A Scattering-Based Approach to the Design, Analysis, and Experimental Verification of Magnetic Metamaterials Made from Dielectrics

by

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Abstract

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The design, modeling, fabrication, and validation of an optical magnetic response in dielectric-based metamaterials are studied. These metamaterials consist of either periodic or random arrays of dielectric particle inclusions, which may be spheres, coated spheres, or completely randomly shaped. It is demonstrated that because of the simple particle shapes and dielectric materials, these metamaterials are quite easy and feasible to implement in a bulk, three-dimensional sample, and the response is isotropic. This is in contrast to other predominant designs of optical metamaterials, which are planar and anisotropic arrays of complicated metallic fishnet or split-ring resonator structures, which require stringent tolerances and sophisticated assembly.

It is shown that SiC is one of many materials from which such infrared magnetic metamaterials can be constructed. A simple SiC powder is used to verify these claims. The milled micropowder of crystalline SiC is comprised of particles of random shapes and sizes. A model of the electromagnetic response of such powders is developed, whereby the induced magnetic dipole response is modeled by equivalently-sized spheres of SiC, whereas the electric dipole response is modeled by a continuous distribution of ellipsoidal particles. Infrared spectroscopic measurements and numerical calculations are performed, verifying both the magnetic and electric response of the powder. An alternate approach is also described, where uniform SiC microspheres are fabricated using more sophisticated nanochemical techniques.

In the final portion of the dissertation, the mutual near-field coupling between ideal magnetic dipoles induced in dielectric spheres is studied. This is implemented for microwave frequencies using large permittivity ceramic spheres. An approximate coupled dipole model of the multiple scattering among the spheres is developed, and a transition matrix method is implemented to calculate the exact scattering
by the clusters. Experimental measurements are performed, confirming the two models. The results for pairs, chains, and rings of spheres indicates that the magnetic dipole modes hybridize in analogy to atomic bonding. A notable result is that certain hybridized magnetic dipole modes may have a net electric dipole moment. The similarity to atomic and molecular bonding should prove useful in conceptualizing and designing more sophisticated metamaterials.
For my mother, and in memory of my father
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Chapter 1

Introduction

There is tremendous variety in the electromagnetic properties of materials. Many glasses are transparent. Minerals may have many colors, and calcite is doubly-refractive. Diffusion in clouds and milk makes them opaque, but bright white. Metals are reflective, but may still have characteristic colours, such as silver, copper, and gold. Going beyond visible attributes, materials may be ferromagnetic, ferroelectric, piezoelectric, pyroelectric, or a whole host of other possibilities. All of these properties depend on atomic-scale phenomena, due to the underlying molecular, ionic, and electronic properties.

The electromagnetic properties of synthetic materials can be engineered similarly by designing phenomena which appear “atomic” or microscopic relative to the wavelengths involved. Such materials are called metamaterials. It is possible to engineer metamaterials with properties which are rare or absent in nature, for example negative permeability or negative refractive index. By widening the scope of available material properties, new applications become possible.

Metamaterials are usually comprised of inclusions embedded in a dielectric host medium. In the early years of metamaterials research the inclusions were metallic microstructures, designed to be resonant based on their geometry. Because the inclusions must be much smaller than the operating wavelength, the scale of the inclusions for optical metamaterials becomes very small indeed, around a micron or smaller. The feature sizes within the geometry of an inclusion become even smaller still. With such sizes two main difficulties arise in the fabrication of metamaterials: the inclusions become difficult to handle due to their often intricate microstructure, and their inherent anisotropy causes great difficulty in assembling bulk three-dimensional isotropic structures. In addition, the ohmic losses of the metals increase, and can become unacceptably large, driving the consideration of non-conductive substances for use as the underlying inclusions.

1.1 Objectives

The contents of this dissertation concentrate on the use of non-magnetic and mostly non-metallic materials in metamaterials. Scattering theory is used as a central theme, whereby it is shown that non-magnetic and compact sub-wavelength particles such as spheres, coated spheres, and ellipsoids can be engineered to have specific magnetic and electric polarizabilities. Using such particles, the following objectives are accomplished:
1. Metamaterials are designed using sub-wavelength dielectric inclusions, either spheres or coated spheres. The spherical inclusions have an inherently simpler geometry than any other metamaterial inclusion design. Due to the isotropy of a sphere, this allows for easy implementation of bulk three-dimensional isotropic metamaterials. Infrared metamaterials with negative permeability, negative permittivity, and negative refractive index are presented.

