

Review of Random Media Homogenization Using Effective Medium Theories

by

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Thesis submitted to the faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

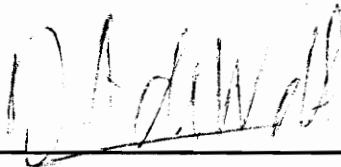
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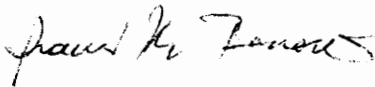
Electrical Engineering

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October, 1992

Blacksburg, Virginia

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(ABSTRACT)

Calculation of propagation constants in particulate matter is an important aspect of wave propagation analysis in engineering disciplines such as satellite communication, geophysical exploration, radio astronomy and material science. It is important to understand why different propagation constants produced by different theories are not applicable to a particular problem. Homogenization of the random media using effective medium theories yields the effective propagation constants by effacing the particulate, microscopic nature of the medium. The Maxwell-Garnet and Bruggeman effective medium theories are widely used but their limitations are not always well understood.

In this thesis, some of the more complex homogenization theories will only be partially derived or heuristically constructed in order to avoid unnecessary mathematical complexity which does not yield additional physical insight. The intent of this thesis is to elucidate the nature of effective medium theories, discuss the theories' approximations and gain a better global understanding of wave propagation equations. The focus will be on the Maxwell-Garnet and Bruggeman theories because they yield simple relationships and therefore serve as anchors in a sea of myriad approximations.

ACKNOWLEDGEMENTS

I am grateful to my committee members Dr. Brown and Dr. Besieris for serving on my committee. I am also grateful to the many teachers and instructors who I felt were the ones that provided me with my primary education. Of particular note (in chronological order) are Val Larsen and Dr. Hardy (English department), Dr. Walker (now with the ESM department formerly with the AOE department), Dr. Dennison (Physics), Dr. de Wolf (EE), and Dr. Brown (EE).

Dr. David de Wolf was my thesis chairman and who allowed me to enjoy an unique learning experience. Simply put, his philosophy about learning, engineering and science has influenced and motivated my thinking on these matters. He also was the source of the single most influential element in my education which I feel would be difficult to achieve with others: academic freedom. This specifically means the time, energy and help in exploring a wide range of topics and musings that amalgamate to form the thinking person that I am (although there is a level of responsibility that accompanies such freedom which I did not always meet). I was given the opportunity to take cover in one of the last bastions of academic freedom which was most likely, the last opportunity I will have to take refuge there. I first met Dr. de Wolf in an undergraduate EM class and became interested in the same things as he when I was trying to figure out how one analyzes wave-particle scattering problems. These questions were long ago

answered. I do have one regret in my dealings with him; I wish I had taken advantage of his expertise much more than I did. It will not be anytime soon if ever, before I have access to such expertise in the EM scattering field again. For my graduate experience, I am grateful.

I would like to heartfully thank the Geology department and in particular the geophysics group which includes Dr. Coruh, Dr. Costain and Dr. Snoke for providing me office space, materials, computer time and equipment and their time, all of which contributed tremendously towards the completion of my thesis and general mental well-being. Their support and the lack of such from my department is an important motivator (but not the only) for my leaving the electrical engineering field.

Many heartfelt thanks to AJ who engaged with me in many stimulating conversations that, quite frankly, made me realize that I hadn't thought through many aspects of both my personal and professional life. His friendship is warmly appreciated and has enriched my life.

Naturally, I must acknowledge the catalyst of my most tremendous growth during my graduate stay—my wife Laura. She has provided me an avenue from which the well-spring of my strength and resolve can now flow with greater vivaciousness than I had thought possible. Her encouragement and her hard work on her master's degree has set an example that will help me become a better person.

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We shall be obliged to have recourse to some hypothesis about the mechanism that is at the bottom of the phenomena.

Lorentz, 1906

Chapter 1

INTRODUCTION

The homogenization of heterogeneous media is a process used to mask the complex structure of matter from macroscopic wave propagation equations. When the specific structure of matter must be considered, the variation of the true field relative to the free space field presents a significant computational impediment. It is desirable to remove this impediment by folding the effects of scattering potentials into effective propagation parameters which then accounts for the scattering phenomenologically. One method of obtaining these propagation parameters is by using effective medium theories.

Effective medium theories attempt to relate macroscopic phenomena to microscopic entities and principles. This is a non-trivial problem in general and all approaches make approximations which simultaneously transform the problem from intractable to solvable and restrict the validity of the theory. Generally, the macroscopic Maxwell's equations are used to hide the microscopic nature of matter—atoms, molecules, electrons. Passing from the microscopic Maxwell equations to the macroscopic Maxwell equations is accomplished by some type of averaging process. Most electrical engineers will use the macroscopic equations whenever possible since the microscopic problem is usually intractable. However, it is impossible to gain physical insight into some phenomena without understanding the microscopic structure.

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For example, it is impossible to understand the physical processes which are described by the optical constants using macroscopic equations and fields. The index of refraction changes quite abruptly at different frequencies due to the change in the physical process such as the change from lattice vibrations to electronic transitions. Also, conductivity is directly influenced by the atomic structure of matter.

Maxwell first proposed the displacement current as a separate and independent phenomenon. It was this proposal which motivated the name for a group of field relationships including Faraday's equation and Ampere's or Gauss's law. However, Maxwell proposed his set of equations without any knowledge of the microstructure of matter. It was not until the early part of the nineteenth century when Lorentz interpreted the macroscopic equations using the language of microscopic processes and microscopic structure that the widespread use of microscopic concepts motivated understanding of the physical processes. Today, the macroscopic equations are justifiably used in many engineering electromagnetic field applications and it is not necessary to utilize microscopic concepts for every problem. But the physical justification and intuition in these applications are often a result of microscopic inspection.

Most media are inhomogeneous and anisotropic at some scale length and lossy over sufficient propagation distances. When these properties greatly influence the phenomena being investigated it is imperative to use a theory which accounts for these properties. Macroscopic equations are inherently easier to use due to the removal of complex physical structure. Hence, models of microscopic matter must be developed so that the microscopic nature of the problem is hidden in macroscopic variables and parameters. Effective medium theories provide this

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connection.

Effective medium theories will allow us to write wave propagation equations in a simpler form. For a broader understanding of such simplification, we wish to point out that all such methods effectively amount to obtaining the mean field in the medium and that any propagation constants that arise in obtaining the mean field are merely useful by-products. Also, the mean field is not always the goal in wave propagation studies. Calculation of the first moment and the and the effective propagation parameters is an intermediate step in dealing with the statistics of wave propagation.

Although we have mentioned that it is desirable to go from microscopic scattering structures to macroscopic wave equations, macroscopic equations derived using macroscopic scattering structures are also important because these relationships allow the homogenization of a medium where the influence on the scattered field from individual constituents of the atomic structure is not as dominant as the overall effect due to the collective behavior of the discrete particles characterized by a macroscopic dielectric function. In this case, consideration of the microscopic nature of matter would be too burdensome and analysis can be more efficiently carried out using macroscopic structures.

1.1 Motivation for the study of effective medium theories

Although effective medium theories are interesting themselves, one specific motivation in this thesis for reviewing effective medium theories is due to the study of high frequency signal attenuation in rain (for reviews, see [20] [35] [36]). As the frequencies used for satellite

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communication moved into the gigahertz region, extinction of the communication signal is also increased. The extinction is caused by the resonance effect present when the particle's radius is on the same order of magnitude as the incident wave. This effect is present in the atmosphere for gigahertz signals and raindrops. When this size criterion is satisfied the particle is said to be in the resonance region. Resonance is characterized by large absorption processes and strong dependence of scattering upon scattering angle. It is well known that scattering from collections of non-spherical particles is not equivalent to scattering from collections of "equivalent" spheres due to shape dependent effects. Raindrops are highly non-spherical and do not resemble ellipsoids or any of the ellipsoid's special cases—oblate or prolate spheroids, spheres or needles—in detail. When resonance effects occur, the specific shape and material properties of the scatterer may become important.

In a transition operator formulation of the multiple scattering problem, all scattering internal to a particle is conveniently hidden inside of the transition operator much like the scattering amplitude (the two are directly and easily related). The transition operator is a linear operator which maps the incident field into the scattered field. Although the operator is linear, the multiple scattering problem is highly non-linear in the electric field because there is more than one particle scattering the incident field and multiple scattering theory must be used (single scattering theory is linear as shown in the Born approximation whereas multiple-scattering theory is highly non-linear). The multiple-scattering problem is comparable to the many-body problem in astrodynamics [31]. Knowledge of the exact form of the transition operator for the particles under study does not itself lead to the solution. Even when the transition

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operator is known exactly (as it is often assumed), solving the equations is a formidable task. In particular, an adequate treatment of resonance absorption in a particulate medium requires detailed knowledge of the transition operator because resonance absorption is highly particle shape dependent. The transition operator can be determined by knowledge of the fields internal to the scatterer. Unfortunately, the fields internal to a scatterer are only known for special particle geometries such as ellipsoids. Because of the highly non-ellipsoidal shape of a raindrop and the dynamic complexity of the raindrops' shapes in flight the transition operator is not known for raindrops [36].

It is desirable to study wave propagation in dense, strong permittivity fluctuating, inhomogeneous, non-spherical particulate media. When the media can be characterized as dense and strongly scattering, correlations between different scatterers and phase fluctuations across a particle must be included in the analysis. The low density and weak scattering multiple scattering approximations such as the Foldy-Twersky integral equation for the coherent field are no longer applicable. Large or small particle assumptions like geometrical optics or Rayleigh scattering can no longer be made and the exact form of the transition operator becomes important. For example, the melting layer in the atmosphere is a layer of particles composed of a mixture of ice and water. Due to the permittivity contrast between the two components and high density of the water-ice particles, the melting layer is a region of strong signal scattering and absorption. In this situation, it is necessary to develop a multiple scattering theory with a transition operator that accurately accounts for high density, strong permittivity fluctuations and inhomogeneous particles. No practical theory that is inclusive of all these problems has

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been developed although some theories address some of these concerns.

It seems natural to conclude that the problem of finding the transition operator for real-world particles can be reduced down to tracking the motion and behavior of the molecules and atoms that compose a raindrop. However, such a model would need to account for the positions and velocities of every atomic sub-unit; a formidable task considering the large number of molecules in a raindrop. To compound the problem, the shape of the raindrop is dependent on its velocity, the wind velocity, precise composition, the temperature, altitude and other variables important at the microscopic scale. Taken together, the list of parameters and variables is impossibly large, largely unknown and this problem generally intractable.

It was initially thought that an older method was able to solve many of the problems mentioned above. This method is the coupled-dipole method (CDM) also known as the discrete-dipole method (DDM) first presented by Purcell and Pennypaker [38] and investigated by Draine [12], Singham [46] [47] [48] and Lakhtakia [28]. The method was also reformulated and named the digitized Green's function algorithm [18].

The CDM is based on a model of the medium that views a particle as a small collection of dipoles whose polarizabilities are tuned to match the bulk properties (the dielectric permittivity in our case) of the desired particle. It is essentially a finite-element approach but is developed without any variational or minimization techniques. Any constituent of a particle in the resonance region would be small compared to the incident wave allowing the constituent's scattering to be modelled in the small particle limit, specifically, the particle can be considered to consist of Rayleigh scatterers modelled as dipoles. The method is attractive because it

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can model non-spherical particles quite easily by placing the dipoles in particular geometries. Inhomogeneous particles could be modelled by tuning the polarizability of neighboring dipoles so that it reflects the corresponding change in the bulk properties of the particle. By increasing the number of dipoles, phase fluctuations across a particle can be modelled implying that this model could account for strong permittivity fluctuations. Recently, Draine [13] reformulated the CDM to use the conjugant gradient method and Fourier transforms to handle a large number of dipoles—up to 40,000. Comparisons to Mie scattering results for the type of particles described above shows however, that even with a large number of dipoles discrepancies between the CDM and Mie theories persist so the results for non-spherical particles are suspect.

Unfortunately, the theory by which the polarizabilities are tuned to match the bulk media constants has been insufficient to provide the desired accuracy. In the CDM, an effective medium theory is invoked to perform the matching between the microscopic structure and the macroscopic propagation constants. Typically, a Clausius-Mossotti (CM) relationship is used but the CM relationship has limitations and researchers in the field have been struggling to replace the CM effective-medium theory with a better relationship in order to improve the accuracy of the CDM model. It is the mapping between the microscopic structure and the macroscopic propagation constants which affects the tuning of the polarizability that is the fundamental problem in the CDM approach.

The motivation for studying effective medium theories is directly related to the above problem. However, effective medium theories are useful in many other areas such as geophysical exploration, remote sensing of ice, remote sensing in forests and dense foliage, solid-state

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physics and the study of conductivity in crystals. It is applicable in any area where it is desirable to efface the details of the material structure and work with macroscopic theories and equations.

1.2 Conceptual and analytic tools

There are some basic concepts which are relevant to the following chapters. Each tool will be used implicitly, we will not attempt to point out which tool is being used at a particular step in the development. Some tools are not applicable to every theory we will discuss.

1.2.1 Ergodic theorem

The ergodic theorem is a poorly understood but useful theorem which allows theories to be developed and experiments to be performed in a timely and efficient manner. Although a proof of the ergodic theorem will not be presented, we will explicitly state how we will use the ergodic theorem.

Engineers routinely use the ergodic theorem without realizing it. Signal-analysis engineers invoke ergodicity to make equivalent the deterministic theory of random processes based on time averages and probabilistic theories based on expected values. Specifically, there is a duality between the probabilistic theory of random processes based on ensemble averages and deterministic theory of random processes based on time averages. For example, the signal-to-noise ratio (SNR) of a communication channel is a probabilistically defined quantity but it is typically measured with time averages. Since noise is a random process, generalized

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harmonic analysis must really be used (which is not exactly the same as Fourier analysis of transient signals). However, since generalized harmonic analysis of random processes is based on ensemble averages and ergodicity allows time averages to be interpreted as expected values (a probabilistic notion) the two can be interchanged. We will make one further note on this topic: generalized harmonic analysis is based on correlation theory but it can be shown that correlations are related to Fourier transforms [37] [16].

When applied to volume averaging, ergodicity allows one to use volume averages based on a spatial domain in place of ensemble averages based on a configuration domain. Since effective medium theories inherently use ensemble averages to calculate fluctuations, ergodicity allows the much simpler and physically realizable volume averages to be used in their place.

1.2.2 Classical descriptions of matter

Maxwell's equations were formulated without an understanding of microscopic media. Although the microscopic aspects of matter were being investigated before Lorentz, it was Lorentz's *The Theory of Electrons* [33] which marked the start of the application of microscopic concepts to understand the macroscopic Maxwell's equations.

In the classical description of matter, all atomic entities such as atoms, electrons and nuclei are considered to be point charges. The location of all entities is known precisely as well as simultaneously known with their velocities in stark contrast to quantum mechanics. Although not strictly belonging to the classical description of matter, it is assumed that the velocities of all particles (especially electrons) involved is much less than the speed of light. This implies

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that it is possible to either specify the motions of particles and calculate the radiation from such motion or to specify the radiation and calculate the motions. Neither viewpoint is particularly accurate if a large amount of radiation is emitted when charges are quickly accelerated. In this case, a treatment which simultaneously handles both motion and radiation is necessary. Such a treatment is used when discussing bremsstrahlung radiation. But for low charged-particle velocities, the radiation will be negligible and the effects of moderate electric fields on charged particle will not introduce additional bookkeeping duties. It is often assumed that point charges scatter energy like dipoles, a convenient assumption that we will make much use of.

It is assumed that infinite self energies of localized particles cannot occur [22]. By assuming that there is a saturation effect, field strengths have upper bounds and it is possible for multi-charge nuclei to have a single coordinate. The important implication is that localized charge clouds can be represented by a single point charge with a cumulative charge magnitude. This allows the use of the classical picture of an atom as being composed of a multi-charged point nucleus with a surrounding electron cloud. Application of an electric field causes the electron cloud to shift its center away from the nucleus creating a dipole. Gauss's law allows the electron cloud to be reduced to a point charge with magnitude q . It is this model of the atom that Lorentz drew on when he used the harmonic oscillator model to describe polarization and absorption.

Although it would be proper to cast all of our problems using the quantum-mechanical media model it is not instructive. It is possible to make general qualitative predictions using classical descriptions of matter and these classical descriptions will reduce the mathematical complexity needed to deal with heterogeneous media. Also, since some of the effects we are

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interested in occur for large aggregates of molecules the quantum-mechanical descriptions are beyond what is minimally needed.

1.2.3 Microscopic and macroscopic Maxwell's equations

When discussing the differences between the microscopic and macroscopic Maxwell's equations it is important to identify two sets of quantities which affect their interpretation: fields and constitutive relationships.

