A homogenization theory for systems of penetrable dielectric particles

M. Ya. Sushko and A. V. Dorosh

Department of Theoretical Physics and Astronomy, Mechnikov National University,
2 Dvoryanska St., Odesa 65026, Ukraine

Abstract

A many-particle theory is presented for the effective quasistatic permittivity of macroscopically homogeneous and isotropic systems of inhomogeneous dielectric particles with different degrees of penetrability. The theory is based upon our original compact-group approach, complemented by the Hashin-Shtrikman variational principle. The governing equation is obtained by summing up the statistical moments for the deviations of the local permittivity in the system from the desired effective permittivity. The latter is, in principle, recoverable from the governing equation as a functional of the constituents’ volume concentrations (expressed through statistical averages of certain products of the particles’ characteristic functions) and permittivity profiles. Under the suggestion that the local permittivity is determined by the shortest distance from the point of interest to the nearest sphere, a complete analysis is carried out for hard and fully penetrable spheres with piecewise-continuous radial permittivities. The results are contrasted with other authors’ analytical theories and simulation data. This comparison validates our theory and also sheds light on possible computational errors caused by the use of rectangular lattices to simulate dispersions of spherical particles.

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1 Introduction

The question of how the statistical microstructure affects the dielectric properties of a particular substance, natural or artificial, is of great importance to a wide range of physical, chemical, biological, and interdisciplinary disciplines [1, 2, 3, 4, 5, 6, 7, 8, 9]. In particular, it lies at the heart of material science whose main objectives include the development of composite materials with desired dielectric parameters. The inverse problem of finding the microstructure of a system from a known response of the latter to an applied electric field is of no less significance.

In this report, we analyze the effective quasistatic permittivity, $\varepsilon_{\text{eff}}$, of those heterogeneous systems which can be viewed as a result of dispersing dielectric particles with different degrees of penetrability (understood as the capability of particles to overlap one another) into uniform dielectric matrices (see, for examples, Figs. 1 and 2). The permittivity $\varepsilon_{\text{eff}}$ characterizes the dielectric response of the system to a probing electrical field with wavelength $\lambda \to \infty$ and is defined as the permittivity of a homogeneous (homogenized) medium producing the same dielectric response to the probing field. In fact, a pure substance with the properties of the homogenized medium may not occur in nature.

1 Corresponding author, e-mail: mrs@ou.edu.ua
The determination of $\varepsilon_{\text{eff}}$ is part of a general many-particle problem called the homogenization of a heterogeneous system. Solving it requires that both polarization and correlation effects of higher orders be taken into account, and it is the long-wave limit where the greatest progress has been achieved (see \cite{1, 2, 3, 4, 5, 6} for a review). Yet even in this case, one is faced with serious difficulties, especially when dealing with aperiodic or random systems. Some facts behind this statement are as follows:

1. One class of homogenization theories, exemplified by \cite{5, 11, 12, 13, 14, 15, 16, 17, 18}, represents attempts to use the multiple scattering theory or, in the quasistatic limit, the Green-function method for boundary-value problems to derive multipolar corrections to the classical Maxwell-Garnett \cite{19, 20} and Bruggeman \cite{21, 22} mixing rules, which were obtained long ago within one-particle and dipolar approximations. The consideration is usually restricted to the evaluation, using the Kirkwood superposition approximation and model pair-distribution functions, of correlation effects in groups of several hard particles. The precise role of the discarded higher-order terms in the iterative series becomes obscure as the filler concentration, or the dielectric filler-host contrast, or both are increased.

2. Similar difficulties are typical of another class of homogenization theories, such as \cite{6, 23, 24, 25, 26, 27, 28, 29, 30, 31}, based upon the perturbation expansion \cite{32} or cluster expansion \cite{33, 34, 35} technique. Their basic idea is to express the average polarization as a formal operator (an ensemble-averaged quantity) acting on the applied field and then use either technique to eliminate the applied field in favor of the average electric field in the system. Besides the knowledge of many-particle distribution functions, one requires the solutions to the electrostatic boundary-value problems for clusters of particles to advance. However, the exact solution is available only for two nonoverlapping spheres \cite{36} and no such solutions exist for overlapping spheres \cite{6, 29}. Even an approximate analysis of the three-sphere boundary problem is extremely difficult \cite{37, 38, 39}.

3. One more class of homogenization theories, termed together as the strong-property-fluctuation theory (SPFT) and represented by \cite{5, 40, 41, 42, 43, 44, 45, 46, 47}, is usually restricted to the use of the second-order truncation (bilocal approximation) for the mass operator series in the Dyson-type equation for the averaged electric field (for a discussion of the third-order approximation, see \cite{47}), Gaussian statistics for the stochastic field, model expressions for the two-point correlation function, and several other approximations.
4. The analysis of the effects of the particles’ inhomogeneity and anisotropy on the overall response of the system is usually reduced to the study of the response of a solitary particle to a uniform field. However, for a system of overlapping particles, the concepts of an individual particle and its polarizability become ill-defined. It is therefore reasonable that the theory of dielectric response of such a system be elaborated in a way that effectively incorporates many-particle effects, but avoids using uncontrolled assumptions about those to the greatest extent possible.

For diluted dispersions of penetrable spheres, such a theory was developed in [29, 30, 31]. However, to our best knowledge, no consistent analytical approach to $\varepsilon_{\text{eff}}$ has been proposed so far for concentrated systems of overlapping particles. Some simulation results for freely overlapping spheres were obtained in [48, 49]. A rather good interpolation of those is given by differential mixing equation [50], derived in a similar manner as the Maxwell Garnett mixing equation, but by including an enhanced background permittivity effect as the volume concentration of particles increases.

The main points of our approach to the problem and the structure of the paper are as follows.

1. We suggest that the dielectric response of a dispersion, $D$, to be homogenized is equivalent to that of an auxiliary model system, $S$, made up by embedding all the constituents of $D$ into a uniform (perhaps imagined) host medium, $M$, with a permittivity $\varepsilon_f$ to be found.

2. The effective permittivity of $S$ (equal to $\varepsilon_{\text{eff}}$ of $D$) is analyzed with the method of compact groups [51, 52, 53]. A compact group is defined as a macroscopic group of inhomogeneities ($D$’s particles and/or regions) within which all the distances between the inhomogeneities are much smaller than the wavelength of probing radiation in the host ($M$). Such groups are assumed to be large enough to reproduce the properties of the entire $S$. In the long-wavelength limit, it is the multi-particle polarization and correlation processes inside compact groups that give the leading contributions to the iterative series for the electric field and induction in $S$. On the hand, with respect to the probing field compact groups are actually point-like. Using the methods of generalized function theory, their contributions can be singled out without going into details of the above processes. The basic relations for $S$ in terms of the compact-group method are summarized in section 2.

3. Finding $\varepsilon_f$ is a separate problem. To solve it, we additionally appeal [54, 55] to the Hashin-Shtrikman variational principle [56] to obtain $\varepsilon_f = \varepsilon_{\text{eff}}$. The details of the solution are outlined in section 2 as well.