2. Infrared metamaterials with a magnetic response are fabricated, measured experimentally, and validated with theoretical models. Two extreme cases are developed and validated: monodisperse SiC spheres (fabricated with an elaborate nanochemical templating technique), and a polydisperse micropowder of randomly shaped SiC particles. A generalized model, which takes into account size and shape dispersions, explains the results.

3. The mutual coupling of ideal magnetic dipoles induced in closely-spaced dielectric particles is studied at microwave frequencies. Theoretical models and experimental results confirm that the clusters support structure-dependent hybridized modes. The use of such clusters as inclusions in metamaterials allows for a much wider range of possibilities are greater flexibility in the engineering of the electromagnetic properties of materials.

1.2 Organization

The organization of the remainder of the dissertation is as follows. An overview of metamaterials research is presented in Chap. 2. Some common implementations and some notable properties are described. A brief background on related aspects of plasmonics is also included.

A summary of some main results from scattering theory will be given in Chap. 3. This material is used throughout the remaining chapters. The magnetic and electric multipole polarizabilities of small particles are derived, as well as the resonant conditions. The transition matrix formalism will be used, since it is concise, flexible, and easily adapted to multiple scattering problems.

An overview of effective medium models begins Chap. 4. The Clausius-Mossotti model is used to derive the effective media properties of metamaterials with dielectric sphere inclusions. A range of materials are discussed, all of which have a large permittivity, which will be shown to be a necessary ingredient in making magnetically-responsive inclusions. Equations are derived to engineer the metamaterial properties. Example designs are given of negative permeability, negative permittivity, and negative refractive index metamaterials.

A fabrication procedure for synthesizing monodisperse SiC microspheres is presented in Chap. 5. The results, after much effort, seem quite promising, yet fall short of adequately corresponding to the effective media model. Because of this, the material presented in Chap. 6 outlines a generalization of the scattering by SiC spheres to model a polydisperse powder of randomly-shaped SiC microparticles. The general model and experimental measurements confirm an infrared magnetic response in the micropowder. In addition, the model explains the shortcomings of the monodisperse SiC sphere samples.

The mutual coupling of finite numbers of ideal magnetic dipoles at microwave frequencies is the topic
of Chap. 7. The ideal magnetic dipoles are obtained with small dielectric spheres of large permittivity. A coupled dipole model is derived which can predict the eigenmodes and eigenfrequencies of a coupled dipole system. Multiple scattering calculations provide an exact theoretical comparison. Pairs, chains, and rings of spheres are analyzed theoretically and measured experimentally, with excellent agreement. It is shown that the magnetic dipoles interact to create hybridized modes, which may be controlled to create a rich variety of metamaterial behaviours.

A summary of the results and conclusions of the dissertation is given in Chap. 8. Suggestions for future directions in research on magnetic effects in dielectric structures are also given.
Chapter 2

Metamaterial Background

The electromagnetic response of a material is characterized by its electric permittivity $\varepsilon$ and its magnetic permeability $\mu$.\(^1\) These properties relate the electric and magnetic flux vectors $\mathbf{D}$ and $\mathbf{B}$ in the material to the electric and magnetic fields $\mathbf{E}$ and $\mathbf{H}$ through the constitutive relations,

$$
\mathbf{D} = \varepsilon \mathbf{E}, \quad (2.1a)
$$

$$
\mathbf{B} = \mu \mathbf{H}. \quad (2.1b)
$$

When fields are applied to the material, the electrons comprising it respond to the stimulus. This microscopic response may in general be quite complicated, but the average response over volumes large compared to the electrons is often rather simple in comparison. The scale of atomic phenomena is on the order of $10^{-10}$ m, and the optical or longer wavelengths that are most commonly used to interact with materials are on the order of $10^{-7}$ m or larger. Thus these wavelengths are at least roughly 1000 times larger than the atomic constituents, and cannot probe the fine details of the material. Only when X-rays or shorter wavelength radiation are used can the atomic-scale phenomena be resolved by Bragg diffraction.