Lorentz [33] suggests that the movement from the microscopic to macroscopic fields is accomplished by averaging over a microscopically large but a macroscopically small volume that contains many particles. This presents conceptual problems when there are not a large number of particles in the volume but the macroscopic fields are still used. Also, such averaging begs the question as to the variance of the average (see Section 1.2.6). Various corrections to the “volume averaging” viewpoint have been made by various authors.

The microscopic fields are often written in lowercase letters. We follow Robinson's [39] lead when we write

$$\begin{aligned}\nabla \cdot \mathbf{b}(\mathbf{r}) &= 0, & \nabla \times \mathbf{e}(\mathbf{r}) + \mu_o \frac{\partial \mathbf{h}(\mathbf{r})}{\partial t} &= 0 \\ \epsilon_o \nabla \cdot \mathbf{e}(\mathbf{r}) &= \sum_n q(n) \delta(\mathbf{r}(n) - \mathbf{r}) \\ \nabla \times \mathbf{h}(\mathbf{r}) - \epsilon_o \frac{\partial \mathbf{e}(\mathbf{r})}{\partial t} &= \sum_n q(n) \dot{\mathbf{r}}(n) \delta(\mathbf{r}(n) - \mathbf{r})\end{aligned}\tag{1.1}$$

All electromagnetic effects in (1.1) are due to point charges located at $\mathbf{r}(n)$ with magnitude q .

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The macroscopic fields are written in uppercase letters and satisfy

$$\begin{aligned}\nabla \cdot \mathbf{B}(\mathbf{r}) &= 0, & \nabla \times \mathbf{E}(\mathbf{r}) + \mu_o \frac{\partial \mathbf{H}(\mathbf{r})}{\partial t} &= 0 \\ \nabla \cdot \mathbf{E}(\mathbf{r}) &= \rho/\epsilon_o, & \nabla \times \mathbf{H}(\mathbf{r}) - \epsilon_o \frac{\partial \mathbf{E}(\mathbf{r})}{\partial t} &= \mathbf{J}\end{aligned}\tag{1.2}$$

where \mathbf{J} and ρ are continuous variables. In both (1.1) and (1.2), the electric and magnetic flux density fields are continuous (there is a form of the field equations where the fields are quantized but we will ignore this form and the associated quantum aspects). It appears that the movement from (1.1) to (1.2) is one of moving between the atomic view of the medium and the view where the medium is considered a continuum. This is not entirely the case however, since (1.2) is used in plasma physics and electron beam tube problems where the medium is not a continuum. Instead, we can view this process as a transition to a scale length where discrete, atomic features are no longer observable. As Robinson points out, this implies a truncation of the variables' spatial Fourier spectrums.

The truncation procedure is compatible with ensemble averaging (Section 1.2.1) especially in the static limit. Ensemble averaging of Maxwell's equations preserves the form of the field equations just as truncation does. Truncation does not depend on statistical ensembles nor has any connection to statistical probabilities, so the two are not equivalent. Truncation rejects available information smaller than the cutoff frequency; ensemble averaging admits that useful information is not available to us. One can work with the macroscopic field equations obtained by truncation and then ensemble average to study the fluctuations. This is routinely done with signal-analysis equipment which responds to a specific range of frequencies but its data is time-averaged. Here, the truncation of the spectrum is intrinsic to the device but the

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time averages are obtained to study the effect of random noise elements whose fluctuations are a manifestation of random process such as thermal noise. Since thermal noise occurs at a microscopic level but is observed at the macroscopic level, it is obviously possible for random microscopic processes to cause macroscopic fluctuations. Specifically, truncation of the Fourier spectrum and subsequent rejection of information below a certain length scale does not eliminate the fluctuation frequencies in the rejected domain [39].

In the medium under consideration, the scatterers will be molecules, atoms or ions. However, we will model them as dielectric bodies. Although we are really dealing with discretized sources and should therefore be working the microscopic to macroscopic problem, our model implies that we are working the macroscopic problem and are attempting to efface the particulates. So while “microscopic” apparently refers to the scale length of atoms, we are working from the outset a “macroscopic” scattering problem. The comments made above imply that microscopic and macroscopic are relative to a scale length; this is still true. We are actually fixing the microscopic scale length to that smaller than an atom so that with our model of the atom, the atom can be a macroscopic dielectric. Adoption of our model is therefore equivalent to the process of truncation. Calculations of the fluctuations using ensemble averages will be our focus.

Effective medium theories apply to both molecular scatterers and particle scatterers with a dielectric permittivity. In the macroscopic problem, fields are continuous and spatially distributed scatterers are taken into account directly in the wave equation as pseudo-sources whereas after ensemble averaging (and hence homogenization) the effects of the scatterers are

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hidden in the spatially constant effective dielectric permittivity.

The constitutive relationships are needed in the field equations so that the number of unknowns does not exceed the number of equations thereby producing an impasse. The constitutive relationships provide a connection between the structure and the fields in a problem and are at the core of effective medium theories. There are two aspects to the constitutive relations: microscopic or molecular and macroscopic.

The macroscopic dielectric constitutive relationship is

$$\begin{aligned} \mathbf{D} &= \epsilon_r \epsilon_o \mathbf{E} = (1 + \chi_e) \epsilon_o \mathbf{E} \\ \mathbf{P} &= \chi_e \epsilon_o \mathbf{E} \end{aligned} \tag{1.3}$$

where the e subscript denotes an electric quantity. Equations (1.3) describe a simple media. The polarization vector \mathbf{P} represents the dipole moment per unit volume. The macroscopic approach to the constitutive relationships does not inquire any deeper definition of \mathbf{P} . \mathbf{P} is usually described and defined as a result of the increase in charge capacity of a parallel plate capacitor due to the creation of dipoles inside a dielectric medium inserted between the plates as compared to the charge capacity with a free space interplate medium. The increase in charge capacity is due to the creation of volume pseudo-charges with density $\rho_v = -\nabla \cdot \mathbf{P}$ and surface pseudo-charges with density $\rho_s = \hat{\mathbf{n}} \cdot \mathbf{P}$. Although the concepts of separated charge units and pseudo-charges are invoked to describe the polarization per unit volume, there is no attempt to be more specific. This is the phenomenological view that the molecular approach produces and it is used to discuss many dielectric effects such as optical activity, birefringence and piezo-electricity.

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In contrast to the phenomenological view, the molecular approach describes P as the sum of multipole moments and elementary interactions between the moments of different charge units. Specific spatial positioning and orientation information is used to calculate P explicitly. The molecular approach utilizes the concepts of a local field and polarizability to arrive at a relationship between the polarization P and the macroscopically applied electric field E_{mac} . Although we have labelled this the molecular view of P , P has units “per volume” indicating that in our context, it is strictly a macroscopic field.

The effective-medium theories that we will discuss rely on the molecular dielectric constitutive view and will be based on the idea of effacing the particulate nature of the medium. We will use ensemble averaging to study the fluctuations and adoption of our atomic model will effectively Fourier truncate the field quantities leaving the field averages statistical physical significance. Moreover, the spatial distributions of the scatterers we will consider is best expressed by an configurational ensemble because the spatial positions are not known exactly and any one member of the ensemble cannot greatly influence the general behavior of the scatterers. We will also discuss homogenization of a random medium whose polarizable units are not atoms and molecules but polarizable particles with a truly defined dielectric permittivity. We will call these macroscopic scatterers to distinguish them from the dielectrics acting as shields over the molecules which we label molecular scatterers. The dielectric permittivity cannot truly be assigned to a particle when the particle is composed only of a single molecular unit because a bulk dielectric permittivity requires the calculation of a volume average. This is evident from (1.3) where $\epsilon_r = 1 - \chi_e$ and χ_e is defined as the polarization response of a macroscopic unit

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to an electric field, $\chi_e = \mathbf{P}/\epsilon_0\mathbf{E}$ (it is also the ratio of the bound charge density to free charge density [19]). Since \mathbf{P} is considered to be the sum of molecular dipole-moment vectors we can expect the equations from the molecular and macroscopic scatterers to be similar, to use similar developmental concepts such as the local field but ultimately to have slightly different interpretations.

1.2.4 Green's functions

Green's functions and their applications to wave propagation are discussed in many advanced electrodynamics textbooks. We only need a small portion of the theory which we repeat here in a concise form.

Green's functions can generally be thought of as the impulse response of a differential equation. The Green's function itself is a singularity function used to describe wave propagation and is sometimes called the propagator because in its most simple application it describes the propagation of a spherical wave due to a point source in a simple medium.

There are advantages and disadvantages to using Green's functions to solve a differential equation. The primary advantage is that it presents a simple formalism to obtain solution integrals to the wave propagation problem. The primary disadvantage is that once you have obtained the solution integral it is often difficult to evaluate directly and the singularity of the Green's function makes it difficult to handle the problem of coincident source and receiver (although methods have been introduced to handle this problem).

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Specifically, we may write the solution to the vector wave equation for the electric field

$$\nabla \times \nabla \times \mathbf{E} - k^2 \mathbf{E} = -\bar{\mathbf{S}}(\mathbf{r})$$

using dyadic Green's functions as

$$\mathbf{E}(\mathbf{r}) = \int_V d^3r' \bar{\mathbf{G}}(\mathbf{r}) \cdot \bar{\mathbf{S}}(\mathbf{r}')$$

where $\bar{\mathbf{G}}(\mathbf{r})$ satisfies

$$\nabla \times \nabla \times \bar{\mathbf{G}}(\mathbf{r}) - k^2 \bar{\mathbf{G}}(\mathbf{r}) = -\bar{\mathbf{I}}\delta(\mathbf{r} - \mathbf{r}')$$

with

$$\bar{\mathbf{G}}(\mathbf{r}) = \left(\bar{\mathbf{I}} + \frac{\nabla \nabla}{k^2} \right) g_o(\mathbf{r}), \quad g_o(\mathbf{r}) = \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{4\pi r}$$

where g_o is the free space Green's function. In the electromagnetic scattering context, the source term $\bar{\mathbf{S}}(\mathbf{r})$ is usually a pseudo-source term containing the medium's dielectric fluctuations. Such an equation is actually the result of the direct application of the electromagnetic equivalence theorem.

1.2.5 Multipole expansions

Multipole expansions of potential fields can be considered either as a Taylor's series expansion of a singular function or as an expression of the physical structure of a system of charges in terms of specific geometrical groupings of charges. In this thesis, we will only deal with ideal dipoles and make the assumption that the entities are charge neutral. The material below borrows from Jackson [22] and Böttcher [5] although it can be found in many basic textbooks.

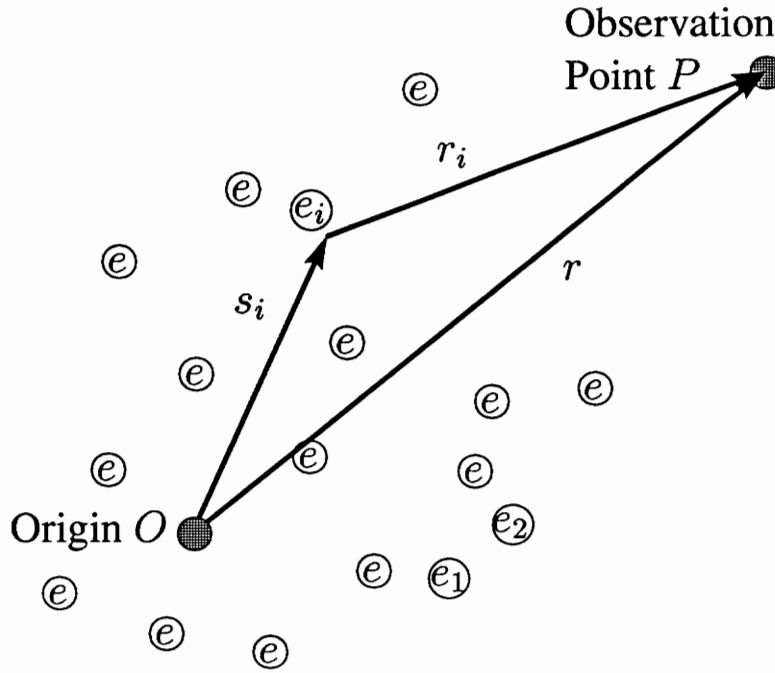


Figure 1.1: Coordinate geometry of an arbitrary charge.

If we consider a cloud of randomly placed charges with each charge having the geometry shown in Figure 1.1, we can write the potential for this cloud as

$$\phi(P) = \sum_i \frac{e_i}{s_i} \tag{1.4}$$

where P is the observation point. The factor $1/s_i$ is merely the distance from the charge to the observation point. If we now do a multi-variable Taylor's expansion of $1/s_i$ about the origin

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we get

$$\begin{aligned} \frac{1}{s_i} &= \frac{1}{r} + x_i \frac{\partial}{\partial x} \left(\frac{1}{r} \right) + y_i \frac{\partial}{\partial y} \left(\frac{1}{r} \right) + z_i \frac{\partial}{\partial z} \left(\frac{1}{r} \right) \\ &+ \frac{1}{2} \left[x_i^2 \frac{\partial^2}{\partial x^2} \left(\frac{1}{r} \right) + 2x_i y_i \frac{\partial^2}{\partial x \partial y} \left(\frac{1}{r} \right) + \dots \right] \\ &+ \dots, \end{aligned} \quad (1.5)$$

where the differentiation is made about the origin. Using (1.5) in (1.4) produces

$$\begin{aligned} \phi(P) &= \sum_i \frac{e_i}{r} - \sum_i \left[e_i x_i \frac{\partial}{\partial x} \left(\frac{1}{r} \right) + e_i y_i \frac{\partial}{\partial y} \left(\frac{1}{r} \right) + e_i z_i \frac{\partial}{\partial z} \left(\frac{1}{r} \right) \right] \\ &+ \frac{1}{2} \sum_i \left[e_i x_i^2 \frac{\partial^2}{\partial x^2} \left(\frac{1}{r} \right) + e_i 2x_i y_i \frac{\partial^2}{\partial x \partial y} \left(\frac{1}{r} \right) + \dots \right] \\ &- \dots. \end{aligned} \quad (1.6)$$

If we now define the moments

$$\begin{aligned} \mathbf{m} &= \sum_i e_i \mathbf{r}_i && \text{dipole} \\ \bar{Q} &= \frac{1}{2!} \sum_i e_i \mathbf{r}_i \mathbf{r}_i && \text{quadrupole} \\ \bar{U} &= \frac{1}{3!} \sum_i e_i \mathbf{r}_i \mathbf{r}_i \mathbf{r}_i && \text{octupole,} \\ &&& \text{etc} \end{aligned} \quad (1.7)$$

and recognize that the first term in (1.6) is the potential at P due to charge $e = \sum_i e_i$ at the origin, we can rewrite (1.6) as

$$\phi(P) = e \frac{1}{r} - \mathbf{m} \cdot \nabla \left(\frac{1}{r} \right) + \bar{Q} \cdot \nabla \nabla \left(\frac{1}{r} \right) - \bar{U} \cdot \nabla \nabla \nabla \left(\frac{1}{r} \right) + \dots. \quad (1.8)$$

The moments defined in (1.7) are not unique and are often seen with different constant factors depending on the author's field. The moments in (1.7) are non-ideal moments. For

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instance, the potential due to a true dipole moment with charges $\pm e$ at positions r_+ and r_- respectively is

$$\begin{aligned}\phi(P) &= \frac{e}{r_+} - \frac{e}{r_-} \\ &= \phi_+(\mathbf{r}) + \phi_-(\mathbf{r}).\end{aligned}\tag{1.9}$$

It is only if we let the distance between the charges decrease to zero while the magnitudes of the charges increase such that the strength of the dipole remains constant that we may define $\mathbf{p} = e\mathbf{l}$ —the ideal dipole moment. The potential due to this ideal dipole moment is

$$\phi(P) = -\mathbf{p} \cdot \nabla \left(\frac{1}{r} \right) = \frac{\mathbf{p} \cdot \hat{\mathbf{r}}}{r^3} = \frac{\mathbf{p} \cdot \mathbf{r}}{r^2}.\tag{1.10}$$

Some simple calculations show that at intermolecular distance the difference between the non-ideal and the ideal dipole potentials is quite large but rapidly diminishes as the observation point moves further from the dipole.

In general it is not possible to convert a non-ideal moment to an ideal moment since it is not generally possible to spatially arrange an arbitrary charge distributions into that matching the ideal charge distributions as in Figure 1.2, but it is possible to find equivalent potentials due to the different moments. As Böttcher points out, you arrive at the same expression as (1.8) if this replacement is made.