4. The permittivity distribution in $S$ is the sum of $\varepsilon_f$ and the contribution $\delta \varepsilon(r)$ due to compact groups of $D$’s constituents embedded in $M$. The $\delta \varepsilon(r)$ is modeled in terms of the characteristic (indicator) functions and permittivity profiles of individual constituents in accordance with the rules defining a model. With $\varepsilon_f$ and $\delta \varepsilon(r)$ known, finding $\varepsilon_{\text{eff}}$ reduces to a calculation and summation of the statistical moments of $\delta \varepsilon(r)$.

5. For dispersions of uniform spheres with different degrees of penetrability, this procedure gives Bruggeman-type equations for $\varepsilon_{\text{eff}}$ as a function of the permittivities and effective volume concentrations of $D$’s constituents. These results and comparison of them with calculations [57, 27, 29, 31], differential mixing rule [50], and extensive simulation data [49] are presented in section 3. The discrepancies with the simulations turn out to be too large to be accepted. We hypothesize that they are caused by the ambiguity in determination of the permittivity value between potential nodes near an arbitrarily-oriented material interface. Setting this value to be different from the permittivities of $D$’s constituents is effectively equivalent to an introduction of thin surface layers covering the spheres.

6. Generalizations of our theory to dispersions of fully penetrable or hard isotropic spheres with piecewise-continuous radial permittivity profiles $\varepsilon = \varepsilon(r)$ are suggested in section 4. In either case, $\varepsilon_{\text{eff}}$ is a functional determined by a certain integral relation. Using the model of two-layer spheres and considering the thickness and permittivity of the surface layer as fitting parameters, simulation data [49]...
can be reproduced within their accuracy. Analytical results for hard spheres are recovered by our theory surprisingly well for all continuous profiles \(e(r)\) considered in there.

(7) The major results of the paper are summarized in section 5.

2 Basics of the compact-group approach

Suppose that a fine dispersion \(D\) consists of a host, with permittivity \(\varepsilon_0\), and dispersed particles, with permittivity \(\varepsilon_1(r)\). To find its effective quasistatic permittivity, we assume that \(D\) is equivalent, in its effective dielectric properties, to a macroscopically homogeneous and isotropic system \(S\) prepared by embedding \(D\)’s constituents into a certain (in general, imagined) uniform medium \(M\), of permittivity \(\varepsilon_f\). According to the compact-group approach \([51, 52, 53]\), \(S\) can be viewed as a set of compact groups of \(D\)’s constituents in \(M\). The local permittivity in \(S\) is modeled as

\[
\varepsilon(r) = \varepsilon_f + \delta\varepsilon(r),
\]

where \(\delta\varepsilon(r)\) is the deviation from \(\varepsilon_f\) due to the presence of a compact group at point \(r\). The explicit form of \(\delta\varepsilon(r)\) depends on the properties of both the embedded particles and the host.

The effective permittivity \(\varepsilon_{\text{eff}}\) of \(S\) (and that of \(D\)) is determined as the proportionality coefficient in

\[
\langle D(r) \rangle = \langle \varepsilon(r) E(r) \rangle = \varepsilon_{\text{eff}} \langle E(r) \rangle,
\]

where \(D(r)\) and \(E(r)\) are the local induction and electric field in \(S\), respectively, and the angular brackets stand for statistical averaging or averaging by integration over the volume \(V\) of \(S\) (that is, \(\langle E(r) \rangle = V^{-1} \int_V E(r) \, dr\), etc). The ergodic hypothesis suggests \([59, 6]\) that for infinite systems, both types of averaging give equal results.

In the long-wavelength limit, the averages in Eq. (2) are formed by those domains of coordinates in the iterative series for \(D(r)\) and \(E(r)\) where the inner electromagnetic field propagators reveal a singular behavior. In other words, it is the effects of multiple reemissions and many-particle correlations within compact groups that contribute to \(\varepsilon_{\text{eff}}\). Their contributions, in the form of statistical moments \(\langle (\delta\varepsilon(r))^n \rangle\), can be singled out from all terms of the iterative series without an in-depth modelling of these processes. As a result,

\[
\langle E(r) \rangle = [1 + \langle Q(r) \rangle] E_0,
\]

\[
\langle D(r) \rangle = \varepsilon_f [1 - 2\langle Q(r) \rangle] E_0,
\]

where

\[
Q(r) = \sum_{n=1}^{\infty} \left( -\frac{1}{\varepsilon_f} \right)^n (\delta\varepsilon(r))^n
\]

and \(E_0\) is the amplitude of the probing field in \(M\).

To illustrate the general formalism, consider a dispersion of uniform hard spheres. In this case,

\[
\delta\varepsilon(r) = (\varepsilon_0 - \varepsilon_f) \left( 1 - \frac{1}{N} \sum_{i=1}^{N} \Pi_i(r, \Omega_i) \right) + (\varepsilon_1 - \varepsilon_f) \sum_{i=1}^{N} \Pi_i(r, \Omega_i),
\]

where \(\Pi_i(r, \Omega_i)\) is the characteristic function for region \(\Omega_i\) occupied by the \(i\)th sphere in a compact group of \(N \gg 1\) spheres:

\[
\Pi_i(r, \Omega_i) = \begin{cases} 1, & \text{if } r \in \Omega_i, \\ 0, & \text{if } r \notin \Omega_i. \end{cases}
\]
Then, by direct integration over $V$, we find from Eqs. (1)–(5) \[53\] :

$$
(1 - c) \frac{\varepsilon_0 - \varepsilon_f}{2\varepsilon_f + \varepsilon_0} + \frac{\varepsilon_1 - \varepsilon_f}{2\varepsilon_f + \varepsilon_1} = \frac{\varepsilon_{\text{eff}} - \varepsilon_f}{2\varepsilon_f + \varepsilon_{\text{eff}}},
$$

(8)

where $c = N_v/V$ is the net volume concentration of the spheres with individual volume $v = 4\pi R^3/3$. Taking $\varepsilon_f = \varepsilon_0$ and $\varepsilon_f = \varepsilon_{\text{eff}}$, we obtain, respectively, the Maxwell-Garnett mixing rule \[19, 20\]

$$
\varepsilon_{\text{eff}} = \varepsilon_0 \left(1 + 2c \frac{\varepsilon_1 - \varepsilon_0}{2\varepsilon_f + \varepsilon_1}\right) / \left(1 - c \frac{\varepsilon_1 - \varepsilon_0}{2\varepsilon_f + \varepsilon_1}\right)
$$

(9)

and the Bruggeman mixing rule \[21, 22\]

$$
(1 - c) \frac{\varepsilon_0 - \varepsilon_{\text{eff}}}{2\varepsilon_f + \varepsilon_0} + c \frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{2\varepsilon_f + \varepsilon_1} = 0.
$$

(10)