Artificial dielectrics [KOCK, 1948; COLLIN, 1991] were first studied to make lightweight lenses for microwave frequencies. Three-dimensional lattices of metal spheres, disks, or strips were used to synthesize the same electromagnetic properties as a large and heavy dielectric lens made of a natural material such as polystyrene. An applied electric field induces a charge imbalance on each inclusion, creating a predominantly electric dipole field response by each inclusion. For a time-dependent source, there will be an accompanying magnetic field excitation, which induces a circulating current on the surface of the metal inclusion. This current circulation is equivalent to an induced magnetic dipole moment.

Each inclusion in an artificial dielectric acts as an abstract polarizable particle, just as the electrons and atoms in a bulk solid. Each inclusion can have an electric polarizability $\alpha_e$ and magnetic polarizability $\alpha_m$. Simple yet often accurate models of the macroscopic properties of artificial dielectrics yield an effective permittivity $\varepsilon_{\text{eff}}$ and an effective permeability $\mu_{\text{eff}}$ as functions of the polarizabilities,

$$
\varepsilon_{\text{eff}} = f (\alpha_e), \quad (2.2a)
$$

$$
\mu_{\text{eff}} = g (\alpha_m), \quad (2.2b)
$$

\(^1\)This is true as long as the medium is not bianisotropic [CHEW, 1995].
where \( f(z) \) and \( g(z) \) depend on the particular homogenization model. These effective media values maintain the validity of the macroscopic constitutive relations (2.1), as long as the wavelength of an applied excitation in the host medium \( \lambda_h \) is much larger than the lattice size \( a \) and the size of the inclusions \( d \),

\[
\lambda_h \gg a > d.
\]  

This long-wavelength condition implies that the inclusions are “sub-wavelength” in size. If the inclusions are spheres of radius \( r_s \), then \( d = 2r_s \). To make this condition more concrete, a common rule of thumb is that

\[
\frac{\lambda_h}{10} \geq a > d
\]  

is sufficient. Diffraction may occur as the host wavelength is decreased and approaches the scale of the underlying structure, \( \lambda_h \approx a/2 \). When this happens the artificial medium is usually referred to as a photonic crystal [Joannopoulos et al., 2008], and simple effective medium models (2.2) usually fail, hence the long-wavelength condition (2.3) or (2.4).

Artificial dielectrics are usually engineered to have electromagnetic properties already found in natural materials. The intent is to create alternatives which are either lighter weight, cheaper, or more structurally applicable than natural materials in certain applications. In contrast, more recent research has illuminated ways to generalize the design of artificial dielectrics to create materials with electromagnetic properties which are otherwise rare or absent in natural materials. Such structures with broader properties than artificial dielectrics have been named metamaterials, where the prefix meta- comes from the Greek, meaning “beyond” or “after”.

### 2.1 Microwave Metamaterials

#### 2.1.1 Artificial Permeability

Perhaps the first metamaterials, although the name did not exist at the time, were composite structures with an artificial permeability. Such structures are made of metal inclusions in a host dielectric, where all of the constituent materials have the permeability of free space \( \mu_0 \). Yet the metal inclusions were designed to have a non-zero magnetic polarizability in the long-wavelength limit, so the composite structure has the artificial permeability \( \mu_{\text{eff}} \neq \mu_0 \). This is the case with metal spheres in a lattice; the induced circulating (eddy) currents on the spheres set up magnetic dipole moments in opposition to the applied magnetic field, following Lenz’s law. The result is that such composites are diamagnetic, \( 0 < \mu_{\text{eff}}/\mu_0 < 1 \) [Collin, 1991; Rousselle et al., 1993].

More recently, more sophisticated designs of the metallic inclusions have made it possible to tailor a wide range of values of magnetic permeability. For some applications it would be desirable to engineer values of permeability that are either unattainable with natural materials, or at frequencies not allowed by natural mechanisms. For example, materials with a high-frequency magnetic response are ferromagnetic materials, ferrites, or garnets, but metamaterials can be designed to have a stronger magnetic response than any natural material at frequencies above 100 GHz [Acher, 2009]. In addition, magnetic metamaterials
may be preferable over naturally magnetic materials due to immunity from external magnetic fields [ACHER, 2009].