We will work only with ideal dipoles and we will assume that we are far enough away from the dipole such that the difference in potential due to non-ideal moments and to ideal moments is negligible. Obviously, at high scatterer densities this assumption might not be as good. Also, we will assume that all entities are charge neutral. This makes the dipole moment independent of position and the dipole moment defined as above unique [1]. Higher

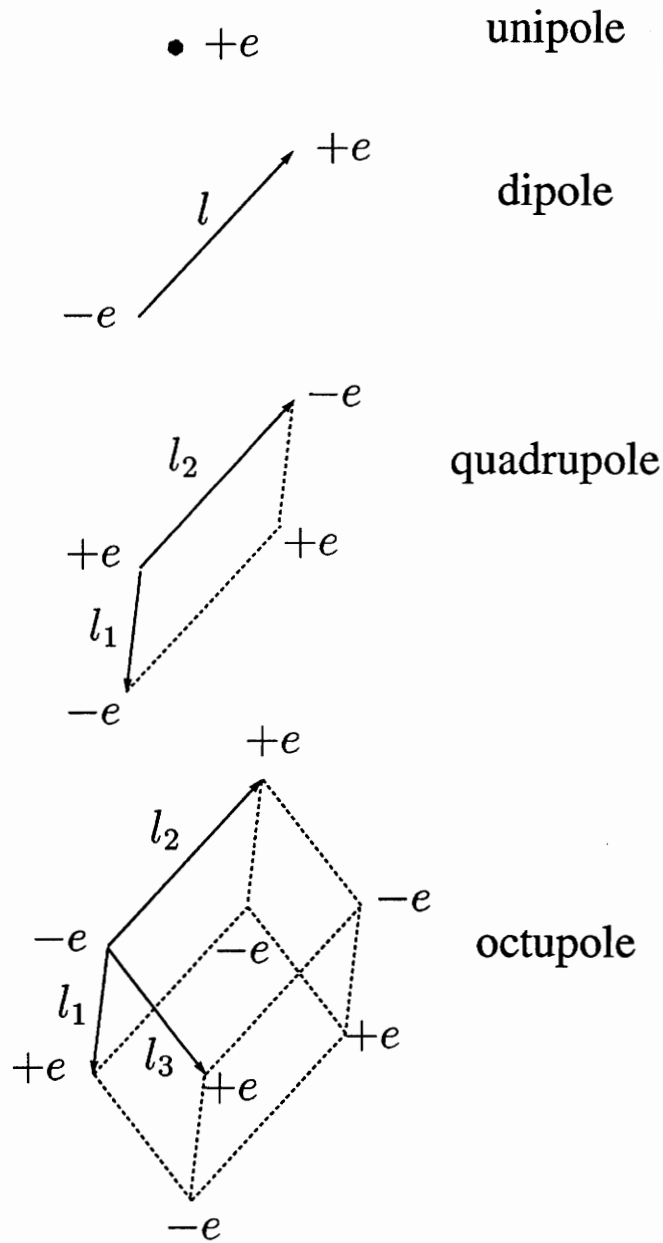


Figure 1.2: Multipole charge distributions

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order moments will be ignored assuming that they contribute little to the potential because they are inversely proportional to the higher powers of the distance as seen in the higher order differentiation of $1/r$ in (1.8).

1.2.6 Random media

Random media descriptions will play an important role in the dense media theories where multiple scattering approaches are needed to yield the effective medium propagation parameters. There are two concepts which we will briefly discuss: the separation of medium parameters into mean values and fluctuations, and coherent versus incoherent fields.

A random medium has parameters that require a stochastic description. These parameters are described using probability theory, and specifically, random functions. Random functions are functions of many parameters typically of space and time. If the time variation of the randomness is small, spatial randomness is the only heterogeneity that is important—an assumption that we will make. A random function of space denoted by $X(\mathbf{r}, \gamma)$ is usually written without the event designator γ .

The medium can be continuous or discrete and the equations resulting from the two different theories often look the same but contain many subtle differences which give rise to different effects. Although it can be argued that at some scale length any medium will appear as a discrete medium, we will assume that the scale length is well defined from the truncation and averaging process when talking about a continuum. In this thesis, we will focus more on the discrete medium and specifically, a two-phase medium characterized by the imbedding of particles into

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a background material with different dielectric properties thereby forming a matrix. In this case, the random function will be the dielectric permittivity dependent on r .

The dielectric permittivity can be written as the sum of a constant part plus a fluctuating part. The notation used depends on the author. For instance, the following have been found in the literature

$$\begin{aligned}\epsilon &= \epsilon_o \epsilon_r & n^2 &= \epsilon_r \\ &= \langle \epsilon \rangle (1 + \delta\epsilon) & &= (n_o + n')^2 \\ &= \langle \epsilon \rangle (1 + \epsilon_1) & &= (n_o + \mu n_1)^2 \\ &= 1 + \mu & &= \langle n \rangle^2 (1 + n_1)^2 \\ & & &= 1 + \mu \\ & & &= 1 + \epsilon\mu\end{aligned}$$

where the spatial dependence of the variables has been dropped. ϵ_r is the relative permittivity, ϵ_o the free space permittivity and the angled brackets denote averages. n is the index of refraction, a quantity used more in optical frequencies. The fluctuating term usually has some assumed statistics. It is quite common to assume that $\langle \delta\epsilon \rangle = 0$, or in $n^2 = (n_o + n')^2$, $\langle n' \rangle = 0$ and the standard deviation of $n' = \mu$. Or in $n^2 = (n_o + \mu n_1)^2$, μ^2 is the variance of n_1 and the standard deviation of $n_1 = 1$. In free space, $\langle n \rangle = 1$. The binomial approximation can also be used yielding $\delta\epsilon = 2n_1$ for the fluctuating term if the fluctuations are small. It is the division of the permittivity into the constant and fluctuating parts that gives rise to the pseudo-sources in the media. These sources do not radiate energy internally generated, but they do scatter incident energy.

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Since the fluctuating term gives rise to the pseudo-sources and the integral equation solution of the wave propagation equations can be iterated (using the Green's function formalism) producing a perturbation expansion in the fluctuation, it is important to ensure that the fluctuations are small so that the infinite series converges. Also, if it is assumed that the constant term in the expression for the permittivity gives rise to coherent propagation, the fluctuating part must give rise to the incoherent field.

Just as the permittivity can be split into two terms, the total field can be split up into the coherent field and the incoherent (fluctuating) field. The coherent field is also known as the mean field, average field, or the first moment of the field. If the field quantity is ψ , we can write

$$\psi(\mathbf{r}) = \langle \psi(\mathbf{r}) \rangle + \delta\psi(\mathbf{r}).$$

where $\langle \psi(\mathbf{r}) \rangle = \langle \psi \rangle$ is a constant due to the averaging process and it is usually assumed that $\langle \delta\psi(\mathbf{r}) \rangle = 0$. A summary of the terminology is in Table 1.1. Whenever there is mention of average fields, we must always ask ourselves about the variances of those averages. If the variances are large, then the knowledge of the average field is insufficient.

Table 1.1: Field definitions in a random media.

$\langle \psi \rangle$	\rightarrow	{	average field mean field coherent field first moment of the field
$\delta \psi$	\rightarrow	{	incoherent field fluctuating field
$ \langle \psi \rangle ^2$	\rightarrow		coherent intensity
$ \delta \psi ^2$	\rightarrow		incoherent intensity
$\langle \delta \psi ^2 \rangle$	\rightarrow	{	average incoherent intensity variance of incoherent field mean square deviation of incoherent field “uncertainty” in mean field
	$=$		$\langle \psi - \langle \psi \rangle ^2 \rangle$
$\langle I \rangle$	\rightarrow		average intensity
	$=$		$\langle \psi ^2 \rangle$
	$=$		$\langle \langle \psi \rangle ^2 \rangle + \langle 2\langle \psi \rangle \delta \psi \rangle + \langle \delta \psi ^2 \rangle$
	$=$		$\langle \psi ^2 \rangle + 2\langle \psi \rangle \langle \delta \psi \rangle + \langle \delta \psi ^2 \rangle$
	$=$		$ \langle \psi \rangle ^2 + \langle \delta \psi ^2 \rangle$.

Chapter 2

SIMPLE EFFECTIVE MEDIUM THEORIES

The “simple” in the title of this chapter refers to electrostatic. The removal of the $e^{i\mathbf{k}\cdot\mathbf{r}}$ in the Green’s function, which is also valid at very low frequencies, allows for a plethora of calculations without worry about the phase of the electromagnetic wave.

The goal of this chapter is to obtain $\bar{\epsilon}_e$ in the expression $\langle \mathbf{D} \rangle = \bar{\epsilon}_e \cdot \langle \mathbf{E} \rangle$. We will see that obtaining $\bar{\epsilon}_e$ is non-trivial and it can be calculated only for certain spatial distributions and shapes of the scatterer. Before the relationship for the effective permittivity can be derived, the polarizability of a single scatterer must be obtained.

2.1 Nature of dielectrics under consideration

The effective permittivity tensor $\bar{\epsilon}_e$ is associated with the dielectric behavior of materials. It directly relates the electric flux density vector \mathbf{D} and the electric field \mathbf{E} . Because $\bar{\epsilon}_e$ is a tensor, the two vectors are not always parallel.

Dielectrics are associated with bound charges whereas conductors are associated with free electrons. In the classical viewpoint, the response of the dielectric is due to the cumulative response of all the bound charges to an electric field. In many dielectrics, and the only type we will consider here, magnetic moment effects are negligible [39]. Also, as Frohlich [15] points

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out, sometimes only 2% of the bound charges participate in the response to an electric field dependent on the medium and electric field but we will not make use of this information and assume that all dipoles equally to the cumulative response.

As we mentioned in Section 1.2.5, we will only consider dipole moments. Using this model, an electric field creates a dipole by separating neutral charges into a positive and negative charges. It is assumed that the dipole is an ideal dipole since the charge separation is assumed small and the observation distances far.

2.2 Historical review

The following brief historical sketch is based mostly on Landauer's [29], Krumhanls's [27] and Böttcher's [5] reviews.

Electrostatic condensor's were first constructed in the mid 1700's. Large amounts of electric charge could be stored on two metal plates separated by an insulating material. The properties of the insulating material were not studied until 1837 when Faraday published results indicating that the condensor's capacity was dependent on the nature of the insulating material which he called the dielectric. It was also Faraday who used the term specific inductive capacity to describe the difference between a condensor filled with a dielectric and a condensor separated by free space. The term specific inductive capacity is now known as the dielectric constant or the dielectric permittivity.

Although Faraday proposed a model of the dielectric composed of metallic globules separated by insulating material, it was Mossotti in 1847 who analyzed the interactions between

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the globules assuming that they were polarizable entities. Mossotti's papers were not widely distributed and his expression remained mostly unknown until 1879 when Clausius rederived the same expression. Also, Lorenz in 1880 derived a similar relationship but used the refractive index (square of the dielectric permittivity). Lorenz gave a derivation of Lorenz's equation based on a model of particles containing elastically bound electrons. Lorenz also introduced the concept of a large sphere centered on a molecule cut out of the dielectric and proposed that there is an internal field (the field that the molecule experiences due to all of the other molecules, now called the local field) different from the applied macroscopic field. In contrast, Mossotti used a small sphere cut out from the surrounding medium that tightly fit around the molecule. Lorenz's large sphere is the approach used today. We will consider a large sphere as Lorenz did and show why the cut out sphere cannot fit closely around the molecule in a later section.

The equations derived from Clausius, Mossotti, Lorenz and Lorenz are known as the Clausius-Mossotti (CM) relationship or the Lorenz-Lorentz relationship (or to make sure that proper credit is given to all, the Clausius-Mossotti-Lorenz-Lorentz relationship). We will refer to it as the CM relationship.

In 1904, J.C. Maxwell-Garnett (MG) rederived the CM relationship for propagating waves [17]. This was in contrast to the electrostatic assumptions made by the above workers (J.C. Maxwell-Garnett is not related to James Clark Maxwell. J.C. Maxwell-Garnett father worked in James Clark Maxwell's laboratory). It was Garnett who first derived the equivalent (or effective) dielectric permittivities for heterogeneous media. The CM relationship is an equation

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containing the polarizability of molecule while the MG is an equation that does not contain the polarizability and contains only the dielectric permittivity. dielectric permittivity.

Workers in the field found that the CM relationship could not explain the experimental results that were being obtained. The discrepancies were mostly associated with “associating” compounds later known as polar compounds. Debye published calculations in 1912 which showed that the dielectric permittivities of associating compounds could be calculated if one attributed the dielectric permittivity to both molecular polarizability and a permanent electric dipole. Debye hypothesized that if the molecule contained a permanent electric dipole component, it would take a finite amount of time after the applied electric was relaxed for the permanent dipole to orient itself. Previously, it had been assumed that a molecule could react instantaneously to the applied electric field. Debye was then able to explain “macroscopic dielectric relaxation” which is characterized by a decrease in the real part of the dielectric permittivity with increasing frequency (known as anomalous dispersion). Anomalous dispersion is usually found near regions of resonant absorption due to an accompanied increase in the imaginary part of the dielectric function.

Based on Debye’s theory, Onsager suggested that the moments produced by a molecule with a permanent dipole moment were contributing to the internal field by the effect the permanent dipole moment had on the surrounding medium. This field is known as the reaction field and its contribution must be subtracted from the internal field. Onsager’s and Debye’s theory accounted for many of the polar liquids which the CM relationship failed to account for.

The modern theory of inhomogeneous media (i.e. dielectrics considered at a small length

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scale) began with Bruggeman in 1935 when he published his effective medium theory. In Bruggeman's theory, the constituents are considered symmetrically whereas in the MG theory the constituents are treated asymmetrically (mathematically, the two components cannot be interchanged without changing the equation). Bruggeman's work is heavily used in solid state physics with the dielectric permittivity replaced by the electrical conductivity. It is not a coincidence that the random medium mathematics which yield the MG theory also yield the same expression for the conductivity.

2.3 Simple Models

We will first derive the Maxwell-Garnett and Bruggeman theories based on a classical model of matter. Relationships such as the MG or Bruggeman are also known as mixing formulae.

The recipe is simple. First we will obtain $\mathbf{p} = \bar{\gamma} \cdot \mathbf{E}_{\text{loc}}$, then relate the local electric field to the macroscopic electric field, then obtain $\bar{\epsilon}_e$.

2.3.1 Classical derivation of the C-M-L-L and MG relationships

The CM relationship can be derived for particles with a dielectric permittivity since dielectric particles are polarized when placed in a uniform electric field. This is also true for molecules. Consideration of both types of scatterers produces the same equations although their interpretation is slightly different. We will first derive the CM relationship then the MG relationship.

We consider an infinite medium composed of molecules, atoms or ions assumed to be dipole

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scatterers. The macroscopic relationships for the electric flux density are

$$\begin{aligned} \mathbf{D} &= \epsilon_o \mathbf{E} + \mathbf{P} = \epsilon_f \epsilon_o \mathbf{E} \\ \mathbf{P} &= (\epsilon_f - 1) \epsilon_o \mathbf{E}, \end{aligned} \tag{2.1}$$

where \mathbf{P} is the dipole moment per unit volume (also known as the polarization vector) and ϵ_f is the effective or relative dielectric permittivity. \mathbf{P} is due to the vector sum of the dipole moments. For moderate field strengths, the dipole moment of a single dipole is related to the field directly acting on the dipole

$$\mathbf{p}_\alpha = \gamma \mathbf{E}_{\text{loc}} \tag{2.2}$$

where γ is the polarizability (after Robinson [39]) of the molecule α and is constant. We have assumed a linear, isotropic relationship between the local field and the molecule's polarization instead of a more general non-linear relationship, $\mathbf{P} = \epsilon_o(\chi_{ij} E_j + d_{ijk} E_j E_k + \dots)$.

The polarization arising from an induced dipole particle density of n_o with identical particles is

$$\mathbf{P} = n_o \gamma \mathbf{E}_{\text{loc}}. \tag{2.3}$$

This also shows that calculation of γ always involves finding the internal field since we can write the polarizability as

$$\gamma = \frac{(\epsilon_f - 1) \epsilon_o}{n_o} \frac{\mathbf{E}}{\mathbf{E}_{\text{loc}}}.$$

The macroscopic field \mathbf{E} is the average field in the medium and is calculated by considering the effects of all dipoles. We wish to calculate \mathbf{E}_{loc} without the effects of particle α . Obviously,

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the two are not equal and a Lorentz correction term must be introduced

$$\mathbf{E}_{\text{loc}} = \mathbf{E} + \mathbf{E}_{\text{cor}} \quad (2.4)$$

to account for the difference.

In the infinite dielectric (or between the plates of an ideal parallel plate capacitor), dipoles far from the observation point are treated as a continuous medium with polarization \mathbf{P} producing a field \mathbf{E}_{far} . Dipoles near the observation point can be explicitly taken into account by knowing their positions (all of the orientations are the same in our problem). This produces a field \mathbf{E}_{near} . The sum of these two field is the correction field,

$$\mathbf{E}_{\text{cor}} = \mathbf{E}_{\text{far}} + \mathbf{E}_{\text{near}}. \quad (2.5)$$

This convenient mathematical procedure arbitrarily divides the domain into two volumes— V_n the near volume and V_f the far volume as shown in Figure 2.1. V_n is known as the Lorentz cavity.