In the general case, $\varepsilon_f$ should be treated as unknown. We determine it consistently \[54, 55\] by combining the compact-group approach with the Hashin-Shtrikman variational principle \[56\]. The relevant functional is written in terms of the local field and permittivity distributions in $S$. Its stationary value is equal to the electric energy stored in $S$ and, by definition, that in $D$. The requirement that two different ways of homogenization – through the linear relation between the induction and the field \[59\] and through the equality of the electric energies stored in the heterogeneous and homogenized systems – give the same result, enables us to conclude that $\mathcal{M}$ is an imagined uniform medium with $\varepsilon_f = \varepsilon_{\text{eff}}$ (except maybe for metamaterials \[60, 61\], not treated here). In this case, Eqs. (2), (3), and (4) reduce to

$$
\langle Q(r) \rangle = \left\langle \frac{\varepsilon(r) - \varepsilon_{\text{eff}}}{2\varepsilon_f + \varepsilon_f(r)} \right\rangle = 0.
$$

(11)

The result $\varepsilon_f = \varepsilon_{\text{eff}}$ corresponds to the Bruggeman-type homogenization, but is not equivalent (see \[55\]) to the classical Bruggeman mean-field approximation \[21\]. It uses no extra model considerations about the geometries and concentrations of the constituents, permittivity distributions (except for their piecewise continuity), and processes in the system. Equation (11) is actually the condition postulated for the stochastic field in the SPFT \[5, 40, 41, 42, 43, 44, 45, 46, 47\] in order to improve the convergence of the iterative series when solving the integral equation for $E(r)$.

For complete proofs of the above statements, the Reader is referred to \[51, 52, 53, 55\].

3 Systems of penetrable uniform spheres

3.1 General formalism

Suppose that the spheres in $D$ are allowed to overlap, the permittivity of the regions of overlap remaining equal to $\varepsilon_1$ (see Fig. 1). Then the permittivity distribution in $S$ can be modeled in form (1) with $\varepsilon_f = \varepsilon_{\text{eff}}$ and

$$
\delta \varepsilon(r) = \Delta \varepsilon_1 \left[1 - \prod_{a=1}^N \left(1 - \chi_a^{(1)}(r)\right)\right] + \Delta \varepsilon_0 \prod_{a=1}^N \left(1 - \chi_a^{(1)}(r)\right),
$$

(12)

where $\Delta \varepsilon_1 = \varepsilon_1 - \varepsilon_{\text{eff}}$, $\Delta \varepsilon_0 = \varepsilon_0 - \varepsilon_{\text{eff}}$, and $\chi_a^{(1)}(r) = \theta(R - |r - r_a|)$ is the characteristic function of the sphere centered at $r_a$ ($\theta(x)$ is the Heaviside function). Due to the orthogonality of the characteristic
functions at $\Delta \varepsilon_1$ and $\Delta \varepsilon_0$ in Eq. (12), we obtain:

$$
\langle (\delta \varepsilon(r))^s \rangle = (\Delta \varepsilon_1)^s \left[ 1 - \left\langle \prod_{a=1}^{N} \left( 1 - \chi_a^{(1)}(r) \right) \right\rangle \right] + (\Delta \varepsilon_0)^s \left\langle \prod_{a=1}^{N} \left( 1 - \chi_a^{(1)}(r) \right) \right\rangle.
$$

(13)

The average of the product in Eq. (13) is the volume concentration of the host, and

$$
\phi(c, \kappa) = 1 - \left\langle \prod_{a=1}^{N} \left( 1 - \chi_a^{(1)}(r) \right) \right\rangle = \left\langle \sum_{1 \leq a \leq N} \chi_a^{(1)}(r) \right\rangle - \left\langle \sum_{1 \leq a < b \leq N} \chi_a^{(1)}(r) \chi_b^{(1)}(r) \right\rangle + \left\langle \sum_{1 \leq a < b < c \leq N} \chi_a^{(1)}(r) \chi_b^{(1)}(r) \chi_c^{(1)}(r) \right\rangle - \ldots
$$

(14)

is the effective volume concentration of spheres [6]. The latter is a function of the dimensionless density $c = Nv/V$ (the ratio of the total volume of spheres to $V$) and the hardness parameter $\kappa$, such that $\kappa = 1$ corresponds to hard (mutually impenetrable) spheres and $\kappa = 0$ to “fully” penetrable (statistically independent) spheres.

The averages in Eq. (14) are calculated using the $s$-sphere distribution functions $F_s(r_1, r_2, \ldots, r_s)$ for a given dispersion. Once $\phi(c, \kappa)$ is known, Eq. (11), treated as an asymptotic series, yields the equation for $\varepsilon_{\text{eff}}$:

$$
(1 - \phi(c, \kappa)) \frac{\varepsilon_0 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_0} + \phi(c, \kappa) \frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_1} = 0.
$$

(15)

Rigorous calculations of $\phi(c, \kappa)$ are possible in the limiting cases of macroscopically homogeneous and isotropic systems of hard or fully penetrable spheres.

In the former case, $F_1(r_1) = 1$, whereas every $F_s(r_1, r_2, \ldots, r_s), s \geq 2$, vanishes for any sphere configuration in which at least one of the center-to-center distances $|r_i - r_j|$ is shorter than $2R$; and so do the products of the characteristic functions for the configurations with all $|r_i - r_j| > 2R$. Then the only nonzero term after the last equality sign in Eq. (14) is

$$
\left\langle \sum_{1 \leq a \leq N} \chi_a^{(1)}(r) \right\rangle = c,
$$

$\phi(c, 1) = c$, and Eq. (15) reduces to the Bruggeman mixing rule (10).

In the latter, the positions of spheres are statistically independent. Then $F_s = \prod_{i=1}^{s} F_1(r_i) = 1$ and $(N \gg 1)$

$$
\left\langle \prod_{a=1}^{N} \left( 1 - \chi_a^{(1)}(r) \right) \right\rangle = \left( 1 - \frac{v}{V} \right)^N \to 1 - f,
$$

(16)

where $f = 1 - e^{-c}$. So, $\phi(c, 0) = f$ and Eq. (15) takes the form

$$
(1 - f) \frac{\varepsilon_0 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_0} + f \frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_1} = 0.
$$

(17)

In deriving Eq. (17), the fact of sphericity of particles (the explicit form of $\chi_a^{(1)}(r)$) was not used. It follows immediately that Eq. (17) should also hold for macroscopically homogeneous and isotropic
systems prepared by embedding $N \gg 1$ freely overlapping regions of arbitrary shape, with individual permittivities $\varepsilon_1$ and volumes $v$, into a host of permittivity $\varepsilon_0$. Moreover, Eq. (17) should remain valid for polydisperse mixtures of such regions, having differing shapes and volumes, $v_\alpha$, provided the number $N_\alpha$ of regions of each sort $\alpha = 1, 2, \ldots, q$ is statistically large: $N_\alpha \gg 1$. The effective volume concentration of such regions $f = 1 - \exp \left( -\sum_{\alpha=1}^{q} N_\alpha v_\alpha / V \right)$ and the volume concentration of the host is $1 - f$.