There are no known materials with an isotropic negative permeability, and ferrites are a rare example of an anisotropic material that can have a negative permeability [VESELAGO, 1968]. Biasing a ferrite with a static magnetic field causes a resonance in the elements of the permeability tensor perpendicular to the bias field. Thus a propagating wave with magnetic field polarized perpendicular to the bias field can be affected by a negative permeability. This has made ferrites commonly used in devices such as isolators, phase shifters, circulators, and Faraday rotators [POZAR, 2005; SALEH AND TEICH, 1991].

By far the most common metal inclusion used to comprise magnetic metamaterials is the split-ring resonator (SRR) [PENDRY ET AL., 1999], which is illustrated in Fig. 2.1. A propagating incident magnetic field \( \mathbf{H}^{\text{inc}} \) parallel to the ring axis induces a circulating current density \( \mathbf{j} \) in the loops. The loop current is equivalent to a magnetic dipole moment \( \mathbf{m} \), as shown in Fig. 2.1. The ring therefore has a magnetic polarizability \( \alpha_m = m/\mathbf{H}^{\text{inc}} \). Since the rings are sub-wavelength in size, the magnetic polarizability contributes to \( \mu_{\text{eff}} \) through (2.2b), and the magnetic dipole resonance is in the long-wavelength regime.

If there were no gaps in the loops, the rings would have only a weak diamagnetic susceptibility already expected of artificial dielectrics [COLLIN, 1991]. But the gaps provide a resonant circuit to the induced current, consisting of the inductance of the rings and the capacitance of the gaps between the rings. These geometry-dependent characteristics can be made large enough that the magnetic moment resonates in the long-wavelength regime. Thus \( \mu_{\text{eff}} \) will also have a resonance, thereby allowing for large values of \( \text{Re} \{ \mu_{\text{eff}} \} \) at frequencies below resonance, and negative permeability at frequencies above resonance, as sketched in Fig. 2.2.

Since an SRR is only magnetically polarized when the incident magnetic field is oriented parallel to the ring axis, an implementation of an isotropic magnetic metamaterial requires a lattice of three orthogonal orientations of SRRs.
Figure 2.2: Typical real (solid) and imaginary (dashed) effective permeability of a split-ring resonator.

2.1.2 Artificial Permittivity

There is a wide range of permittivity values that may be found in natural materials. However, negative permittivity is not too common, although it is still easily found. Indeed, many metals have negative permittivity at infrared and visible frequencies, and many dielectric crystals have negative permittivity at far infrared frequencies. Nonetheless, it is desirable to be able to engineer a negative permittivity at any frequency range.

The most common design of a negative permittivity metamaterial is a mesh of very thin metal wires [Pendry et al., 1996]. There are two main consequences to using very thin wires: the electron density is decreased due to confinement in the thin wires, and the effective mass of the electrons is increased due to the self inductance of the wires. Both effects tend to decrease the plasma frequency from the ultra-violet to any specified frequency. As with the SRRs, an implementation of an isotropic negative permittivity requires a lattice of three orthogonal orientations of thin wires.

2.1.3 Negative Index of Refraction

There is no known natural substance with a negative index of refraction. The theoretical consequences of a material with simultaneously negative permittivity and permeability were first studied by Veselago [1968]. It was found that such a material must have a negative index of refraction,

\[ n = -\sqrt{\frac{\varepsilon}{\varepsilon_0 \mu_0}} \]  (2.5)
The negative square root is the valid solution when both $\varepsilon < 0$ and $\mu < 0$ [Smith and Kroll, 2000]. Generalizing this for complex effective media values,

$$n_{\text{eff}} = n'_{\text{eff}} + i n''_{\text{eff}} = \sqrt{\frac{\varepsilon_{\text{eff}} \mu_{\text{eff}}}{\varepsilon_0 \mu_0}}$$

such that $n''_{\text{eff}} \geq 0$, (2.6)

where the condition on the imaginary part is valid for passive structures.