Contributions from \mathbf{E}_{far} are due to the pseudo charge density. There is a charge density of $\rho_v = -\nabla \cdot \mathbf{P} = 0$ in the far volume and a pseudo surface charge density $\rho_s = \hat{\mathbf{n}} \cdot \mathbf{P}$, with $\hat{\mathbf{n}}$ the outward unit normal on the far volume's surface (it points into the near volume) due to the artificial boundary between the far and near volume. If we assume the near volume is spherical, $\mathbf{E}_{\text{far}} = \mathbf{P}/3\epsilon_o$ where \mathbf{P} is the polarization of the medium, obtained by integrating the surface pseudo-charge density over the surface of the Lorentz cavity.

Contributions from \mathbf{E}_{near} are due to the contributions from individual dipoles in the near volume. For some special geometries such as the type we will assume, $\mathbf{E}_{\text{near}} = 0$. We will

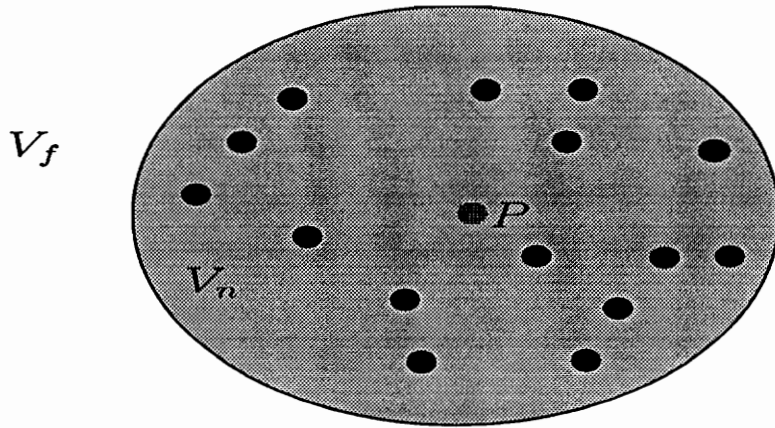


Figure 2.1: Geometry of the Lorentz cavity

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comment on this assumption shortly.

With E_{far} and E_{near} obtained above, E_{cor} becomes

$$E_{\text{cor}} = E_{\text{far}} + E_{\text{near}} = E_{\text{far}} = \frac{P}{3\epsilon_o} \quad (2.6)$$

and the local field is

$$E_{\text{loc}} = E + E_{\text{cor}} = E + \frac{P}{3\epsilon_o}. \quad (2.7)$$

Using (2.3), we can write the relationship between the local field and the applied field explicitly as

$$E_{\text{loc}} = \frac{E}{1 - n_o\gamma/3\epsilon_o}. \quad (2.8)$$

Moreover, substituting our local field expression directly into (2.1) to obtain the relation between P and E produces

$$P = n_o\gamma \left(E + \frac{P}{3\epsilon_o} \right) \rightarrow P = \frac{3n_o\gamma}{3\epsilon_o - n_o\gamma} \epsilon_o E. \quad (2.9)$$

Comparison to (2.1) implies,

$$\frac{n_o\gamma}{3\epsilon_o} = \frac{\epsilon_f - 1}{\epsilon_f + 2} \quad \leftrightarrow \quad \epsilon_f = \frac{1 - 2n_o\gamma/3}{1 - n_o\gamma/3} \quad (2.10)$$

which is the Clausius-Mosotti relationship. In the form with the index of refraction instead of the dielectric permittivity, (2.10) is known as the Lorentz-Lorenz relationship.

It is necessary to calculate the polarizability of a single molecule in order to obtain the effective dielectric permittivity. This involves a complicated quantum-mechanical calculation in the exact case, but we assumed that molecules respond as dipoles which greatly simplifies

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the calculation. The perturbation of the potential created by a homogeneous sphere filled with dielectric ϵ_α in an uniform electrostatic field is equivalent to a perturbation caused by an ideal dipole. We may replace the molecule modeled as a dipole with a sphere of dielectric ϵ_α and the radius of the sphere indicating the extent of the molecule.

The field inside this homogeneous dielectric sphere can be obtained from the well-known electrostatics result,

$$\mathbf{E}_{\text{int}} = \frac{3}{\epsilon_\alpha + 2} \mathbf{E}_{\text{loc}} \quad (2.11)$$

where the sphere is embedded in free space. The polarizability of this sphere is

$$\gamma = \frac{3(\epsilon_\alpha - 1)}{\epsilon_\alpha + 2} v_\alpha = 4\pi a^3 \frac{\epsilon_\alpha - 1}{\epsilon_\alpha + 2} \quad (2.12)$$

where v_α is the volume of the sphere. Substitution of (2.12) into (2.10) produces

$$\epsilon_f = \frac{1 + 2f \frac{\epsilon_\alpha - 1}{\epsilon_\alpha + 2}}{1 - f \frac{\epsilon_\alpha - 1}{\epsilon_\alpha + 2}} \quad (2.13)$$

where $f = n_o v_\alpha$, the volume fraction of the dielectric spheres. Equation (2.13) is the Maxwell-Garnett relationship. It may be written in an alternative form known as the Rayleigh mixing formula,

$$\frac{\epsilon_f - 1}{\epsilon_f + 2} = f \frac{\epsilon_\alpha - 1}{\epsilon_\alpha + 2}.$$

We wish to extend this result to anisotropic media. In this, we follow the notation of de Wolf [11]. We will consider all molecules as ellipsoids that respond as dipoles. The dipoles are embedded in a background “matrix” dielectric ϵ_m in which homogeneous wave propagation occurs.

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In the general problem, the polarizability is a dyadic. The constitutive relationships in this medium are

$$\begin{aligned} \mathbf{D} &= \epsilon_o \mathbf{E} + \mathbf{P} = \bar{\epsilon}_f \epsilon_m \mathbf{E} \\ \mathbf{P} &= (\bar{\epsilon}_f - \bar{\mathbf{1}}) \epsilon_m \mathbf{E}. \end{aligned} \tag{2.14}$$

The linear relationship between the polarization of one dipole and the local field is

$$\bar{\mathbf{p}} = \bar{\gamma} \mathbf{E}_{\text{loc}}. \tag{2.15}$$

As we did in (2.3), we may write the polarization vector as the sum of the contributions from the individual dipole moments (assumed to be identical) as

$$\mathbf{P} = \sum_{\alpha} \bar{\mathbf{p}} = n_o \bar{\mathbf{p}} = n_o \bar{\gamma} \mathbf{E}_{\text{loc}}. \tag{2.16}$$

Again, \mathbf{E}_{loc} is the field acting on dipole α and it is the sum of the macroscopic field \mathbf{E} and a correction term \mathbf{E}_{cor}

$$\mathbf{E}_{\text{loc}} = \mathbf{E} + \mathbf{E}_{\text{cor}}, \tag{2.17}$$

with the correction term accounting for the field at the observation point due to all dipoles except α .

By dividing the domain into near and far, we may account for the far dipoles by the field from the volume pseudo-charge density \mathbf{P} via $\nabla \cdot \mathbf{P} = 0$ and the surface pseudo-charge density $\rho_s = \hat{\mathbf{n}} \cdot \mathbf{P}$ resulting from the formation of dipoles near the surface of the dielectric. Because the flux of \mathbf{P} is zero, the volume charge does not contribute to the local field. The contribution due to the charges on the surface of the ellipsoid has been solved in [4, p 421] or [50, Sec. 3.27]

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and we write it similar to de Wolf and Sihvola [45],

$$\mathbf{E}_{\text{far}} = \frac{\bar{\mathbf{L}}\mathbf{P}}{\epsilon_m} \quad (2.18)$$

with

$$\begin{aligned} \bar{\mathbf{L}} &= \sum_j \lambda_j \hat{\mathbf{u}}_j \hat{\mathbf{u}}_j \\ \lambda_j &= \frac{a_1 a_2 a_3}{2} \int_0^\infty \frac{dq}{(a_i^2 + q) f(q)}, \end{aligned} \quad (2.19)$$

where $f(q) = [(q + a_1^2)(q + a_2^2)(q + a_3^2)]^{1/2}$.

As we did in the scalar, spherical case, the contribution of the dipoles in the near volume is assumed to be zero, $\mathbf{E}_{\text{near}} = 0$. The total correction field then is only (2.18) and the local field can be written

$$\mathbf{E}_{\text{loc}} = \mathbf{E} + \frac{\bar{\mathbf{L}}\mathbf{P}}{\epsilon_m} \quad (2.20)$$

which leads to the relation between the local field and the macroscopic field as

$$\mathbf{E}_{\text{loc}} = \mathbf{E} + \mathbf{E}_{\text{cor}} = \frac{\mathbf{E}}{\bar{\mathbf{1}} - \bar{\mathbf{L}} \frac{n_o \bar{\gamma}}{\epsilon_m}} \quad (2.21)$$

where we have represented multiplication by the inverse with the division notation and care must be taken to insure that the matrix operations are performed in the correct order.

Using the constitutive relationships and (2.21), we obtain

$$\mathbf{P} = (\bar{\epsilon}_f - \bar{\mathbf{1}}) \epsilon_m \mathbf{E} = n_o \bar{\gamma} \mathbf{E}_{\text{loc}} = n_o \bar{\gamma} [\bar{\mathbf{1}} - \bar{\mathbf{L}} n_o \bar{\gamma} / \epsilon_m] \mathbf{E} \quad (2.22)$$

which leads to the result,

$$\bar{\epsilon}_f = \frac{\bar{\mathbf{1}} - (\bar{\mathbf{L}} - \bar{\mathbf{1}}) n_o \bar{\gamma} / \epsilon_m}{\bar{\mathbf{1}} - \bar{\mathbf{L}} n_o \bar{\gamma} / \epsilon_m} \quad (2.23)$$

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and reduces to (2.10) if the particles are spheres and the background medium is free space.

To obtain the equivalent to the CM relationship it is necessary to calculate the relationship between the polarizability of an ellipsoid and E_{loc} . We saw that in the case of the sphere, this involved finding the internal field, the same is true here. Again, we consult [4, p 145, eqn 5.32] to find that

$$\mathbf{p} = 4\pi\epsilon_m abc \frac{\epsilon_1 - \epsilon_m}{3\epsilon_m + 3L_3(\epsilon_1 - \epsilon_m)} \mathbf{E}_o$$

which translated into our notation yields

$$\gamma_j = v_\alpha \epsilon_m \frac{\epsilon_\alpha - 1}{1 + \lambda_j(\epsilon_\alpha - 1)}$$

along the three main axes of the ellipsoid. This expression assumes the electrostatic field is oriented along the z -axis. When modified to handle fields oriented along all three principal axes we obtain the expression,

$$\bar{\gamma} = \epsilon_m v_\alpha (\epsilon_\alpha - 1) \bar{\tau} \quad (2.24)$$

where

$$\bar{\tau} = \sum_{j=1}^3 \Lambda_j \hat{u}_j \hat{u}_j$$

$$\Lambda_j = \frac{1}{1 + \lambda_j(\epsilon_\alpha - 1)}.$$

Using the purely algebraic identity

$$\bar{L} = -\frac{\bar{\tau} - \bar{\mathbf{1}}}{\bar{\tau}(\epsilon_\alpha - \bar{\mathbf{1}})}$$

and (2.24) in (2.23) yields

$$\bar{\epsilon}_f = \frac{\bar{\mathbf{1}} + f(\epsilon_\alpha \bar{\tau} - \bar{\mathbf{1}})}{\bar{\mathbf{1}} + f(\bar{\tau} - \bar{\mathbf{1}})}. \quad (2.25)$$

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Equation (2.25) is the equivalent of the MG relationship for ellipsoids. Sihvola [45] has produced the same expression in different form with the ellipsoidal scatterers having a distribution of orientations.

2.3.2 Comments on the simple derivation of the CM and MG relationships

We made few comments on the assumptions made in the derivation of the CM and MG relationships. The intent of this section is to remedy this situation.

In both derivations, the contributions from E_{near} was assumed zero. The near field contributions were due to the dipoles in the Lorentz volume. It was assumed that this volume was macroscopically small but microscopically large so that it contained a large number of dipoles. The assumption that $E_{\text{near}} = 0$ is equivalent to ignoring short-range interactions. Although the dipole electric field falls off as $1/r^3$, the contribution from distant dipoles, outside the Lorentz sphere, provided the only correction to the macroscopic field when calculating the local field. The Lorentz sphere must be chosen sufficiently large to have the same dielectric properties as a macroscopic sample to assure that fluctuations across the sphere are small. If the fluctuations are large, the cumulative response of the dipoles at the observation point will not be zero and the volume will not be representative of the medium. There are configurations of the interior dipoles which yield a zero net field contribution. For spherical molecules arranged on a cubic lattice or for a completely random molecule spatial arrangement, the field contribution is zero. It is also important to have a microscopically large cavity so that the fluctuations due to different configurations, representing different members of an ensemble, are small. Although we have

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not mentioned anything about ensemble averaging in our derivation, we see that we must pick a representative volume of the media in which to do our calculations, an idea inherent in ensemble averaging.

The volume fraction of scatterers must be low. It is not apparent that there is any restriction on the volume fraction f . However, as it was quickly found experimentally, the MG relationship is only good for low volume fractions or for $f = 1$. The low volume fraction restriction is a direct result of the implicit assumption that the local field is uniform everywhere outside of dielectric particle α . This is clearly false. The field outside a dielectric particle is the sum of the electrostatic field plus a perturbation due to the presence of the dielectric. Just outside the sphere, the field is

$$\mathbf{E} = \mathbf{E}_{\text{loc}} - \nabla \left(\frac{\mathbf{p} \cdot \hat{\mathbf{r}}}{4\pi\epsilon_m r^2} \right)$$

where the dipole expression is just the gradient of the potential from (1.8) and \mathbf{p} is the polarization due to the sphere proportional to a^3 as seen from the CM calculations. This implies that the error is $O(a^3/r^3)$ and if the separation of particles is less than several radii the error and becomes significant.

The MG relationship is only valid for non-polar molecules. Polar molecules have a permanent dipole moment which must be taken into account with other theories such as Onsager's or Kirkwood's [6]. Water has a large permanent dipole moment. There are articles in the literature concerning the application of MG to scattering from raindrops and about the applicability of MG to other problems where it is not clear the non-polar assumption is valid. For example, Bohren [3] clearly indicates that MG is suitable in calculations of scattering from rain. The

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conflict is over the interpretation of polarizability. There are different types of polarizability involved in determining the CM relationship. Each polarizability is related to a specific physical process of dielectric response. For example, the polarizability of a dielectric sphere is due to the response of every volume element whereas in a conducting sphere, the polarization is due to true surface charges. Polarizabilities may be linearly added to yield the total polarizability. The different types are electronic, due to the displacement of the electron cloud; atomic, due to molecules with electrons strongly attracted to other charge centers; orientation (or dipole), due to permanent dipole moments (they exist in the absence of fields) and space-charge, due to trapped carrier electrons at interfaces (they cause boundary scattering). At high frequencies (not the electrostatic case), the permanent dipole can no longer follow the changes in polarization of the field but the atomic and electronic polarizabilities are the same as in static fields. In this situation, the CM relationship can be used to study both polar and non-polar molecules. Also, if the molecules are truly randomly oriented, the contribution of these permanent dipole moments would be zero as was discussed previously.

It was assumed that a molecule could be assigned a specific dielectric permittivity. This is obviously not true because a single molecule does not a dielectric make. According to macroscopic theory, the polarizability is a function of the dielectric permittivity of the polarizable body. In order to use macroscopic theory, the molecules must be viewed as small ellipsoids with an internal dielectric constant ϵ_a . Given the dimensions of the molecule, this constant can be calculated from simple relationships. However, such a construct is only a model and any attempts at a complete characterization of the molecule using the dielectric constant is

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fallacious. The molecule is modeled as a dielectric sphere but is still small enough that a dipole moment suffices to describe its radiation pattern.

The cavity shape and the shape of the interior particles should be the same. This follows directly from the equivalence principal. The equivalence principal states that the removal or creation of a surface must be accompanied by the creation or removal of a current. The creation of the Lorentz cavity surface implies that the field surrounding the cavity is perturbed just as the placement of any dielectric in an electrostatic field produces a perturbation. The interior particles contribute a surface current to the surface of the Lorentz cavity in addition to the pseudo-charges introduced from the continuum and P . Since the introduction of the Lorentz cavity should produce no net effect on the medium it is necessary for the surface charge produced by the interior particles to cancel the effects the Lorentz cavity has introduced to the electrostatic field. If the interior particles are positioned on a cubic lattice and they all have the shape and orientation, the cumulative sum of the particles' depolarization factors will cancel the effect of the Lorentz cavity's depolarization factor producing no net effect in the medium. Previous derivations of the MG relationship have usually invoked the more mystical process of creating a Lorentz cavity while holding the polarization constant in the surround medium. From the explanation above, we see this is not necessary. If we choose the shape of the Lorentz cavity different from the interior particles' shapes, we are forced into additional bookkeeping duties to account for the extra surface charge density.