3.2 Systems of soft particles

For dispersions of soft spheres, with $0 < \kappa < 1$, the determination of $\kappa$ and theoretical calculation of $\phi(c, \kappa)$ are nontrivial problems. One way is to define $\kappa$ through the pair distribution function $F_2(r_1, r_2) = F_2(|r_1 - r_2|)$ by the relation [62, 63]

$$F_2(r) = 1 - \kappa, \quad r < 2R.$$ 

Assuming the direct correlation function and the pair potential to be zero for $r > 2R$, one can use the Percus-Yevick approximation for $F_2(r)$ and the generalized Kirkwood superposition approximation for $F_s(r_1, r_2, \ldots, r_s)$ at $s > 2$ to obtain the estimate [64]

$$\phi(c, \kappa) \approx \sum_{n=1}^{\infty} \left( -1 \right)^{n+1} \frac{c^n}{n!} \left( 1 - \kappa \right)^{n(n-1)/2}. \tag{18}$$

This, in particular, reproduces the above limiting values: $\phi(c, 0) = f$, $\phi(c, 1) = c$. The equation for $\varepsilon_{\text{eff}}$ still has form (15).

Note that the concept of hard particles implies the existence of a sharp change in density at the particle-host interface. In fact, not many interfaces fulfill this condition. Particles may contain pores, be gel-type penetrable or somewhat deformable, have “hairy” adjacent polymer layers, etc. Given permittivity data for a system of such “soft” particles, we can use Eq. (15) to recover $\phi(c, \kappa)$ and then Eq. (18) to estimate $\kappa$. In this way, the effective hardness of particles can be defined operationally.

3.3 Dilute dispersions

It is of crucial importance to verify the applicability of our theory to diluted dispersions, for which a number of reliable results exist in the literature and, on the other hand, the concept of compact groups may seem most vulnerable.

In the limit $\phi(c, \kappa) \to 0$, Eq. (15) can be represented as

$$\frac{\varepsilon_{\text{eff}}}{\varepsilon_0} = 1 + 3\beta\phi(c, \kappa) + \left( 3\beta^2 + 6\beta^3 \right) \phi^2(c, \kappa) + O \left( \beta^3 \phi^3(c, \kappa) \right), \tag{19}$$

where $\beta = (\varepsilon_1 - \varepsilon_0) / (\varepsilon_1 + 2\varepsilon_0)$. For $\phi(c, \kappa)$ given by Eq. (18) and $c \to 0$, Eq. (19) takes the form

$$\frac{\varepsilon_{\text{eff}}}{\varepsilon_0} = 1 + 3\beta c + \left[ \frac{3}{2} (1 - \kappa) \beta + 3\beta^2 + 6\beta^3 \right] c^2 + O \left( \beta c^3 \right). \tag{20}$$

The first two addends on the right of Eq. (20) give the classical Maxwell-Garnett result [19, 20]. The next addend is a $c^2$-correction. For a dilute hard-sphere gas ($\kappa = 1$), its leading term $3\beta^2 c^2$ agrees with those in Jeffrey’s result [57]

$$\frac{\varepsilon_{\text{eff}}}{\varepsilon_0} = 1 + 3\beta c + \left[ 3\beta^2 + 6A(\beta)\beta^3 \right] c^2 + O \left( c^3 \right) \tag{21}$$
and result [27]; the other term, \( \sim \beta^3 c^2 \), differs from its counterparts in [57] [27] by a \( \beta \)-dependent coefficient \( A(\beta) < 0.252 \). For low-contrast dispersions with \( \delta = |\varepsilon_1 - \varepsilon_0|/\varepsilon_0 \ll 1 \), all the results agree, to \( O(\delta^2) \), with one another and with relation [59]

\[
\varepsilon_{\text{eff}} = \varepsilon - \frac{1}{3\varepsilon} (\varepsilon - \varepsilon_f)^2,
\]

valid to \( O(\delta^2) \) for any mixture in which the local variations of permittivity are weak.

If the spheres are penetrable \((0 \leq \kappa < 1)\), the volume concentration \( \phi(c, \kappa) \) is a more preferable parameter than \( c \). Through order \( c^2 \), \( \phi(c, \kappa) = c - \frac{1}{2}(1 - \kappa)c^2 \equiv \phi_2 \) and Eq. (19) approaches Torquato’s result [29] [31] [30]

\[
\frac{\varepsilon_{\text{eff}}}{\varepsilon_0} = 1 + 3\beta\phi_2 + [3\beta^2 + 6(0.21068 + 0.35078(1 - \kappa))]\phi_2^2,
\]

except for the numerical factor in front of \( \beta^3 \phi_2^2 \). Note that for dispersions of fully penetrable spheres, Eq. (22) is expected to be a good approximation provided \( \phi_2^2 < 0.2 \) [31].

So, the agreement of Eq. (19) with results [27] [29] [31] [57] for dilute dispersions with low \( \delta \) is exact through order \( \beta^3 \phi_2^2 \). At the same time, the \( O(\beta^3 \phi_2^2) \)-corrections are of greater magnitude in our theory. This fact can be interpreted as a manifestation of many-particle polarization and correlation effects, coming into play as \( \delta \) increases and effectively taken into account by Eq. (19).

### 3.4 Comparison with numerical experiment

To further test our theory, we contrast it with differential mixing equation [50], proposed for mixtures with wide-ranging permittivity contrast \( k = \varepsilon_1/\varepsilon_0 \), and numerical \( \nu \)-model [19]

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_0}{\varepsilon_{\text{eff}} + 2\varepsilon_0 + \nu(\varepsilon_{\text{eff}} - \varepsilon_0)} = f \frac{\varepsilon_1 - \varepsilon_0}{\varepsilon_1 + 2\varepsilon_0 + \nu(\varepsilon_{\text{eff}} - \varepsilon_0)},
\]

derived as a fit to the set of over 4000 simulation results for \( k \) varying from 1/102 to 102. The dimensionless fitting function \( \nu = \nu(k, f) \) was proposed to be

\[
\nu(f, k) = \begin{cases} 
1.27 + 1.43 e^{-0.043k}f^2 + (-2.76 - 0.9 e^{-0.043k})f + 2.35, & k > 1, \\
1.06f^2 + (-1.23 + 0.44 e^{-5.95k})f + 1.7, & k < 1.
\end{cases}
\]

The permittivity \( \varepsilon_{\text{eff}} \) was determined by calculating the electrostatic field energy of samples placed in a homogeneous electric field. The computational domain, of size \( 100 \times 100 \times 100 = 1000000 \) cells, was restricted with periodic boundary conditions. The potentials were different on the faces perpendicular to the field and the same on the other faces. The diameter of randomly positioned spheres was 20 cells.

The finite difference approximation was used in [19] to solve the equation for potential. The local permittivity value in the difference equation was ambiguous when the cubic grid cell included the surface of a sphere. In such cases, it was taken to be equal to certain weighted averages of \( \varepsilon_0 \) and \( \varepsilon_1 \). That is, a third phase, with poorly defined permittivity \( \varepsilon_2 \), was actually introduced.