Veselago [1968] demonstrated theoretically that a material with simultaneously negative permittivity and permeability would possess many novel and initially counter-intuitive properties. He found that in such a material, and contrary to the common situation, that the electric field, magnetic field, and wavevector form a left-handed triplet, while as usual the electric field, magnetic field, and Poynting vector form a right-handed triplet. This implies that the plane wave solutions are backward waves, such that the phase velocity $v_p$ is negative and the group velocity $v_g$ is positive [Lindell et al., 2001],

$$v_p = \frac{\omega}{k} < 0 \quad \text{and} \quad v_g = \frac{\partial \omega}{\partial k} > 0.$$ (2.7)

The Doppler shift and Cherenkov radiation are reversed in a such a medium. Most dramatically, however, is the reversal of Snell’s law. A plane wave incident at an oblique angle on a slab of $n < 0$ will be refracted to the same side of the normal. Veselago [1968] noted that this could be used to make a planar lens.

Research into negative index metamaterials was thereafter inactive for over thirty years, until the field was revived with great interest when Pendry [2000] found that such a planar lens with $n = -n_h$ (where $n_h$ is the index of the host) could perfectly re-construct the source at the image plane not only by correctly refracting the propagating components of the source, but more importantly by amplifying the evanescent components of the field within the metamaterial lens. The goal of attaining such a “perfect” lens has been a great motivation for metamaterials research.

The first negative index metamaterial was constructed for microwave frequencies by combining lattices of SRRs (negative permeability) and a thin-wire mesh (negative permittivity) [Smith et al., 2000; Shelby et al., 2001]. These inclusions have also been used for optical metamaterials, which will be discussed in the next section. Lastly, however, it is noted that there are two other major classes of metamaterials. Loaded transmission line media can be designed to have a negative index for guided waves, which has proven quite successful for making compact microwave devices [Eleftheriades et al., 2002; Eleftheriades and Balmain, 2005]. It seems, however, that such designs rely on lumped or distributed loading capacitive and inductive elements, which makes them unsuitable for optical metamaterials. An effect similar to a negative index has been found to occur in photonic crystals [Notomi, 2000; Wheeler et al., 2005a; Luo et al., 2002], where careful selection of Bragg diffraction modes can yield negative refraction as governed by Snell’s Law, without a true long-wavelength index of refraction. Since the physical mechanisms for this effect is different, these structures will not be discussed further.
Many variations on the srr and wire mesh designs have been developed for fabricating metamaterials for optical frequencies. Here “optical” is taken to mean infrared and visible frequencies. This section provides a summary of some of the many variations.

### 2.2 Optical Metamaterials

It is not difficult to engineer a negative permittivity at optical frequencies. Indeed, this can be achieved by using the plasmon-polariton resonances in metal nanoparticles, which have been used to color stained glass for centuries [Maier and Atwater, 2005]. The resonant coupling of the electromagnetic field to the free electrons (plasma) in the metal shifts the plasma frequency of the metal to shape-dependent frequencies, which are easily shifted to visible light. These resonances are electric dipole modes, so metal nanoparticles may be used as inclusions in optical artificial permittivity metamaterials.

An artificial permeability, however, is much more difficult to fabricate for optical frequencies [Shalaev,
Figure 2.4: Fishnet structure with an optical negative index. Reprinted with permission from DOLLING ET AL. [2007]. Copyright (2007) OSA.

2007]. The most straightforward path has been to fabricate srrs at increasingly small scales [YEN ET AL., 2004], as shown in Fig. 2.3(a), but the detailed geometry of the double srrs makes them difficult to fabricate smaller than on the micron scale. Simplified geometries have arisen: srrs with a single ring [LINDEN ET AL., 2004], as shown in Fig. 2.3(b); staples [ZHANG ET AL., 2005b], as shown in Fig. 2.3(c); and paired rods or strips [YUAN ET AL., 2007; SHVETS AND URZHUMOV, 2006; PODOLSKIY ET AL., 2003]. The feature size in some of these structures is smaller than 100 nm. Even though these inclusions are used for their magnetic polarizability, their miniaturization is aided by the plasmonic effects inherent in the metals of which they are composed [URZHUMOV AND SHVETS, 2008].

In the optical regime it has been found unnecessary to integrate two distinct inclusions to provide simultaneous negative permeability and permittivity to form a negative index structure. Indeed, the fishnet structure shown in Fig. 2.4 seems to be the best optical negative index metamaterial design so far [ZHANG ET AL., 2005b; DOLLING ET AL., 2007].