It is assumed that the scatterers in the far volume are in a continuum with dielectric permittivity ϵ_m , the background medium. \bar{L}/ϵ_m as seen in (2.20). This is an expression of

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the relation of the fields internal and the fields external (a depolarization factor which we will discuss further) to a scatterer. P is calculated using the polarization of the scatterer at the observation point and then applied to all scatterers including those in the far volume by the multiplication of n_o . This directly implies that the “continuum” composed of scatterers in the far volume assumed to have a polarization P have an effective dielectric permittivity of ϵ_m instead of ϵ_f . This approximation is only true for tenuous distributions, that is, when $\epsilon_f - \epsilon_m \ll 1$.

Only three parameters were important in the derivations: the particle density n_o , the polarizability $\bar{\gamma}$ and the local field E_{loc} . Also, all of the development was motivated by defining the effective permittivity then attempting to find an expression for it. To obtain an expression for the permittivity it was necessary to obtain an ensemble average. This is not apparent in the above equations but it is expressed in the parameter n_o which is how the “per volume” gets into P . Since all of the particle’s locations were assumed to be known exactly, the one volume referred to n_o was the ensemble member. Since there was no configurational uncertainty, the volume average in n_o is exact and the variance of our permittivity is zero. For the model considered and subject to its assumptions, it is an exact result.

Calculation of the MG relation using ellipsoids embedded in a background medium ϵ_m requires one actually to deal with macroscopic scatterers and in this case, the polarizability must be interpreted as a macroscopic polarizability. Only when the background medium is free space can this polarizability be interpreted as the molecular polarizability. The form of the resulting equations will be identical. However, in the molecular case, the polarizability is

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a property of the molecule and is independent of macroscopic parameters. Frohlich [15] has shown this quantity is proportional to the density of the dielectric while with the macroscopic polarizability no such conclusion can be made.

The CM and MG relationships were derived assuming the dielectric had infinite support. In the case of finite domain, there will be contributions to the local field from the presence of additional dielectric surfaces. We saw that when a dielectric is placed in an electrostatic field, the induced dipoles create a surface pseudo-charge density. As Bleaney [1] points out, if the applied field is E_0 and the dielectric body B is the domain where one is solving for the effective permittivity, the Lorentz sphere L and the surface of B will contribute to the local field at the observation point (Figure 2.2). This is a more difficult problem than the single surface of surface charge encountered in the CM derivation and in this case there is a physical surface. When the dielectric body has finite support, the polarization depends on the shape of the body in contrast to the infinite support of the CM derivation. In the case of an infinite slab of dipoles with an electrostatic field perpendicular to the slab, the complexity is somewhat relaxed since because the field in the slab is easily determined by a simple ratio of dielectric permittivities.

In general, the CM relationship cannot be used with the optical theorem because it yields a real ϵ_f even when it must be complex to account for specific types of attenuation. Bohren [2] has commented that in general the refractive index of any medium is dependent on both the dielectric permittivity and relative permeability. Although it is always assumed that $\mu = 1$ and we expect a material to be non-magnetic if its components are, this is not true. The assumption that all scatterers scatter as point dipoles can be severely tested if we let the size of the scatterer

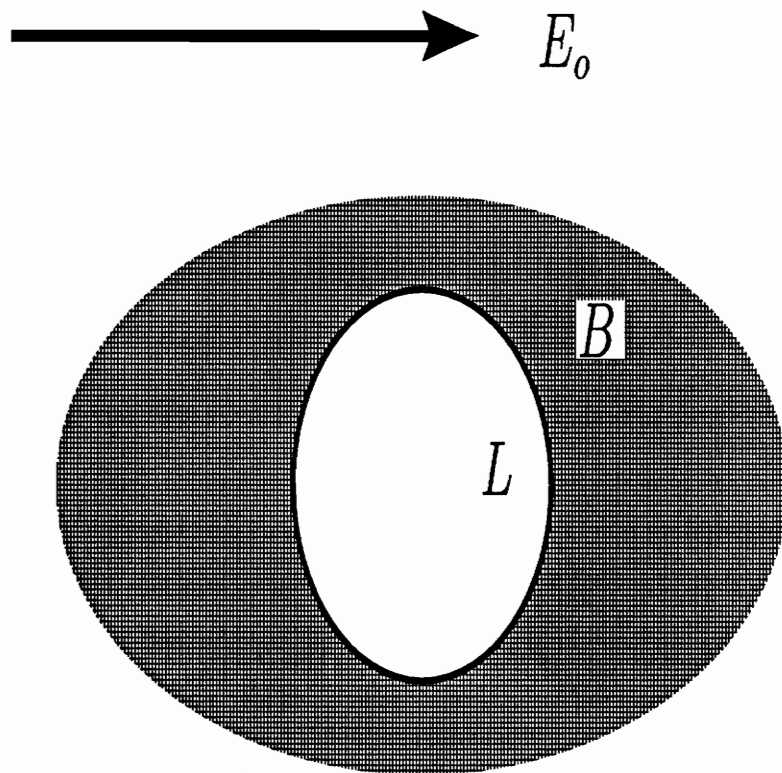


Figure 2.2: Bleaney's finite domain dielectric problem

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become large. In this case, the fluctuation across the scatterer itself would need to be calculated in order to correctly determine the internal field and hence the polarizability. Clearly, this is a difficult calculation. Substitution of a real ϵ_α into MG yields a real ϵ_f that is also independent of particle shape (since the scatterers are assumed to be dipoles). In inhomogeneous media however, shape-dependent absorption is important as is attenuation from multiple-scattering, both of which are ignored by effective-medium theories. Since molecules are modelled as dielectric spheres, it is possible to introduce a complex ϵ_α . This would correspond to introducing atomic absorption processes. We will comment on this aspect in the next chapter. Bohren draws the conclusion that if absorption and scattering are important processes in the medium, and the heterogeneities cannot be considered point dipoles, then effective medium theories such as those derived above are inadequate.

2.4 Electrostatic derivations of Maxwell-Garnett and Bruggeman

2.4.1 Integral equation derivation

The classical derivation of the MG relationship was performed using electrostatics and dipole scattering. The goal of this section is to derive MG directly from Maxwell's electrostatic equations. We will arrive at the MG relationship without assuming dipole scattering. This is similar to Rayleigh scatterers and then determining that scattering from Rayleigh scatterers and scattering from dipoles is equivalent [4], [60]. For our approach, we have borrowed heavily from the much quoted derivation by Stroud [51] and we will show how the classical derivation above maps into Stroud's derivation.

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We will assume that the observation point is inside an arbitrary finite volume f . Without time dependent fields, Maxwell's equations are

$$\begin{aligned}\nabla \times \mathbf{E}(\mathbf{r}) &= 0 & \nabla \times \mathbf{H}(\mathbf{r}) &= 0 \\ \nabla \cdot \mathbf{B}(\mathbf{r}) &= 0 & \nabla \cdot \mathbf{D}(\mathbf{r}) &= 0\end{aligned}$$

All of the above field are macroscopic. We define $\bar{\epsilon}_e$ by

$$\langle \mathbf{D} \rangle \equiv \bar{\epsilon}_e \langle \mathbf{E} \rangle \quad (2.26)$$

where the angled brackets denote ensemble averages. Equation (2.26) expresses the intent of finding the average macroscopic flux density \mathbf{D} . Calculation of the average flux density and effective dielectric permittivity will efface the cell structure of the medium.

An electrostatic field \mathbf{E}_o is applied to the volume V bounded by surface S . We will let

$$\bar{\epsilon}(\mathbf{r}) = \bar{\epsilon}_g + \delta\bar{\epsilon}(\mathbf{r}) \quad (2.27)$$

where $\bar{\epsilon}_g$ is an arbitrary constant that we will conveniently set later and $\delta\bar{\epsilon}(\mathbf{r})$ is the fluctuation about $\bar{\epsilon}_g$. Substitution of (2.27) into $\mathbf{D} = \bar{\epsilon} \cdot \mathbf{E}$, and averaging produces

$$\langle \mathbf{D} \rangle = \bar{\epsilon}_g \langle \mathbf{E} \rangle + \langle \delta\bar{\epsilon} \mathbf{E} \rangle. \quad (2.28)$$

$\langle \mathbf{E} \rangle = \mathbf{E}_o$ the applied electric field. It is necessary to find $\langle \delta\bar{\epsilon} \mathbf{E} \rangle$. Notice that the last term in (2.28) acts much like the polarization term in $\mathbf{D} = \epsilon_o \mathbf{E} + \mathbf{P}$.

Gauss's law allows us to write

$$\nabla \cdot (\bar{\epsilon}(\mathbf{r}) \mathbf{E}(\mathbf{r})) = \nabla \cdot (\bar{\epsilon}(\mathbf{r}) \nabla \Phi(\mathbf{r})) = 0 \quad (2.29)$$

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where $E = \nabla\Phi$ and Φ is a scalar potential. Upon using (2.27), we obtain the following boundary value problem,

$$\begin{aligned}\nabla \cdot \bar{\epsilon}_g \nabla \Phi(\mathbf{r}) &= -\nabla \cdot \delta \bar{\epsilon}(\mathbf{r}) \nabla \Phi \quad \text{in } V, \\ \Phi(\mathbf{r}) &= \Phi_o(\mathbf{r}) \equiv -E_o \cdot \mathbf{r} \quad \text{on } S.\end{aligned}\tag{2.30}$$

The scalar potential was introduced to obtain a differential equation whose solution could be written using a Green's function. We define a Green's function as

$$\begin{aligned}\nabla \cdot (\bar{\epsilon}_g(\mathbf{r}) \nabla G(\mathbf{r}, \mathbf{r}')) &= -\delta(\mathbf{r} - \mathbf{r}') \quad \mathbf{r}' \in V, \\ G(\mathbf{r}, \mathbf{r}') &= 0 \quad \mathbf{r}' \in S,\end{aligned}\tag{2.31}$$

even though it has different boundary conditions than Φ . This allows us to write

$$\Phi(\mathbf{r}) = \Phi_o(\mathbf{r}) + \int_V d^3r' G(\mathbf{r}, \mathbf{r}') \nabla' \cdot (\delta \bar{\epsilon}(\mathbf{r}') \nabla' \Phi(\mathbf{r}'))\tag{2.32}$$

with the primes ∇' indicating that the derivatives are taken with respect to the integration variables. Applying the operator $[\nabla \cdot \bar{\epsilon}_g \nabla(\cdot \cdot)]$ to (2.32) will reproduce (2.30). Integrating by parts using a specialized form of Gauss's law (Green's theorem),

$$\begin{aligned}\int_V d^3r \nabla \cdot A &= \int_S d^3r A \cdot dS \\ A &= \psi \Delta \phi \\ \int_V d^3r \psi \Delta \phi &= \int_S \psi \nabla \phi \cdot dS - \int_V d^3r \nabla \psi \cdot \nabla \phi,\end{aligned}$$

allows us to transfer the differentiation to the Green's function. Letting $\psi = G$ and $\Delta \phi = \nabla \cdot \nabla \Phi$ in the above expression we obtain

$$\int_V d^3r' G(\mathbf{r}, \mathbf{r}') \nabla \cdot \nabla \Phi(\mathbf{r}') = \int_S G(\mathbf{r}, \mathbf{r}') \nabla \Phi \cdot dS' - \int_V d^3r' \nabla G(\mathbf{r}, \mathbf{r}') \cdot \nabla \Phi(\mathbf{r}')$$

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but since $G(\mathbf{r}, \mathbf{r}') = 0$ on the boundary, the first term on the right hand side is zero. Using the above expression with (2.32) and operating on the resultant equation with the gradient operator produces,

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_o(\mathbf{r}) - \int_V d^3\mathbf{r}' \delta\bar{\epsilon} \mathbf{E}(\mathbf{r}') \nabla' \nabla G(\mathbf{r}, \mathbf{r}') \quad (2.33)$$

This integral equation is similar to (1.2.4), with a Green's function defined in (2.31) and $\delta\bar{\epsilon} \mathbf{E}(\mathbf{r}')$ acting like a “pseudo-source”. We had previously used $\langle \mathbf{E}(\mathbf{r}) \rangle = \mathbf{E}_o$, and after ensemble averaging (2.33), we must let $\langle \delta\bar{\epsilon} \mathbf{E}(\mathbf{r}) \rangle = 0$ to obtain the same result. This is known as the self-consistent condition because it will again produce an average field of \mathbf{E}_o . We will comment on self consistent approximations later in this section and in the following chapter.

Defining the function $\bar{S}(\mathbf{r})$ as

$$\delta\bar{\epsilon}(\mathbf{r}) \mathbf{E}(\mathbf{r}) = \bar{S}(\mathbf{r}) \mathbf{E}_o(\mathbf{r}) \quad (2.34)$$

shows that $\bar{S}(\mathbf{r})$ is a normalized pseudo-source. If we multiply (2.33) by $\delta\bar{\epsilon}(\mathbf{r})$, the equation describing scattering caused by fluctuations of $\bar{\epsilon}(\mathbf{r})$ is

$$\bar{S}(\mathbf{r}) = \delta\bar{\epsilon}(\mathbf{r}) + \delta\bar{\epsilon}(\mathbf{r}) \int_V d^3\mathbf{r}' \nabla \nabla' G(\mathbf{r}, \mathbf{r}') \bar{S}(\mathbf{r}'). \quad (2.35)$$

This is an integral equation of the second kind since $\bar{S}(\mathbf{r})$ appears both under and outside the integral. Successive substitutions of $\bar{S}(\mathbf{r}')$ under the integral using the expression (2.35) itself produces a Born series [49]). We will not follow this procedure here.

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Equations (2.27), (2.28) and (2.34) lead to

$$\begin{aligned}
 \langle D \rangle &= \bar{\epsilon}_e \langle E \rangle = \bar{\epsilon}_e E_o \\
 &= \bar{\epsilon}_g \langle E \rangle + \langle \delta\epsilon E \rangle \\
 &= \bar{\epsilon}_g \langle E \rangle + \langle \bar{S} E_o \rangle \\
 &= \bar{\epsilon}_g E_o + \langle \bar{S} \rangle E_o \\
 &= (\bar{\epsilon}_g + \langle \bar{S} \rangle) E_o \\
 &= (\bar{\epsilon}_g + \langle \bar{S} \rangle) \langle E \rangle
 \end{aligned} \tag{2.36}$$

which shows,

$$\bar{\epsilon}_e(\mathbf{r}) = \bar{\epsilon}_g + \langle \bar{S}(\mathbf{r}) \rangle. \tag{2.37}$$

By setting $\langle \bar{S}(\mathbf{r}) \rangle = 0$ we are removing the pseudo-sources caused by the inhomogenities. We can use this to define an effective medium theory—a theory where the pseudo-sources caused by the media's inhomogenities are removed from the wave propagation equations.

Calculation of $\langle \bar{S}(\mathbf{r}) \rangle$ can performed using (2.35). Consider a media composed of two constituents as in Figure 2.3 and let $\mathbf{r} \in v_i$ where the i indicates the arbitrary i th cell. The particles fill all space and neither can be identified as the background material or the particle material This assumption breaks (2.35) into two integrals: one part inside v_i and one part outside v_i

$$\begin{aligned}
 \bar{S}(\mathbf{r}) &= \delta\bar{\epsilon}_i(\mathbf{r}) + \delta\bar{\epsilon}_i(\mathbf{r}) \int_{v_i} d^3r' \bar{S}(\mathbf{r}') \nabla' \nabla G(\mathbf{r}, \mathbf{r}') \\
 &\quad + \delta\bar{\epsilon}_i(\mathbf{r}) \int_{V-v_i} d^3r' \bar{S}(\mathbf{r}') \nabla' \nabla G(\mathbf{r}, \mathbf{r}')
 \end{aligned} \tag{2.38}$$

with $\delta\bar{\epsilon}_i(\mathbf{r}) = \bar{\epsilon}(\mathbf{r}) - \bar{\epsilon}_g$ the dielectric permittivity fluctuation of the i th cell. To obtain a closed form of $\langle S(\mathbf{r}) \rangle$ we will use a closure hypothesis.