The results for \( \varepsilon_{\text{eff}} \) obtained in the framework of our approach, equation [50], and \( \nu \)-model (23) at \( k = 51 \) are shown in Fig. 3 all are within the Hashin-Shtrikman bounds. The relative deviation \( \text{Dev} = (\varepsilon_{\text{eff}} - \varepsilon_{\text{eff}})/\varepsilon_{\text{eff}} \cdot 100\% \) between the results is shown in Fig. 3. For \( f \gtrsim 0.2 \), our theory predicts higher values for \( \varepsilon_{\text{eff}} \); a possible reason is that the uncontrolled \( \varepsilon_2 \) took intermediate values between \( \varepsilon_0 \) and \( \varepsilon_1 \). If so, the appearance of the maximum in Fig. 4 is explained readily: as \( f \) increases, the net
volume and, therefore, the accumulating effect of the interfacial layers should first increase and then, when the spheres begin to overlap considerably, decrease. That fact that our theory is in rather good agreement with analytical differential mixing equation [50] (see Fig. 3) seems to support our suggestion.

Note that a statistically small number of spheres and anisotropy of the computing domain may also be factors contributing to Dev.

4 Systems of penetrable heterogeneous spheres

4.1 Equation for $\varepsilon_{\text{eff}}$

The preceding analysis naturally leads to the problem of finding $\varepsilon_{\text{eff}}$ for systems of heterogeneous particles. For hard particles, its formal solution within the compact-group approach was obtained in [52, 53, 55]. Here, we analyze the case where: 1) the particles are fully penetrable isotropic spheres embedded into an isotropic and homogeneous host of permittivity $\varepsilon_{0}$; 2) their permittivity profile is described by a piecewise-continuous radial function $e = \varepsilon(r)$; 3) the local permittivity value $\varepsilon(r)$ in the system is determined, according to [54, 65], by the distance $l \equiv \min_{a} |r - r_{a}|$ from the point of interest $r$ to the center of the nearest sphere. An example of such a system is shown in Fig. 2.

Following the line of reasoning [54, 65], suppose first that every sphere, of radius $R$, consists of $M$ concentric spherical layers with outer radii $R_{j}$ and constant permittivities $\varepsilon_{j}, j = 1, 2, \ldots, M (R_{1} < R_{2} < \ldots < R_{M})$.

Figure 3: $\varepsilon_{\text{eff}}/\varepsilon_{0}$ versus $f$ for a dispersion of fully penetrable uniform spheres according to Eq. (17) (solid curve), $\nu$-model (23) (dashed one), and differential mixing equation [50] at $k = 51$ (middle dotted one); the outermost dotted curves represent the Hashin-Shtrikman bounds [56].

Figure 4: The relative deviations of $\varepsilon_{\text{eff}}$ given by Eq. (17) and that by Eq. (33) at $a = 0.93$, $\varepsilon_{2}/\varepsilon_{0} = 5$ (curves 1 and 2, respectively) from $\varepsilon_{\text{eff}}$ given by $\nu$-model (23) as functions of $f$; $k = 51$. 

Introducing the characteristic functions $\chi^{(i)}(r) = \theta(R_i - |r - r_a|)$ for spheres with centers at points $r_a$ and radii $R_i$, we rewrite Eq. (25) in form (1) with $\varepsilon_f = \varepsilon_{\text{eff}}$ and

$$\begin{align*}
\delta\varepsilon(r) &= \Delta\varepsilon_1 \left[ 1 - \prod_{a=1}^{N} (1 - \chi^{(1)}_a(r)) \right] \\
&\quad + \sum_{j=2}^{M} \Delta\varepsilon_j \left[ 1 - \prod_{a=1}^{N} (1 - \chi^{(j)}_a(r)) \right] \prod_{b=1}^{N} (1 - \chi^{(j-1)}_b(r)) + \Delta\varepsilon_0 \prod_{b=1}^{N} (1 - \chi^{(M)}_b(r)),
\end{align*}$$

(26)

where $\Delta\varepsilon_0 = \varepsilon_0 - \varepsilon_{\text{eff}}$ and $\Delta\varepsilon_j = \varepsilon_j - \varepsilon_{\text{eff}}$. By doing so, we change from a given system, $D^*$, to the associated system, $S^*$, used for the homogenization of $D^*$ (as discussed in sections 1 and 2).

The moments of $\delta\varepsilon(r)$ are

$$
\langle \langle \delta\varepsilon(r) \rangle^s \rangle = f(n, R_1) (\Delta\varepsilon_1)^s + \sum_{j=2}^{M} [f(n, R_j) - f(n, R_{j-1})] (\Delta\varepsilon_j)^s + [1 - f(n, R_M)] (\Delta\varepsilon_0)^s,
$$

(27)

where

$$f(n, R_j) = 1 - \left\langle \prod_{a=1}^{N} (1 - \chi^{(j)}_a(r)) \right\rangle = 1 - e^{-4\pi n R_j^3/3}$$

(28)

and $n = N/V$ is the particle number density.

Now, passing to the limits $M \to \infty$, $|R_j - R_{j-1}| \to 0$ and taking into account the differentiability of $f(n, r)$ in $r$, we can generalize Eq. (27) to the case where the sphere’s permittivity profile is a piecewise-continuous function $e = e(r)$:

$$
\langle \langle \delta\varepsilon(r) \rangle^s \rangle = \int_0^R \frac{\partial f(n, r)}{\partial r} [\Delta\varepsilon(r)]^s dr + (1 - f(n, R)) (\Delta\varepsilon_0)^s,
$$

(29)

where $\Delta\varepsilon = e(r) - \varepsilon_{\text{eff}}$. Then Eqs. (28) and (11) give the desired equation for $\varepsilon_{\text{eff}}$:

$$
e^{-4\pi n R^3/3} \frac{\varepsilon_0 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_0} + 4\pi n \int_0^R r^2 e^{-4\pi n r^3/3} \frac{e(r) - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + e(r)} dr = 0.
$$

(30)

Changing to the dimensionless variable $u = r/R$, we can represent it as

$$
e^{-c} \frac{\varepsilon_0 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_0} + 3c \int_0^1 u^2 e^{-cu^3} \frac{e(u) - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + e(u)} du = 0.
$$

(31)
The analogous equation for a dispersion of hard spheres with a piecewise-continuous permittivity profile \( e = e(r) \) reads \[52, 53, 55\]

\[
(1 - c) \frac{\varepsilon_0 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_0} + 3c \int_0^1 u^2 \frac{e(u) - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + e(u)} du = 0. \tag{32}
\]

### 4.2 Comparison with analytical results for inhomogeneous spheres

For low values of \( k \) and \( c \), both electromagnetic interactions and spatial correlations are small. In this case, the Maxwell-Garnett- and Bruggeman-type approaches should give close results. This fact was used in \[55\] to test Eq. (32) by contrasting its solutions with analytical results \[58\] for mixtures of hard spheres with continuous radial permittivity profiles. The quasi-static polarizability of spheres and then \( \varepsilon_{\text{eff}} \) were calculated in \[58\] using (a) the internal field method (one finds the dipole moment by integrating the product of the field and the permittivity over the sphere’s volume) and (b) the external field method (one finds the field perturbation due to the sphere and then the amplitude of an equivalent dipole). Both methods gave the same results, free of ambiguities typical of the above computer simulations.

