conductivity of the fibers. Therefore, imperfect contacts may result in a large low-frequency shift of dielectric loss. Because of a low value and wide distribution of the conductivity of contacts, this loss forms a very smooth dispersion curve, which is seen in Fig. 10.

The same may be true for composites filled with carbon black or carbon nanotubes, which are known to have the percolation type of frequency dispersion at microwaves, see, e.g., [20]. Dielectric loss appearing at low frequencies might be associated with very prolate conductive clusters, if the conductivity of clusters is on the same order of magnitude as the conductivity of inclusions. Account for the imperfect contacts would allow for more realistic assumptions on the shape of conducting clusters.

In principle, the effect of contacts may be understood as a presence of a comparatively low-conductive shell covering the surface of conducting inclusions. For an individual inclusion, the presence of such a shell leads to a low-frequency shift of the loss peak, without change in its shape. To get an agreement with the measured data, a distribution of these conductivities should be included in the model. By the analogy to the Cole-Cole dispersion law, such distribution would results in the power frequency dependences of the permittivity. Hence the difference between measured critical indices and universal values derived from geometrical considerations can be observed, but there is no theory explaining and quantifying such phenomena in the literature.

The available data of the microwave permeability of composites filled with magnetic fibers are consistent with the dilute limit approximation [53, 54].

5. Conclusions

The problem of describing of the effective permittivity as a function of concentration of inclusions in a metal-dielectric mixture is well studied. However, newly developed mixing rules still appear in the literature. This means that the solution for the problem is not satisfactory to some extent, and is typically related to the description of frequency dependences of material parameters.

The above consideration allows for determining the validity limits of various mixing rules. These limits are dependent on the difference between the susceptibilities of inclusions and the host matrix, and on the elongation of inclusions.

For microwave permeability, the difference is typically not high, and the effective properties of composites are well described by the MG mixing rule. For lower frequencies, the intrinsic permeability may be high, and a more sophisticated mixing rule may be needed. For composites containing platelet and fibrous magnetic inclusions, the microwave permeability is described by the dilute limit approximation. The same is true for composites with dielectric fibers.

For microwave permittivity of a metal-dielectric mixture, the difference is typically large, and the effective properties are determined by the morphology of the composite. But fitting of measured data to the theoretical results is typically rather simple, because the frequency dispersion of permittivity is a rare occasion at microwaves. In metal-dielectric composites, the region of frequency dispersion is located at much higher frequencies, as can be estimated from typical conductivity of metals and feasible dimensions of inclusions.

For simultaneous modeling of the permittivity and permeability of composites with conducting inclusions, sophisticated mixing rules are unavoidable, with an account for a distribution of inclusions in shape. This case is the most difficult, because both concentration and frequency dependences of material parameters may be non-trivial.

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