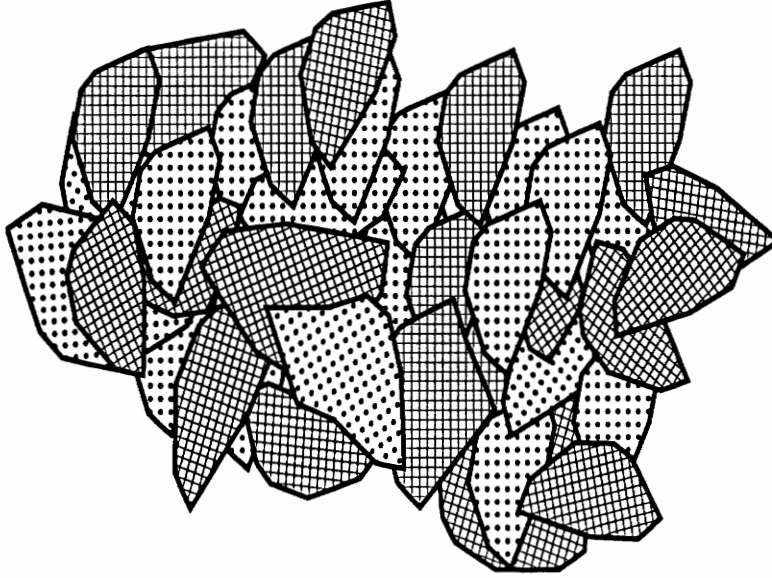


Figure 2.3: Stroud's composite media. The cells are assumed to have isotropic dielectric properties.

The closure hypothesis we will use, sets the pseudo-sources external to the i th cell equal to their average. This is equivalent to treating the region external to the i th cell as a continuum. This closure hypothesis is related to the assumption in the MG derivation that the volume of scatterers external to the inclusion volume may be considered a continuum with a significant computational simplification as a result. In essence, it replaces the media external to the scatterer with a continuum and accounts for the discrete external pseudo-sources by replacing them with an average source. Using the closure hypothesis on the last term in (2.38) produces

$$\delta\bar{\epsilon}(\mathbf{r}) \int_{V-v_i} d^3r' \bar{\mathbf{S}}(\mathbf{r}) \nabla' \nabla G(\mathbf{r}, \mathbf{r}') \approx \delta\epsilon(\mathbf{r}) \int_{V-v_i} d^3r' \langle \bar{\mathbf{S}} \rangle \nabla' \nabla G(\mathbf{r}, \mathbf{r}') \quad (2.39)$$

where $\mathbf{r} \in v_i$ and $\langle \bar{\mathbf{S}} \rangle = \langle \bar{\mathbf{S}}(\mathbf{r}) \rangle$ ($\langle \bar{\mathbf{S}} \rangle$ is a constant). This is not the same approximation made by Foldy [14] who assumed that the average effective field at scatterer i was the average effective field at the point \mathbf{r}_i when scatterer i was not present. The averaging process did not

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involve $G(\mathbf{r}, \mathbf{r}')$ because \bar{S} is the random function not $G(\mathbf{r}, \mathbf{r}')$ [49] (see Appendix A).

With the assumption that the cells are ellipsoids, the field in the i th cell is uniform [23]. Upon using (2.39) in (2.38), integrating by parts using a tensorial form Gauss's divergence [9, page 582] and using the boundary conditions in (2.31) we can write the full expression for the permittivity fluctuation (Equation (2.40) on page 53) or more succinctly if we use dyadic notation

$$\bar{S}_i = \delta\bar{\epsilon}_i - \delta\bar{\epsilon}_i \int_{S'} \nabla' G(\mathbf{r}, \mathbf{r}') \cdot \hat{\mathbf{n}} \times (\bar{S}_i - \langle \bar{S} \rangle). \quad (2.41)$$

The integration by parts has allowed us to combine the two integrals over different volumes into one integral over the same surface. The outward unit normal vector for the external volume is opposite to that of the outward unit normal one for the interior volume and it has produced the negative sign on $\langle \bar{S} \rangle$. If we now assume that the volume V is infinite, the Green's function defined in (2.31) becomes the free space Green's function whose value depends only on $|\mathbf{r} - \mathbf{r}'|$.

By letting,

$$V\bar{\Gamma}_i = - \int_{S'} d^2r' \nabla' G(\mathbf{r} - \mathbf{r}') \cdot \hat{\mathbf{n}} \quad (2.42)$$

we can write,

$$\bar{S}_i = \delta\bar{\epsilon}_i + \delta\bar{\epsilon}_i \bar{\Gamma}_i (\bar{S}_i - \langle \bar{S} \rangle). \quad (2.43)$$

Solving for \bar{S}_i produces,

$$\bar{S}_i = \frac{\delta\bar{\epsilon}_i (\bar{\mathbf{1}} - \bar{\Gamma} \langle \bar{S} \rangle)}{\bar{\mathbf{1}} - \delta\bar{\epsilon} \bar{\Gamma}}. \quad (2.44)$$

$$\begin{pmatrix} S_i^{zz} & S_i^{zy} & S_i^{zx} \\ S_i^{yz} & S_i^{yy} & S_i^{yx} \\ S_i^{xz} & S_i^{zy} & S_i^{zz} \end{pmatrix} = \begin{pmatrix} \delta\epsilon_i^{zz} & \delta\epsilon_i^{zy} & \delta\epsilon_i^{zx} \\ \delta\epsilon_i^{yz} & \delta\epsilon_i^{yy} & \delta\epsilon_i^{yx} \\ \delta\epsilon_i^{xz} & \delta\epsilon_i^{zy} & \delta\epsilon_i^{zz} \end{pmatrix} - \begin{pmatrix} \delta\epsilon_i^{zz} & \delta\epsilon_i^{zy} & \delta\epsilon_i^{zx} \\ \delta\epsilon_i^{yz} & \delta\epsilon_i^{yy} & \delta\epsilon_i^{yx} \\ \delta\epsilon_i^{xz} & \delta\epsilon_i^{zy} & \delta\epsilon_i^{zz} \end{pmatrix} \\
 \begin{pmatrix} \delta\epsilon_i^{zz} & \delta\epsilon_i^{zy} & \delta\epsilon_i^{zx} \\ \delta\epsilon_i^{yz} & \delta\epsilon_i^{yy} & \delta\epsilon_i^{yx} \\ \delta\epsilon_i^{xz} & \delta\epsilon_i^{zy} & \delta\epsilon_i^{zz} \end{pmatrix} = \begin{pmatrix} \int_{S'} d^2\mathbf{r}' n_x \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial x} & \int_{S'} d^2\mathbf{r}' n_x \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial y} & \int_{S'} d^2\mathbf{r}' n_x \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial z} \\ \int_{S'} d^2\mathbf{r}' n_y \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial x} & \int_{S'} d^2\mathbf{r}' n_y \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial y} & \int_{S'} d^2\mathbf{r}' n_y \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial z} \\ \int_{S'} d^2\mathbf{r}' n_z \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial x} & \int_{S'} d^2\mathbf{r}' n_z \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial y} & \int_{S'} d^2\mathbf{r}' n_z \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial z} \end{pmatrix} \begin{pmatrix} S_i^{zz} - \langle S \rangle_{zz} & S_i^{zy} - \langle S \rangle_{zy} & S_i^{zx} - \langle S \rangle_{zx} \\ S_i^{yz} - \langle S \rangle_{yz} & S_i^{yy} - \langle S \rangle_{yy} & S_i^{yx} - \langle S \rangle_{yx} \\ S_i^{xz} - \langle S \rangle_{xz} & S_i^{zy} - \langle S \rangle_{zy} & S_i^{zz} - \langle S \rangle_{zz} \end{pmatrix} \\
 = \begin{pmatrix} \delta\epsilon_i^{zz} - \delta\epsilon_i^{zz} \int_{S'} d^2\mathbf{r}' \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial x} & \delta\epsilon_i^{zy} - \delta\epsilon_i^{zy} \int_{S'} d^2\mathbf{r}' \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial y} & \delta\epsilon_i^{zx} - \delta\epsilon_i^{zx} \int_{S'} d^2\mathbf{r}' \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial z} \\ \delta\epsilon_i^{yz} - \delta\epsilon_i^{yz} \int_{S'} d^2\mathbf{r}' \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial x} & \delta\epsilon_i^{yy} - \delta\epsilon_i^{yy} \int_{S'} d^2\mathbf{r}' \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial y} & \delta\epsilon_i^{yx} - \delta\epsilon_i^{yx} \int_{S'} d^2\mathbf{r}' \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial z} \\ \delta\epsilon_i^{xz} - \delta\epsilon_i^{xz} \int_{S'} d^2\mathbf{r}' \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial x} & \delta\epsilon_i^{zy} - \delta\epsilon_i^{zy} \int_{S'} d^2\mathbf{r}' \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial y} & \delta\epsilon_i^{zz} - \delta\epsilon_i^{zz} \int_{S'} d^2\mathbf{r}' \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial z} \end{pmatrix}$$

Equation 2.40: Equation for the fluctuation in the permittivity in full matrix form for Stroud's theory.

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Although it is improper to divide one tensor (or dyadic) by another, such expressions really represent multiplication by the inverse; the division notation should not pose any difficulties.

Equation (2.44) may now be averaged and it's substitution into (2.37) produces

$$\bar{\epsilon}_e = \bar{\epsilon}_g + \frac{\left\langle \frac{\delta \bar{\epsilon}_i}{\bar{\mathbf{1}} - \delta \bar{\epsilon} \bar{\Gamma}} \right\rangle}{\left\langle \bar{\mathbf{1}} - \delta \bar{\epsilon} \bar{\Gamma} \right\rangle}. \quad (2.45)$$

Since the ensemble averaging is equivalent to volume averaging we may write

$$\begin{aligned} \left\langle \frac{\delta \bar{\epsilon}_i}{\bar{\mathbf{1}} - \delta \bar{\epsilon} \bar{\Gamma}} \right\rangle &= \lim_{V \rightarrow \infty} \frac{1}{V} \sum_i \frac{v_i}{\bar{\mathbf{1}} - \delta \bar{\epsilon} \bar{\Gamma}} = \sum_i \frac{f_i}{\bar{\mathbf{1}} - \delta \bar{\epsilon} \bar{\Gamma}} \\ \left\langle \frac{1}{\bar{\mathbf{1}} - \delta \bar{\epsilon} \bar{\Gamma}} \right\rangle &= \lim_{V \rightarrow \infty} \frac{1}{V} \sum_i \frac{v_i \delta \bar{\epsilon}_i}{\bar{\mathbf{1}} - \delta \bar{\epsilon} \bar{\Gamma}} = \sum_i \frac{f_i \delta \bar{\epsilon}_i}{\bar{\mathbf{1}} - \delta \bar{\epsilon} \bar{\Gamma}} \end{aligned} \quad (2.46)$$

where the summation is over the number of constituents in the medium, f_i is a constituent partial volume fraction with $\sum_i f_i = 1$.

Although Stroud originally derived the effective conductivity, we have recast it to derive a similar expression for the effective permittivity. Before we derive the MG and Bruggeman theories we would like to comment on several assumptions that were made:

- *The field is uniform in the crystal.* This was made more for mathematical convenience and allowed us to derive an expression for the effective permittivity explicitly.
- *The field outside the crystal is $\langle \bar{S} \rangle$.* As was mentioned before, this is equivalent to the assumption in the MG derivation of lumping the effects of distant scatterers in a continuum.
- *V is large so that the Green's function becomes the free space Green's function.* We could have made this assumption at the beginning.
- *An ensemble average is equivalent to a volume average.* This was discussed in 1.2.1.

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- *There is an applied electrostatic field.* The time-independent theories are easier to work with. We will remove the time-independence in a later discussion and derive equivalent results assuming the incident electric field is time-harmonic. The effective permittivity derived here is the static dielectric permittivity.
- *Each cell has a dielectric function.* This implies that we are not working with molecular entities. Instead, this derivation is strictly macroscopic.
- *There is no boundary scattering.* Stroud mentions the neglect of boundary scattering in the original derivation. This refers to defects such as dislocations and to current carriers. Although these are important in solid state physics where they can cause significant changes in conductivity they are not relevant to the permittivity discussion where the effects we are interested in are due to bound charges. While no real material can be lossless at all frequencies, we assume that in the zero frequency limit, the number of current carriers is very small and their effect on the dielectric permittivity through scattering is negligible.

Using (2.45), we wish to derive the Bruggeman and MG relationships. If we make the following assumptions

- there are two constituents labelled A and B with volume fractions of f and $1 - f$ respectively,
- the cells are isotropic such that $\bar{\epsilon}_A = \bar{1}\epsilon_A$ and that $\bar{\epsilon}_B = \bar{1}\epsilon_B$,
- every cell is spherical
- the self-consistent condition holds,

we obtain the Bruggeman expression. For electrostatic problems we must use the electrostatic Green's function for our effective medium

$$G(\mathbf{r} - \mathbf{r}') = \frac{1}{4\pi\epsilon_e} \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

which satisfies (2.31) with free space Green's function boundary conditions and $\epsilon_g = \epsilon_e$. Using

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this Green's function in (2.42) for a spherical volume yields,

$$\bar{\Gamma} = \int_{S'} d^2r' \nabla G(\mathbf{r} - \mathbf{r}') = \int_V d^3r' \Delta G(\mathbf{r} - \mathbf{r}') = -\frac{\bar{\mathbf{1}}}{3\epsilon_e} \quad (2.47)$$

Using the last assumption, $\langle \bar{S} \rangle = 0$, (2.45) and (2.46) we can obtain

$$\begin{aligned} \langle \bar{S} \rangle &= 0 \\ &= \frac{\left\langle \frac{\delta \bar{\epsilon}}{\bar{\mathbf{1}} - \delta \bar{\epsilon} \bar{\Gamma}} \right\rangle}{\langle \bar{\mathbf{1}} - \delta \bar{\epsilon} \bar{\Gamma} \rangle} \\ &= \frac{f(\epsilon_A - \epsilon_e)}{1 - (\epsilon_A - \epsilon_e)\Gamma_A} + \frac{(1-f)(\epsilon_B - \epsilon_e)}{1 - (\epsilon_B - \epsilon_e)\Gamma_B} \\ &= f \frac{\epsilon_A - \epsilon_e}{\epsilon_A + 2\epsilon_e} + (1-f) \frac{\epsilon_B - \epsilon_e}{\epsilon_B + 2\epsilon_e}, \end{aligned} \quad (2.48)$$

or

$$f \frac{\epsilon_A - \epsilon_e}{\epsilon_A + 2\epsilon_e} + (1-f) \frac{\epsilon_B - \epsilon_e}{\epsilon_B + 2\epsilon_e} = 0, \quad (2.49)$$

This is Bruggeman's relationship and it can be rewritten into the Polder-van Santen form as

$$\frac{\epsilon_e - 1}{3\epsilon_e} = f \frac{\epsilon_A - 1}{\epsilon_A + 2\epsilon_e} + (1-f) \frac{\epsilon_B - 1}{\epsilon_B + 2\epsilon_e}. \quad (2.50)$$

Bruggeman's theory is used more in solid state physics and studies of conductivity. It is a symmetrical theory, replacing dielectric A by dielectric B and B by A will produce the same relationship. Also, note we specifically assumed that all the cells (of both dielectrics) were spheres. This is obviously wrong because space cannot be completely filled by spheres. Bohren [4] has pointed out that scattering of non-spherical particles is not equivalent to scattering by

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equal-volume spheres so we expect that the above result to be an approximation to a medium completely filled by only two types of material. Bohren has mentioned that scattering by non-spherical particles should naturally be shape dependent, a result we see above quite clearly in (2.49) due to the presence of $\bar{\Gamma}$.

If we make the same assumptions as we did for deriving the Bruggeman relationship but do not use the self-consistent expression and select dielectric B as the reference material, $\epsilon_o = \epsilon_B$, $\Gamma_i = -1/3\epsilon_B$ and we have from (2.45)

$$\begin{aligned}
 \epsilon_e(\mathbf{r}) &= \epsilon_B + \langle S(\mathbf{r}) \rangle \\
 &= \epsilon_B + \frac{\left\langle \frac{\delta \bar{\epsilon}}{\bar{\mathbf{I}} - \delta \bar{\epsilon} \bar{\Gamma}} \right\rangle}{\left\langle \bar{\mathbf{I}} - \delta \bar{\epsilon} \bar{\Gamma} \right\rangle} \\
 &= \epsilon_B + \frac{\frac{f(\epsilon_A - \epsilon_B)}{1 - (\epsilon_A - \epsilon_B) \frac{-1}{3\epsilon_B}} + \frac{(1-f)(\epsilon_B - \epsilon_B)}{1 - (\epsilon_B - \epsilon_B) \frac{-1}{3\epsilon_B}}}{\frac{f}{1 - (\epsilon_A - \epsilon_B) \frac{-1}{3\epsilon_B}} + \frac{1-f}{1 - (\epsilon_B - \epsilon_B) \frac{-1}{3\epsilon_B}}} \\
 &= \epsilon_B + \frac{3f \left(\frac{\epsilon_A - \epsilon_B}{\epsilon_A + 2\epsilon_B} \right)}{1 - f \frac{\epsilon_A - \epsilon_B}{\epsilon_A + 2\epsilon_B}}.
 \end{aligned} \tag{2.51}$$

This is the Maxwell-Garnett solution. Sometimes the ϵ_B is pulled into the second term on the right hand side producing,

$$\epsilon_e = \frac{\epsilon_B + 2f \left(\frac{\epsilon_A - \epsilon_B}{\epsilon_A + 2\epsilon_B} \right)}{1 - f \frac{\epsilon_A - \epsilon_B}{\epsilon_A + 2\epsilon_B}}. \tag{2.52}$$

If the background medium is free space, $\epsilon_B = 1$ and we have

$$\epsilon_e = \frac{1 + 2f \left(\frac{\epsilon_A - 1}{\epsilon_A + 2} \right)}{1 - f \frac{\epsilon_A - 1}{\epsilon_A + 2}}. \tag{2.53}$$

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The MG relationship is not symmetric upon interchanging the background and scatterer dielectric functions. We will comment on this feature in the next chapter.