Figure 5 represents our results obtained by Eqs. (32) and (31) for \( \varepsilon_{\text{eff}} \) of dispersions of inhomogeneous hard and fully penetrable dielectric particles embedded in a medium of permittivity \( \varepsilon_0 = 1 \) and having the following permittivity profiles (\( 0 \leq u \leq 1 \)): homogeneous \( e(u) = 2 \varepsilon_0 \) (denoted as H); linear \( e(u) = \varepsilon_0 (2 - u) \) (L); parabolic \( e(u) = \varepsilon_0 (2 - u^2) \) (P); Gaussian \( e(u) = \varepsilon_0 (1 + e^{-u^2}) \) (G; this is different from the Gaussian packet used in \[58\] since we consider spheres with sharp boundaries). The agreement of our results \[55\] with analytical results \[58\] for inhomogeneous hard spheres is surprisingly good. It is
recalling our remark (see subsection 3.4) that the procedure used in [49] to determine the local permittivity of the low permittivity contrasts between the regions, its relative magnitude is not very high (5% and 2.4% for L, P and G, respectively; f ∈ [0, 0.7]). No increase is observed for homogeneous penetrable spheres, as expected.

4.3 Further comparison with the numerical experiment

4.3 Further comparison with the numerical experiment

For fully penetrable two-layer spheres, with the inner-sphere radius aR (a ≤ 1) and permittivity ε_1 and the outer-sphere radius R and permittivity ε_2, Eq. (33) can be represented as

\[(1 - f) \frac{ε_0 - ε_{eff}}{2ε_{eff} + ε_0} + \left[1 - (1 - f)^{α^3}\right] \frac{ε_1 - ε_{eff}}{2ε_{eff} + ε_1} + \left[(1 - f)^{α^3} - (1 - f)\right] \frac{ε_2 - ε_{eff}}{2ε_{eff} + ε_2} = 0.\] (33)

Recalling our remark (see subsection 3.4) that the procedure used in [49] to determine the local permittivity value near the sphere-host interfaces is equivalent to the introduction of a third phase, we expect that Eq. (33) is capable of reproducing the ν-model results within the accuracy of the fitting procedure employed in [49] to obtain Eqs. (23) and (24). Based on Figs. 6 and 7 in [49], we estimate that accuracy to be no better than 10% for f ∈ [0.20, 0.65].

The results predicted by model (33) for a = 0.93, ε_2/ε_0 = 5, and k = 51, simulations [49], ν-model [23], and differential mixing equation [50] are compared in Figs. 6, 7, and 8. The maximum deviation of our theory from the ν-model does not exceed 7.5% on the entire interval f ∈ [0, 1]. For narrower intervals of f, it can be greatly reduced by minor variations in a and ε_2.
The authors of [49] also studied mixtures of hard dielectric spheres with volume fractions $c < 0.3$. The results converged rather poorly when the grid step size was reduced. To improve their convergence, the local permittivity near the sphere-host interfaces was found by using the minimum estimation within the numerical technique employed, rather than the average of limit estimations. The final results for $\varepsilon_{\text{eff}}$ at $k = 51$ are presented in Fig. 8 and can be described by the $\nu$-model with $\nu \approx 0.3$, which is rather close the Maxwell–Garnett model ($\nu = 0$). They give us another opportunity to test our approach.

Consider a dispersion of hard two-layer spheres, with the inner-sphere radius $aR$ ($a \leq 1$) and permittivity $\varepsilon_1$ and the outer-sphere radius $R$ and permittivity $\varepsilon_2$. According to Eq. (32), the equation for its $\varepsilon_{\text{eff}}$ is

$$ (1 - c) \frac{\varepsilon_0 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_0} + a^3 c \frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_1} + (1 - a^3) c \frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_2} = 0. \quad (34) $$

In our view, the just-mentioned choice of the local permittivity in [49] is equivalent to a decrease in $\varepsilon_2$, or $a$, or both, as compared to those for the model of penetrable two-layer spheres. In particular, for two sets of parameters, $a = 0.82$, $\varepsilon_2/\varepsilon_0 = 4.1$ and $a = 0.79$, $\varepsilon_2/\varepsilon_0 = 5$, Eq. (34) reproduces the $\nu$-model result for hard uniform spheres with an accuracy of no worse than 3.5% (see Fig. 8 and 9). This fact is another evidence for the efficiency and consistency of our approach.
5 Conclusion

The main results of this study can be summarized as follows.

1. Using the compact-group approach \[51, 52, 53, 54, 55\], complemented by the Hashin-Shtrikman variational theorem \[56\], we developed a many-particle theory for finding the effective quasistatic permittivity \(\varepsilon_{\text{eff}}\) of dispersions of dielectric particles with different degrees of penetrability. According to it:

   (a) a dispersion to be homogenized is dielectrically equivalent to a macroscopically homogeneous and isotropic system prepared by embedding the constituents of the real dispersion into an imagined medium having the looked-for permittivity (Bruggeman-type homogenization);

   (b) the governing equation for \(\varepsilon_{\text{eff}}\) is obtained from Eq. (11) by summing up the statistical moments for the deviations of the local permittivity values in the model system from \(\varepsilon_{\text{eff}}\). These moments are determined by the properties of the dispersion’s constituents, such as their geometric parameters, permittivity profiles, degree of penetrability, etc.;

   (c) \(\varepsilon_{\text{eff}}\) is found from the governing equation as a functional of the dispersion’s constituents’ permittivity profiles and volume concentrations, the latter being expressed through the statistical averages of certain products of the particles’ characteristic functions.

2. The theory was applied to dispersions of spheres with a piecewise-continuous radial permittivity profile under the suggestion that for overlapping spheres, the local permittivity value is determined by the shortest distance from the point of interest to their centers. In this case, \(\varepsilon_{\text{eff}}\) satisfies certain integral relations, which were analyzed in detail.

3. The efficiency of the theory was demonstrated by contrasting its results with:

   (a) rigorous calculations \[27, 29, 31, 57\] for dilute dispersions of uniform spheres with different degrees of penetrability;

   (b) analytical calculations \[58\] for low-contrast dispersions \((1 \leq \varepsilon_1/\varepsilon_0 \leq 2)\) of hard spheres with different permittivity profiles and volume concentrations \(c \in [0, 0.4]\);

   (c) differential mixing equation \[50\] for high-contrast \((\varepsilon_1/\varepsilon_0 \gg 1)\) random mixtures of uniform spheres with effective volume concentrations \(f \in [0, 1]\);

   (d) computer simulations \[49\] for intermediate-contrast \((\varepsilon_1/\varepsilon_0 = 51)\) dispersions of hard \((c \in [0, 0.3])\) and freely overlapping \((f \in [0, 1])\) uniform spheres.

The agreement of the results with calculations \[27, 29, 31, 57, 58\] is very good and with equation \[50\] satisfactorily good. The agreement with simulation data \[49\] is achieved under the assumption that an uncontrolled use of weighted averages for the local permittivity values near the surfaces of spheres, which is typical of the finite difference method, is equivalent to the introduction of an interphase layer (of certain thickness and permittivity) between the spheres and the matrix. The neglect of this fact may cause considerable computational errors when rectangular grids are used to simulate dielectric properties of systems of particles with arbitrary oriented surfaces.
References

[1] C.F. Bohren and D.R. Huffman, Absorption and Scattering of Light by Small Particles, John Wiley & Sons, New York, 1983.

[2] D.J. Bergman and D. Stroud, Physical Properties of Macroscopically Inhomogeneous Media, Solid State Phys., 46 (1992) 147–269.

[3] C.-W. Nan, Physics of Inhomogeneous Inorganic Materials, Prog. Mater. Sci., 37 (1993) 1–116.

[4] A. Sihvola, Electromagnetic Mixing Formulas and Applications, IEE Electromagnetic Waves Series 47, The Institution of Engineering and Technology, London, 1999.

[5] L. Tsang and J.A. Kong, Scattering of Electromagnetic Waves: Advanced Topics, John Wiley & Sons, New York, 2001.

[6] S. Torquato, Random Heterogeneous Materials: Microstructure and Macroscopic Properties, Springer, New York, 2002.

[7] H. Morgan and N.G. Green, AC Electrokinetics: Colloids and Nanoparticles, Research Studies Press Ltd., Baldock, Hertfordshire, England, 2003.

[8] A.V. Delgado et al., Measurement and Interpretation of Electrokinetic Phenomena (IUPAC Technical Report), Pure Appl. Chem., 77 (2005) 1753–1805.

[9] H. Ohshima (Ed.), Electrical Phenomena at Interfaces and Biointerfaces. Fundamentals and Applications in Nano-, Bio-, and Environmental Sciences, John Wiley & Sons, Hoboken, New Jersey, 2012.

[10] M. Lax, Multiple Scattering of Waves. II. The Effective Field in Dense Systems, Phys. Rev. B, 85 (1952) 621–629.

[11] W. Lamb, D.M. Wood, and N.W. Ashcroft, Long-wavelength Electromagnetic Propagation in Heterogeneous Media, Phys. Rev. B, 21 (1980) 2248–2266.

[12] L. Tsang and J.A. Kong, Multiple Scattering of Electromagnetic Waves by Random Distributions of Discrete Scatterers with Coherent Potential and Quantum Mechanical Formalism, J. Appl. Phys., 51 (1980) 3465–3485.

[13] V.A. Davis and L. Schwartz, Electromagnetic Propagation in Close-packed Disordered Suspensions, Phys. Rev. B, 31 (1985) 5155–5165.

[14] U. Geigenmüller and P. Mazur, The Effective Dielectric Constant of a Dispersion of Spheres, Physica A, 136 (1986) 316–369.

[15] F. Claro and R. Rojas, Correlation and Multipolar Effects in the Dielectric Response of Particulate Matter: An Iterative Mean-field Theory, Phys. Rev. B, 43 (1991) 6369–6375.

[16] L. Fu, P.B. Macedo, and L. Resca, Analytic Approach to the Interfacial Polarization of Heterogeneous Systems, Phys. Rev. B, 47 (1993) 13818–13829.
[17] V.L. Kuz’min, Contribution of Multiple Scattering to the Dielectric Constant of a Randomly Inhomogeneous Medium, Zh. Eksp. Teor. Fiz., 127 (2005) 1173–1180 [JETP, 100, (2005) 1035–1041].

[18] P. Mallet, C.A. Guérin, and A. Sentenac, Maxwell-Garnett Mixing Rule in the Presence of Multiple Scattering: Derivation and Accuracy, Phys. Rev. B, 72 (2005) 014205 (9pp).

[19] J.C. Maxwell, A Treatise on Electricity and Magnetism, Vol. 1, 1st ed., Clarendon Press, Oxford, 1873, pp. 362–365.

[20] J.C.M. Garnett, Colours in Metal Glasses and in Metallic Films, Phil. Trans. R. Soc. Lond. A, 203 (1904) 385–420.

[21] D. Bruggeman, Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen, Ann. Phys. (Leipzig), 24 (1935) 636–664.

[22] R. Landauer, The Electrical Resistance of Binary Metallic Mixtures, J. Appl. Phys., 23, 779–784 (1952).

[23] W.F. Brown, Dielectric Constants, Permeabilities, and Conductivities of Random Media, Trans. Soc. Rheol., 9 (1965) 357–380.

[24] G.K. Batchelor, Sedimentation in a Dilute Dispersion of Spheres, J. Fluid Mech., 52 (1972) 245–268.

[25] D.J. Jeffrey, Group Expansions for the Bulk Properties of a Statistically Homogeneous, Random Suspension, Proc. R. Soc. London Ser. A, 338 (1974) 503–516.

[26] B.U. Felderhof, G.W. Ford, and E.G.D. Cohen, Cluster Expansion for the Dielectric Constant of a Polarizable Suspension, J. Stat. Phys., 28 (1982) 135–164.

[27] B.U. Felderhof, G.W. Ford, and E.G.D. Cohen, Two-Particle Cluster Integral in the Expansion of the Dielectric Constant, J. Stat. Phys., 28 (1982) 649–672.

[28] J.D. Ramshaw, Dielectric Polarization in Random Media, J. Stat. Phys., 25 (1984) 49–75.

[29] S. Torquato, Bulk Properties of Two-phase Disordered Media. I. Cluster Expansion for the Effective Dielectric Constant of Dispersions of Penetrable Spheres, J. Chem. Phys., 81 (1984) 5079–5088.

[30] S. Torquato, Bulk Properties of Two-phase Disordered Media. II. Effective Conductivity of a Dilute Dispersion of Penetrable Spheres, J. Chem. Phys., 83 (1985) 4776–4785.

[31] S. Torquato, Effective Electrical Conductivity of Two-phase Disordered Composite Media, J. Appl. Phys., 58 (1985) 3790–3797.

[32] W.F. Brown, Solid Mixture Permittivities, J. Chem. Phys., 23 (1955) 1514–1517.

[33] V.M. Finkel’berg, Virial Expansion in the Problem of Electrostatic Polarization of a System of Many Bodies, DAN SSSR, 152 (1963) 320–323 [Sov. Phys. Dokl., 8 (1964) 907–910].