2.4.2 Transition operator derivation

The transition operator approach provides an elegant way to obtain the same results as in the previous section. In addition to the transition operator approach, we will use the operator formalism. We will again assume electrostatic fields and a grain material as in Stroud's derivation. Our dielectric tensor may be written

$$\bar{\epsilon}(\mathbf{r}) = \bar{\epsilon}_g + \delta\bar{\epsilon} \quad (2.54)$$

where $\bar{\epsilon}_g$ is an arbitrary tensorial constant that we conveniently set later. We wish to find the effective dielectric constant $\bar{\epsilon}_e$ in the expression

$$\langle \mathbf{D} \rangle = \bar{\epsilon}_e \langle \mathbf{E} \rangle \quad (2.55)$$

and the brackets denote ensemble averages. From the electrostatic equation

$$\nabla \cdot \mathbf{D} = 0 \quad (2.56)$$

and assuming that the Green's function $G(\mathbf{r}, \mathbf{r}')$ satisfies

$$\nabla \cdot (\bar{\epsilon}(\mathbf{r}) G(\mathbf{r}, \mathbf{r}')) = \delta(\mathbf{r} - \mathbf{r}') \quad (2.57)$$

we can write an integral equation like (2.33) for the electric field

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_o + \int_{V'} d^3r' \bar{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \mathbf{E}(\mathbf{r}') \delta\bar{\epsilon}. \quad (2.58)$$

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Here, $\bar{G}(\mathbf{r}, \mathbf{r}')$ is a Green's function tensor defined as

$$\bar{G}(\mathbf{r}, \mathbf{r}') = \nabla \nabla G(\mathbf{r}, \mathbf{r}'). \quad (2.59)$$

If we now use operator notation where the \bar{G} symbol implies volume integration we can write the above integral as

$$\mathbf{E} = \mathbf{E}_o + \bar{G} \delta\bar{\epsilon} \mathbf{E} \quad (2.60)$$

which can be iterated into an infinite series

$$\mathbf{E} = \mathbf{E}_o + \bar{G} \delta\bar{\epsilon} \mathbf{E}_o + \bar{G} \delta\bar{\epsilon} \bar{G} \delta\bar{\epsilon} \mathbf{E}_o + \bar{G} \delta\bar{\epsilon} \bar{G} \delta\bar{\epsilon} \bar{G} \delta\bar{\epsilon} \mathbf{E}_o + \dots \quad (2.61)$$

If we define the transition matrix (T-matrix) as

$$\bar{T} = \delta\bar{\epsilon} + \delta\bar{\epsilon} \bar{G} \delta\bar{\epsilon} + \delta\bar{\epsilon} \bar{G} \delta\bar{\epsilon} \bar{G} \delta\bar{\epsilon} + \dots \quad (2.62)$$

we can write

$$\mathbf{E} = \mathbf{E}_o + \bar{G} \bar{T} \mathbf{E}_o. \quad (2.63)$$

where \bar{T} now contains the perturbation series and no further iterative substitution is required.

From (2.62) we see that T is

$$\bar{T} = \frac{\delta\bar{\epsilon}}{\mathbf{1} - \bar{G} \delta\bar{\epsilon}}. \quad (2.64)$$

We wish to express the system's T-matrix in terms of the t-matrix for an individual cell α .

$$\bar{\xi}_\alpha(\mathbf{r}) = \begin{cases} \delta\bar{\epsilon}(\mathbf{r}) & \text{if } \mathbf{r} \in v_\alpha \\ 0 & \text{if } \mathbf{r} \notin v_\alpha. \end{cases} \quad (2.65)$$

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so that we can rewrite (2.64) as

$$\bar{t}_\alpha = \frac{\bar{\xi}_\alpha}{\mathbf{I} - \bar{G} \bar{\xi}_\alpha}. \quad (2.66)$$

This converts the continuum transition operator into a discrete transition operator where a single \bar{t}_α signifies the mapping of the field that would exist at \mathbf{r} if the particle was not present compared to the field that does exist because the particle is present where the single particle is embedded in an infinite medium. It represents the perturbation of the incident field due to the scatterer. This is slightly different in concept from the travelling wave transition operator where the transition operator maps the incoming travelling wave into the outgoing travelling wave. Since a dielectric sphere will become polarized in an uniform electric field, \bar{t}_α is obviously connected with this polarization. This implies that the perturbation of the applied uniform represented by \bar{t}_α electric field is caused by polarization, an effect we expected.

It is convenient to rewrite the infinite series in (2.66) using \bar{t}_α as

$$\bar{T} = \sum_\alpha \bar{t}_\alpha + \sum_\alpha \sum_{\beta \neq \alpha} \bar{t}_\alpha \bar{G} \bar{t}_\beta + \sum_\alpha \sum_{\beta \neq \alpha} \sum_{\gamma \neq \beta} \bar{t}_\alpha \bar{G} \bar{t}_\beta \bar{G} \bar{t}_\gamma + \dots \quad (2.67)$$

where the first term on the right hand side represents contributions to the perturbed electrostatic field from the effects of one particle at a time, the second term represents the contributions to the perturbed electrostatic field from the effects of two particles at a time, etc. Gubernatis [30] points out correctly that truncation after the first term in (2.67) produces a perturbation of infinite order in $\delta\bar{\epsilon}_i\alpha$ instead of a perturbation series of first order in $\delta\bar{\epsilon}_i\alpha$ if (2.62) was used.

By comparing (2.63) and (2.60) we see that analogous to (2.34),

$$\delta\bar{\epsilon} E = \bar{T} E_o. \quad (2.68)$$

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We can immediately interpret the transition operator as a pseudo-source just as we did with $\bar{S}(\mathbf{r})$ (2.34). Also, the perturbation expression for \bar{T} in (2.67) is of infinite order in $\delta\bar{\epsilon}$ which is the same as that for (2.58) upon iteration.

We now ensemble average (2.63) to produce

$$\langle \mathbf{E} \rangle = \mathbf{E}_o + \langle \bar{\mathbf{G}} \bar{\mathbf{T}} \rangle \mathbf{E}_o. \quad \longleftrightarrow \quad \mathbf{E}_o = \frac{\langle \mathbf{E} \rangle}{\bar{\mathbf{1}} + \langle \bar{\mathbf{G}} \bar{\mathbf{T}} \rangle}. \quad (2.69)$$

Using (2.54), we may write

$$\mathbf{D} = \bar{\epsilon}_g \mathbf{E} + \delta\bar{\epsilon} \mathbf{E} \quad (2.70)$$

which when used with (2.68) and averaged produces

$$\langle \mathbf{D} \rangle = \bar{\epsilon}_g \langle \mathbf{E} \rangle + \langle \bar{\mathbf{T}} \rangle \mathbf{E}_o. \quad (2.71)$$

With the definition of \mathbf{E}_o from (2.69), we can write (2.71) as

$$\bar{\epsilon}_e = \bar{\epsilon}_g + \frac{\langle \bar{\mathbf{T}} \rangle}{\bar{\mathbf{1}} + \langle \bar{\mathbf{G}} \bar{\mathbf{T}} \rangle} \quad (2.72)$$

which is our expression for the effective permittivity using the transition operator formalism.

If we truncate our expression for the T-matrix after the first term in (2.67),

$$\bar{\mathbf{T}} \approx \sum_{\alpha} \bar{\mathbf{t}}_{\alpha} \quad (2.73)$$

we obtain the equivalent of (2.45). The terms $\bar{\mathbf{T}}$ and $\bar{\mathbf{S}}$ are not equivalent because they are associated with different integral equations, $\bar{\mathbf{T}}$ with (2.63) and $\bar{\mathbf{S}}$ with (2.35). The main difference between these integral equations is that the perturbation of the latter is obtained by iteration while in the former, the perturbation is contained directly in $\bar{\mathbf{T}}$.

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We wish to verify explicitly that the definitions (2.45) and (2.72) of the effective dielectric permittivity are equal,

$$\frac{\langle \sum_{\alpha} \bar{t}_{\alpha} \rangle}{1 + \langle \bar{G} \sum_{\alpha} \bar{t}_{\alpha} \rangle} \equiv \frac{\sum_i \frac{f_i \delta \bar{\epsilon}_i}{\bar{\mathbf{I}} - \delta \bar{\epsilon}_i \bar{\Gamma}_i}}{\sum_i \frac{f_i}{\bar{\mathbf{I}} - \delta \bar{\epsilon}_i \bar{\Gamma}_i}}. \quad (2.74)$$

First, we write $\bar{\Gamma}_i$ as the operator \bar{G} . Since $\bar{t}_{\alpha} = \bar{\xi}_{\alpha} / (\bar{\mathbf{I}} - \bar{G} \bar{\xi}_{\alpha})$ and ensemble averages are equivalent to volume averages, the numerators in (2.74) are equivalent. Also,

$$\begin{aligned} \bar{t}_{\alpha} &= \frac{\bar{\xi}_{\alpha}}{(\bar{\mathbf{I}} - \bar{G} \bar{\xi}_{\alpha})} = \delta \bar{\epsilon} + \delta \bar{\epsilon} \bar{G} \delta \bar{\epsilon} + \delta \bar{\epsilon} \bar{G} \delta \bar{\epsilon} \bar{G} \delta \bar{\epsilon} + \dots \\ \frac{1}{\bar{\mathbf{I}} - \delta \bar{\epsilon}_i \bar{\Gamma}_i} &= 1 + \bar{G} \delta \bar{\epsilon} + \bar{G} \delta \bar{\epsilon} \bar{G} + \bar{G} \delta \bar{\epsilon} \bar{G} \delta \bar{\epsilon} \bar{G} + \dots, \end{aligned} \quad (2.75)$$

where in both cases we assume that $\mathbf{r} \in v_{\alpha}$. If we consider cells 1, 2, 3, ..., the denominators of (2.74) can be written

$$\begin{aligned} 1 + \langle \bar{G} \sum_{\alpha} \bar{t}_{\alpha} \rangle &= 1 + \bar{G} (\delta \bar{\epsilon}_1 + \delta \bar{\epsilon}_1 \bar{G} \delta \bar{\epsilon}_1 + \delta \bar{\epsilon}_1 \bar{G} \delta \bar{\epsilon}_1 \bar{G} \delta \bar{\epsilon}_1 + \dots) \\ &\quad + \bar{G} (\delta \bar{\epsilon}_2 + \delta \bar{\epsilon}_2 \bar{G} \delta \bar{\epsilon}_2 + \delta \bar{\epsilon}_2 \bar{G} \delta \bar{\epsilon}_2 \bar{G} \delta \bar{\epsilon}_2 + \dots) \\ &\quad + \dots \\ \frac{1}{\bar{\mathbf{I}} - \delta \bar{\epsilon}_i \bar{\Gamma}_i} &= f_1 (1 + \bar{G} \delta \bar{\epsilon}_1 + \bar{G} \delta \bar{\epsilon}_1 \bar{G} + \bar{G} \delta \bar{\epsilon}_1 \bar{G} \delta \bar{\epsilon}_1 \bar{G} + \dots) \\ &\quad + f_2 (1 + \bar{G} \delta \bar{\epsilon}_2 + \bar{G} \delta \bar{\epsilon}_2 \bar{G} + \bar{G} \delta \bar{\epsilon}_2 \bar{G} \delta \bar{\epsilon}_2 \bar{G} + \dots). \end{aligned} \quad (2.76)$$

Since $\sum_i f_i = 1$, the two are equivalent and we obtain identical results for the Bruggeman and MG relationships as we did in the previous section.

For the transition operator derivation, the self-consistent condition is

$$\langle \bar{T} \rangle = 0, \quad \bar{T} \approx \sum_{\alpha} \bar{t}_{\alpha}. \quad (2.77)$$

Since \bar{t}_{α} is the transition operator for a single grain embedded in the medium $\bar{\epsilon}_g$, (2.77) is a sum of the average contributions of each grain. This motivates the name ‘‘single site’’ approximation.

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In contrast to the integral equation derivation, the transition operator approach clearly shows that interactions between grains are neglected in both cases, although in the self-consistent approach with $\langle \bar{T} \rangle = 0$, interactions between grains is incorporated in an average way. Specifically, correlations between scatterers is zero.

The nonself-consistent approximation is also known as the average T-matrix approximation (ATA). An implication of the truncated T-matrix (2.73) is the imbedding of the grain in a uniformly polarized medium. Since the truncated T-matrix only accounts for single grains embedded in an infinite medium, it appears that the MG or Bruggeman relationships are based on a superpositioning of scatterers that do not feel the effect of other scatterers. However, the factor $(\bar{\mathbf{I}} - \langle \bar{\mathbf{G}}\bar{\mathbf{T}} \rangle)^{-1}$ can be viewed as a correction factor to $\langle \bar{\mathbf{T}} \rangle$. This implies that the grains are embedded in a uniformly polarized medium rather than ϵ_g . We commented on this feature in Section 2.3.2.

2.5 Comments on MG and Bruggeman relationships

We saw in the last section that the self-consistent expression gives the effective permittivity of an inhomogeneous medium and that the grains are considered to be imbedded in a uniformly polarized medium with permittivity ϵ_m . This is shown in (2.20). Obviously, there is some non-self-consistency in this statement. To be “fully self-consistent” (in the sense of [25]) we must use

$$E_{\text{loc}} = E + \frac{\bar{\mathbf{L}}P}{\epsilon_f}. \quad (2.78)$$

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If we perform the same analysis and assume isotropic spherical scatterers, this leads to

$$\epsilon_f = \epsilon_m + \frac{3f(\epsilon_\alpha - \epsilon_m)\epsilon_f}{3\epsilon_f + (\epsilon_\alpha - \epsilon_m)(1 - f)} \quad (2.79)$$

which is clearly a transcendental equation. Equation (2.79) is also known as the “coherent potential” or “quasicrystalline approximation with coherent potential”(QCA-CP) MG relationship. The fully self-consistent approximation does not remove the low concentration restriction imposed because the local field was assumed to act everywhere on particle α . This will be discussed in the next chapter.

There are other models of the dielectric permittivity that are in use, some roughly based on the results presented above, others purely empirical. Sihvola [45] [44] has discussed many of these and showed except for the empirical relationships, they mostly follow from an assumption similar to that used immediately above, namely, the continuum external to the Lorentz cavity has an apparent permittivity of $\epsilon_a(\epsilon_m, \epsilon_\alpha, \epsilon_f)$ rather than ϵ_f or ϵ_m . With this assumption, (2.20) can then be written

$$E_{\text{loc}} = E + \frac{\bar{L}P}{\epsilon_a}. \quad (2.80)$$

We should also observe that both the Bruggeman and MG relationships express a very intuitive concept. Both of theories are similar to perturbation expressions in the dielectric permittivity fluctuation. The expression for the MG relationship for isotropic spheres of dielectric ϵ_α with background ϵ_m is

$$\epsilon_e = \epsilon_m + \frac{3f\left(\frac{\epsilon_\alpha - \epsilon_m}{\epsilon_\alpha + 2\epsilon_m}\right)}{1 - f\frac{\epsilon_\alpha - \epsilon_m}{\epsilon_\alpha + 2\epsilon_m}}. \quad (2.81)$$

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Obviously, ϵ_m is the effective permittivity if there no fluctuations in the medium. Notice that $\epsilon_e \approx \epsilon_m$ if either the volume fraction is small $f \ll 1$ or the fluctuations are small $|(\epsilon_\alpha - \epsilon_m)/\epsilon_m| \ll 1$. However, $f \ll 1$ is the defining relationship because if the fluctuations are strong, the single-scatter approximation implies that they must be separated by a larger distance, decreasing the volume fraction. The volume fraction is decreased because n_o is decreased. Although n_o is the ratio of the number of particles to the total volume of the medium, assumed to be infinite, we mentioned above that it can be seen as a representation of an ensemble average. Since the elements of the ensemble are finite volumes with scatterers, and the separation between scatterers is increased, the number of scatterers in a member's volume is decreased. This implies that the ensemble value n_o decreases and it follows that there is a similar decrease in $f = n_o v_\alpha$.