[34] V.M. Finkel’berg, Dielectric Permittivity of Mixtures, Zh. Tekh. Fiz., 34 (1964) 509–518.
[35] V.M. Finkel’berg, Mean Field Strength in an Inhomogeneous Medium, Zh. Exp. Teor. Fiz., 46 (1964) 725–731 [Sov. Phys. JETP, 19 (1964) 494–498]

[36] G.B. Jeffery, On a Form of the Solution of Laplace’s Equation Suitable for Problems Relating to Two Spheres, Proc. R. Soc. Lond. A, 87 (1912) 109–120.

[37] B. Cichocki and B.U. Felderhof, Dielectric Constant of Polarizable, Nonpolar Fluids and Suspensions, J. Stat. Phys., 53 (1988) 499–521.

[38] J.W. Ju and T.M. Chen, Effective Elastic Moduli of Two-phase Composites Containing Randomly Dispersed Spherical Inhomogeneities, Acta Mechanica, 103 (1994) 123–144.

[39] V.A. Buryachenko, Multiparticle Effective Field and Related Methods in Micromechanics of Composite Materials, Appl. Mech. Rev., 54 (2001) 1–47.

[40] Yu.A. Ryzhov, V.V. Tamoškin, and V.I. Tatarski, Spatial Dispersion of Inhomogeneous Media, Zh. Exp. Teor. Fiz. 48 (1965) 656–665 [Sov. Phys. JETP, 21 (1965) 433–438].

[41] Yu.A. Ryzhov and V.V. Tamoškin, Radiation and Propagation of Electromagnetic waves in Randomly Inhomogeneous Media (Review), Izv. VUZ., Radiofiz., 13 (1970) 273–300 [Radiophys. Quantum Electron., 13 (1970) 273–300].

[42] V.V. Tamoškin, The Average Field in a Medium Having Strong Anisotropic Inhomogeneities, Izv. VUZ., Radiofiz., 14 (1971) 285–292 [Radiophys. Quantum Electron. 14 (1971) 228–233].

[43] L. Tsang and J.A. Kong, Scattering of Electromagnetic Waves from Random Media with Strong Permittivity Fluctuations, Radio Sci., 16 (1981) 303–320.

[44] N.P. Zhuch, Strong-fluctuation Theory for a Mean Electromagnetic Field in a Statistically Homogeneous Random Medium with Arbitrary Anisotropy of Electrical and Statistical Properties, Phys. Rev. B, 50 (1994) 15636–15645.

[45] B. Michel and A. Lakhtakia, Strong-property-fluctuation Theory for Homogenizing Chiral Particulate Composites, Phys. Rev. E, 51 (1995) 5701–5707.

[46] T.G. Mackay, A. Lakhtakia, and W.S. Weiglhofer, Strong-property-fluctuation Theory for Homogenization of Bianisotropic Composites: Formulation, Phys. Rev. E, 62 (2000) 6052–6064; Erratum, Phys. Rev. E, 63 (2001) 049901(E).

[47] T.G. Mackay, A. Lakhtakia, and W.S. Weiglhofer, Third-order Implementation and Convergence of the Strong-property-fluctuation Theory in Electromagnetic Homogenization, Phys. Rev. E, 64 (2001) 066616 (9pp).

[48] O. Pekonen, K. Kärkkäinen, A. Sihvola, and K. Nikoskinen, Numerical Testing of Dielectric Mixing Rules by FDTD Method, J. Electromagn. Waves Applicat., 13 (1999) 67–87.

[49] K. Kärkkäinen, A. Sihvola, and K. Nikoskinen, Analysis of a Three-Dimensional Dielectric Mixture with Finite Difference Method, IEEE Trans. Geosc. Remote Sensing, 39 (2001) 1013–1018.

[50] L. Jylhä and A. Sihvola, Equation for the Effective Permittivity of Particle-filled Composites for Material Design Applications, J. Phys. D: Appl. Phys., 40 (2007) 4966–4973.
[51] M.Ya. Sushko, Dielectric Permittivity of Suspensions, Zh. Eksp. Teor. Fiz., 132 (2007) 478–484 [JETP, 105 (2007) 426–431].

[52] M.Ya. Sushko and S.K. Kris’kiv, Compact Group Method in the Theory of Permittivity of Heterogeneous Systems, Zh. Tekh. Fiz., 79 (2009) 97–101 [Tech. Phys., 54 (2009) 423–427].

[53] M.Ya. Sushko, Effective Permittivity of Mixtures of Anisotropic Particles, J. Phys. D: Appl. Phys., 42 (2009) 155410 (9pp).

[54] M.Ya. Sushko. Effective Dielectric Constant of Systems of Penetrable Particles, in: L.A. Bulavin (Ed.), 7th International Conference Physics of Liquid Matter: Modern Problems. May 27–30, 2016, Kyiv, Ukraine, p. 133.

[55] M.Ya. Sushko, Effective Dielectric Response of Dispersions of Graded Particles, Phys. Rev. E, 96 (2017) 062121 (8pp).

[56] Z. Hashin and S. Shtrikman, A Variational Approach to the Theory of the Effective Magnetic Permeability of Multiphase Materials, J. Appl. Phys., 33 (1962) 3125–3131.

[57] D.J. Jeffrey, Conduction Through a Random Suspension of Spheres, Proc. R. Soc. London Ser. A, 335 (1973) 355–367.

[58] A. Sihvola and I.V. Lindell, Polarizability and Effective Permittivity of Layered and Continuously Inhomogeneous Dielectric Spheres, J. Electromagn. Waves and Applicat., 3 (1989) 37–60.

[59] L.D. Landau, E.M. Lifshitz, L.P. Pitaevskii, Course of Theoretical Physics, Vol. 8: Electrodynamics of Continuous Media, 2nd ed., Nauka, Moscow, 1982; Pergamon, Oxford, 1984.

[60] V.G. Veselago, Electrodynamics of Substances with Simultaneously Negative Values of $\varepsilon$ and $\mu$, Usp. Fiz. Nauk, 92 (1967) 517–526 [Sov. Phys. Usp., 10 (1968) 509–514].

[61] T.G. Mackay and A. Lakhtakia, A Limitation of the Bruggeman Formalism for Homogenization, Optics Comm., 234 (2004) 35–42.

[62] L. Blum and G. Stell, Polydisperse Systems. I. Scattering Function for Polydisperse Fluids of Hard or Permeable Spheres, J. Chem. Phys., 71 (1979) 42–46.

[63] J.J. Salacuse and G. Stell, Polydisperse Systems: Statistical Thermodynamics, with Applications to Several Models Including Hard and Permeable Spheres, J. Chem. Phys., 77 (1982) 3714–3725.

[64] P.A. Rikvold and G. Stell, Porosity and Specific Surface for Interpenetrable Spheres Models of Two-phase Random Media, J. Chem. Phys., 82 (1985) 1014–1020.

[65] M.Ya. Sushko and A.K. Semenov, A Mesoscopic Model for the Effective Electrical Conductivity of Composite Polymeric Electrolytes, ArXiv: 1810.11892 [cond-matt.mtrl-sci], 28 Oct 2018.