A real perturbation expansion in terms of the fluctuations $\delta\epsilon = \epsilon_\alpha - \epsilon_m$ is

$$\begin{aligned}\epsilon_f(\text{Maxwell-Garnett}) &= \epsilon_m + f\delta\epsilon - \frac{f(1-f)\delta\epsilon^2}{3\epsilon_m} + \frac{f(1-f)^2\delta\epsilon^3}{9\epsilon_m^2} + \dots, \\ \epsilon_f(\text{Bruggeman}) &= \epsilon_m + f\delta\epsilon - \frac{f(1-f)\delta\epsilon^2}{3\epsilon_m} + \frac{f(1-f)^2\delta\epsilon^3}{9\epsilon_m^2} + \dots,\end{aligned}\quad (2.82)$$

after Bohren [3] and Kohler [25] (who did the perturbation in terms of f). This shows that up to $O(f^2)$ the two are equivalent. It is obvious that a similar expansion on (2.79) produces a solution dissimilar to the above implying they are not closely related. The perturbation series highlights another aspect of these equations, in the limit $|(\epsilon_\alpha - \epsilon_m)/\epsilon_m| \ll 1$,

$$\epsilon_f \approx \epsilon_m + f\delta\epsilon = \epsilon_m + f(\epsilon_\alpha - \epsilon_m) = f\epsilon_\alpha + (1-f)\epsilon_m,$$

showing that the effective permittivity is just the average of the two permittivities.

Chapter 3

COMPLEX EFFECTIVE MEDIUM THEORIES

The more complex effective medium theories are those that involve time-dependent fields, the subject of this chapter.

3.1 Adoption of electrostatic results

The identification of similar potential expressions between a dielectric sphere and an ideal dipole motivate the substitution of the dipole for the sphere in the electrostatic limit. The extension to time-dependent theories and low frequencies is also made and for particle volumes small compared to the incident wavelength, Rayleigh scattering is shown to be equivalent to scattering from a dipole. In the same spirit, we may use the results derived for electrostatic fields in Chapter 2 as low-frequency solutions for time-dependent fields. The only requirement that must be enforced is that

$$\delta < \frac{2\pi}{\lambda} \tag{3.1}$$

where δ is a characteristic chord length of the scattering particles. This simply makes the phase change in the numerator of the Green's function, $e^{i\mathbf{k}\cdot\mathbf{r}}/4\pi\epsilon_0 r$ negligible and produces low-frequency results. The quasi-static limit may be written $k_0^3 V_\alpha \ll 1$.

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The transition to time-dependent fields and the adoption of the results from the electrostatic derivations, motivates an additional comment about the chord length condition and losses. We mentioned in Chapter 2 that the MG relationships could model absorption losses by atomic processes. These processes would appear in the ϵ_α . The chord length condition shows that the MG relationship should not be applied to particles whose radii are on the same order of magnitude as the incident travelling wave since this would violate the quasi-static approximation used to adopt the electrostatic results. Since this chord length to wavelength size relationship should not be used, shape dependent absorption present when the ratio is approximately unity can not be modeled. The absence of this loss mechanism from the model cannot be overlooked and could be a source of significant deviations from theoretical calculations and experimental data; it was probably the source of the errors found in [34].

The MG relationship includes loss by atomic processes such as electronic resonance (an absorption process). This type of loss appears as an imaginary ϵ_α . However, the MG relationship does not include scattering losses. Since extinction is equal to scattering plus absorption [60], we really need to include scattering losses in the MG relationship [26]. We may do this by considering scattering caused by dipoles (Rayleigh scattering). We will assume that ϵ_α is real and hence scattering dominates over absorption. Bohren [4] has pointed out that if absorption is present in Rayleigh scatterers it usually dominates over scattering losses.

Without absorption loss, the scattering loss is measured by the ratio of scattered power to input power. The input wave is traversing a medium of ϵ_f . As we assumed in the derivation MG, there is no correlation between scatterers (independent scattering). The effective wavenumber

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$K = K_R + iK_I$ becomes $K^2 \approx K_R^2 + i2K_RK_I$ when $K_I \ll K_R$ and $K_R = k\sqrt{\epsilon_f}$. Since $\epsilon_f - 1 = \gamma$, dipole α has a dipole moment of

$$\mathbf{p}_\alpha = \hat{\mathbf{k}}_i \frac{3v_\alpha (\epsilon_\alpha - 1) / (\epsilon_\alpha + 2)}{1 - f (\epsilon_\alpha - 1) / (\epsilon_\alpha + 2)} \mathbf{E}_o e^{i\mathbf{K}_R \cdot \mathbf{r}_\alpha}.$$

Substitution into the expression for the scattered field of dipole α ,

$$\mathbf{E}_{s\alpha} = \frac{w^2 \mu_o e^{ikR_\alpha}}{4\pi R_\alpha} \hat{\mathbf{k}}_s \times \hat{\mathbf{k}} \times \hat{\mathbf{k}} \mathbf{p}_\alpha$$

and summed over all of the dipoles and combined with the incident \mathbf{E} , yields K_R ,

$$K_I = \frac{P_s}{P_i} = f \frac{k^5 a^3}{K_R} \left| \frac{(\epsilon_\alpha - 1) / (\epsilon_\alpha + 2)}{1 - f (\epsilon_\alpha - 1) / (\epsilon_\alpha + 2)} \right|^2.$$

A cylinder with unit length was used as the integration volume when considering the power input and output giving K_I the correct dimensions. The above expression introduces an imaginary correction term into ϵ_f . The MG relationship, modified to account for Rayleigh scattering losses, can be written

$$\epsilon_f = \frac{1 + 2fy}{1 - fy} + 2ifk^3 a^3 y^2 \quad (3.2)$$

where $y = (\epsilon_\alpha - 1) / (\epsilon_\alpha + 2)$.

3.2 Foldy-Twersky integral equation, the effective field approximation and MG

The Foldy-Twersky integral equation (FTIE) (also known as the effective field approximation EFA) has been thoroughly reviewed and investigated by many authors [8] [7] [56] [26] [53] [55] [54] [21] [14] [58] [59] [57] [31] [32].

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The FTIE considering scalar wave propagation is

$$\langle \psi(\mathbf{r}_e) \rangle = \phi_i(\mathbf{r}_e) + n_o \int_V d^3\mathbf{r}_o v_o^e \langle \psi(\mathbf{r}_o) \rangle \quad (3.3)$$

where $v_o^e \langle \psi(\mathbf{r}_o) \rangle$ represents the field at \mathbf{r}_e due to the scatterer at \mathbf{r}_o with the total average field $\langle \psi(\mathbf{r}_o) \rangle$ incident upon it. ϕ_i is the free-space field. The FTIE accounts for multiple-scattering in a limited way, ignoring both repeated scattering within a particle and repeated scattering from different particles. There are three assumptions inherent made in (3.3): the fractional volume of scatterers is small, correlations between particles is negligible, the average field is a scalar. These assumptions have much in common with those used to derive the MG relationship with Rayleigh scattering correction.

For the FTIE approximation, the effective permittivity is

$$\epsilon_f = 1 + 3fy + 2ifk^3 a^3 y^2. \quad (3.4)$$

Compared to (3.2), we see that there are slight discrepancies. Brown [7] has noted that when the domain becomes infinite the FTIE is equivalent to the the single scatter approximation with no internal particle scattering. Since we may write

$$\frac{3fy}{1 - fy} = 3fy + 3(fy)^2 + 3(fy)^3 + \dots,$$

where y is a constant, we see that to $O(f^2)$ the two agree. f is usually small so this error is negligible. The imaginary component of the dielectric permittivity contains terms of $O(f^3)$ which if expanded in a power series shows that only a small amount of loss is allowed. At the present time, there is no clear physical explanation of the $O(f^2)$ terms. The above is consistent with our comments on the limits of the MG with Rayleigh scattering loss relationship. The error

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bound is similar to that between the MG and Bruggeman relationships as we noted at the end of Chapter 2. It is evident that the comments made about the MG relationship apply equally well to the FTIE and that the FTIE has the Rayleigh scattering attenuation built into the formulation whereas we added it explicitly in (3.2). The same conclusions about the Bruggeman theory can be made because the Bruggeman is equivalent to MG to $O(f^2)$. These appear to be new conclusions about the obvious relationship between MG and FTIE.

The MG relationship also shows why the average internal and external field have the same form, they are linearly related through the relationship

$$E_{\text{int}} = \frac{3}{\epsilon_{\alpha} - 1} E_{\text{ext}}.$$

The transition operator approach to MG also shows why the FTIE scattering amplitude is similar to the free space scattering amplitude in an infinite medium. The FTIE dispersion relation is

$$(k')^2 = k^2 + 4\pi n_o f \longrightarrow k' \approx k + 2\pi f/k_o$$

We saw in Section 2.4.2 that the transition operator is truncated leaving only single-particle terms. Each single transition operator is proportional to a scattering amplitude. By truncating the transition operator and leaving only single-particle scattering orders, we are setting the real scattering amplitude to the scattering amplitude of the particle in free space.

Chapter 4

CONCLUSIONS

We can make the following general conclusions about effective medium theories:

- The homogenization of random media using effective medium theories can be viewed merely as a process of obtaining the coherent field $\langle E \rangle$ or $\langle G \rangle$.
- The analytic difficulty in wave propagation in a random media is from simultaneously combining the motion of Green's functions and the structure of the medium in one equation. We discussed two ways of solving these problems: using a decoupling assumption (closure hypothesis) or a perturbational approach.
- Effective medium theories provide an intuitive, physical viewpoint about the approximations being made. They can be used in a simple way to understand more complex theories.
- Nearly all derivations of effective medium theories assume that an effective permittivity exists at the outset of the problem. Solutions are then obtained in a manner that is consistent with this assumption. Effective medium theories usually can be recognized by the presence of three parameters: the local field, the particle density, and the polarizability.

CHAPTER 4. CONCLUSIONS

- All theories ignore internal particle scattering and hence, they cannot describe phase changes across the particle. This limits the applicability of effective medium theories to low frequencies.

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Appendix A

ENSEMBLE AVERAGING AND GREEN'S FUNCTIONS

There is often confusion about both ensemble averaging and calculating the ensemble average. We are not going to address the problem fully here but we will comment on why the Green's function in (2.39) is not included in the average that was performed. Our brief comments are based on [43, pages 148-152] and [49, page 125].

As we mentioned in the text (page 51), the specific and simple reason that $G(\mathbf{r}, \mathbf{r}')$ is not included in the average is that it is not a random variable. In the random media under consideration, the random variable is the dielectric permittivity. This randomness is caused by the spatial distribution of the permittivity fluctuations. The Green's function in (2.39) is a deterministic function.

A source of possible confusion is the averaging performed in (2.4) and the averaging performed on the stochastic (or random) Green's function used when one desires to calculate the average field in a random media due to a point source with both the source and observation point in the scattering volume. This latter type of problem is governed by the equation (in the scalar formulation)

$$\Delta G(\mathbf{r}, \mathbf{r}_o) + k_o^2[1 + \mu(\mathbf{r})]G(\mathbf{r}, \mathbf{r}_o) = \delta(\mathbf{r} - \mathbf{r}_o) \quad (\text{A.1})$$

APPENDIX A. ENSEMBLE AVERAGING AND GREEN'S FUNCTIONS

subject to a outgoing radiation condition at $|\mathbf{r} - \mathbf{r}_o| \rightarrow \infty$ and $\mu(\mathbf{r})$ is the fluctuation about a constant background dielectric permittivity (or the square of the refractive index) folded into k_o^2 and whose variance is $\ll 1$. Here, $G(\mathbf{r}, \mathbf{r}_o)$ is a random Green's function but we could just have easily let the symbol for the scalar field be $\psi(\mathbf{r}, \mathbf{r}_o)$. The $G(\mathbf{r}, \mathbf{r}_o)$ is retained because the Green's function is *defined* as the response to an impulse source and the G symbol is traditional.

The typical procedure after developing (A.1) is to write the solution in terms of an integral equation

$$G(\mathbf{r}, \mathbf{r}_o) = G_o(\mathbf{r}, \mathbf{r}_o) - k^2 \int d^3\mathbf{r}' G_o(\mathbf{r}, \mathbf{r}') \mu(\mathbf{r}') G(\mathbf{r}', \mathbf{r}_o) \quad (\text{A.2})$$

and to iterate it by successive substitutions producing a Born series

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}_o) &= G_o(\mathbf{r}, \mathbf{r}_o) - k^2 \int d^3\mathbf{r}_1 G_o(\mathbf{r}, \mathbf{r}_1) \mu(\mathbf{r}_1) G_o(\mathbf{r}_1, \mathbf{r}_o) \\ &+ k^4 \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 G_o(\mathbf{r}, \mathbf{r}_1) \mu(\mathbf{r}_1) G_o(\mathbf{r}_1, \mathbf{r}_2) \mu(\mathbf{r}_2) G_o(\mathbf{r}_2, \mathbf{r}_o) \\ &- k^6 \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 G_o(\mathbf{r}_o, \mathbf{r}_1) \mu(\mathbf{r}_1) G_o(\mathbf{r}, \mathbf{r}_2) \mu(\mathbf{r}_2) G_o(\mathbf{r}_2, \mathbf{r}_3) \mu(\mathbf{r}_3) G_o(\mathbf{r}_3, \mathbf{r}_o) \\ &+ \dots \end{aligned} \quad (\text{A.3})$$

where $G_o(\mathbf{r}, \mathbf{r}_o)$ is the free space Green's function. Most authors then assume a linear inhomogeneous medium where the Green's function obeys reciprocity $G(\mathbf{r}, \mathbf{r}_o) = G(\mathbf{r}_o, \mathbf{r})$ which allows for another rewriting of the iterated series that clearly shows its interpretation as scattering from the initial point $\mathbf{r}_o \rightarrow \mathbf{r}_1 \rightarrow \mathbf{r}_2 \rightarrow \mathbf{r}_3 \dots \mathbf{r}$ where \mathbf{r} is the observation point. If $\mu(\mathbf{r})$ is assumed to obey Gaussian statistics then all $2n$ point correlations can be expressed in terms of 2 point correlations and all odd correlations are zero

$$\langle \mu(\mathbf{r}_1) \dots \mu(\mathbf{r}_{2n-1}) \rangle = 0$$

APPENDIX A. ENSEMBLE AVERAGING AND GREEN'S FUNCTIONS

$$\langle \mu(\mathbf{r}_1) \cdots \mu(\mathbf{r}_{2n}) \rangle = \sum \mathcal{K}_\mu(\mathbf{r}_i, \mathbf{r}_j) \cdots \mathcal{K}_\mu(\mathbf{r}_p, \mathbf{r}_q)$$

\mathcal{K}_μ is the covariance and the summation is made over all possible pairs of the points $\mathbf{r}_1 \cdots \mathbf{r}_{2n}$.

With these assumptions, we can ensemble average (A.3) to obtain the mean Green's function (and hence the mean field in the random media)

$$\begin{aligned} \langle G(\mathbf{r}, \mathbf{r}_o) \rangle &= G_o(\mathbf{r}, \mathbf{r}_o) + k^4 \int d^3r_1 d^3r_2 G_o(\mathbf{r}_o, \mathbf{r}_1) G_o(\mathbf{r}_1, \mathbf{r}_2) G_o(\mathbf{r}_2, \mathbf{r}) \mathcal{K}_\mu(\mathbf{r}_1, \mathbf{r}_2) \\ &+ k^8 \int d^3r_1 d^3r_2 d^3r_3 d^3r_4 G_o(\mathbf{r}_o, \mathbf{r}_1) G_o(\mathbf{r}_1, \mathbf{r}_2) G_o(\mathbf{r}_2, \mathbf{r}_3) G_o(\mathbf{r}_3, \mathbf{r}) \\ &\quad \times [\mathcal{K}_\mu(\mathbf{r}_1, \mathbf{r}_2) \mathcal{K}_\mu(\mathbf{r}_3, \mathbf{r}_4) + \mathcal{K}_\mu(\mathbf{r}_1, \mathbf{r}_3) \mathcal{K}_\mu(\mathbf{r}_2, \mathbf{r}_4) + \mathcal{K}_\mu(\mathbf{r}_1, \mathbf{r}_4) \mathcal{K}_\mu(\mathbf{r}_2, \mathbf{r}_3)] \\ &+ \cdots \end{aligned} \tag{A.4}$$

Typically, the next step is to convert the iterated averaged integrals into Feynman diagrams, topologically re-sort the integrals, define a mass operator and produce Dyson's equation for the mean field due to a point source. We will not perform these steps and we point interested readers to the previously mentioned references.

VITA

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