Despite the tremendous progress in fabricating such nanostructures for metamaterials, they all suffer from several drawbacks. Reliance on sophisticated lithographic techniques, while allowing for precise detail in two dimensions, usually results in only single layer structures. Although four and ten layer structures have been made [LIU ET AL., 2008a; VALENTINE ET AL., 2008], substantial improvement in fabrication techniques must occur before bulk, three-dimensional metamaterials can be made. The inherent anisotropy of the inclusions also limits their generality. Lastly, the losses due to the metal of the inclusions can be large at optical frequencies.

2.2.2 Metamaterials Comprised of Dielectric Resonators

One way to simplify metamaterials is to replace the complicated resonant inclusion such as the srr with a sphere of a (complex) dielectric permittivity. A dielectric sphere can support leaky (also called

\[ \mu = \mu_0 \]

\[^2\text{In this work all of the constituent materials will be assumed to be non-magnetic, } \mu = \mu_0.\]
virtual) cavity resonances [BOHREN AND HUFFMAN, 1983]. Of these, it is well known that dielectric spheres can support magnetic dipole modes [GASTINE ET AL., 1967; FUCHS AND KLIEWER, 1968; RUPPIN AND ENGLMAN, 1970]. Indeed, the scattering from a sphere is in general a superposition of an infinite number of multipole modes [BOHREN AND HUFFMAN, 1983; MISHCHENKO ET AL., 2002; VAN DE HULST, 1981]. The trick, however, is to design spheres to have a magnetic polarizability while remaining very small compared to the wavelength in the host medium, thus satisfying (2.3). This may be accomplished by choosing a sphere material with a large permittivity, whereby the fundamental resonant mode of a sphere is one with a circulating displacement current. Thus the sphere becomes magnetically polarized, as shown in Fig. 2.5.

The fundamental magnetic dipole mode of large permittivity spheres has been used to make waveguide filters [AFFOLTER AND ELIASSON, 1973] and dielectric resonator antennas [KAIFEZ AND GUILLON, 1998]. Usually in such applications the large permittivity materials are selected to make the resonators compact, and to increase the quality factor of the resonances.

Dielectric resonators can also be designed to have an electric polarizability in the long-wavelength regime. This has been known for quite some time for metal spheres; the electric dipole resonance is a consequence of the plasma dispersion [BOHREN AND HUFFMAN, 1983]. A quantum of the resulting mode of coupled light and electrons is called a plasmon-polariton.

It seems that LEWIN [1947] was the first to derive the effective media values of a composite of spheres. The results demonstrated that non-magnetic constituents could form a composite with a non-unity permeability. Similar results have been found in research on improving effective medium models of composites of metal nanoparticles [DOYLE, 1989], magnetic microstructures [GRIMES AND GRIMES, 1991], and microwave eddy currents [ROUSSELLE ET AL., 1993]. These reports predate the interest in metamaterials, so none of them considered engineering particular artificial permeabilities.

Spheres designed to have resonances in the long-wavelength limit (2.3) have resonant fields localized within and nearby the sphere. Therefore the resonances in the effective media properties $\varepsilon_{\text{eff}}$ and $\mu_{\text{eff}}$ do not depend intimately on neighboring particles, and the dispersion properties are independent on the lattice structure. Only when the wavelength is shortened out of the long-wavelength regime can the details of the lattice be probed, and diffraction will occur. This diffraction is the very same Bragg scattering as occurs in photonic crystal [JOANNOPoulos ET AL., 2008]. So although a lattice of spheres may at first appear to be a photonic crystal, the goal for designing metamaterials is to engineer resonances in the
long-wavelength regime which will contribute to $e_{\text{eff}}$ and $\mu_{\text{eff}}$, and to avoid wavelengths which approach the diffraction regime of photonic crystals.

The recent investigation of spherical or cylindrical inclusions for metamaterials began with a report on the magnetic polarizability of ferroelectric cylinders, and the negative permeability of an array of such rods [O’Brien and Pendry, 2002]. Other early publications presented theoretical research on microwave metamaterials comprised of magneto-dielectric spheres [Holloway et al., 2003] and ferroelectric spheres [Vendik and Gashinova, 2004], or infrared metamaterials comprised of phonon-polaritonic dielectric rods or spheres [Huang et al., 2004; Wheeler et al., 2005b, 2006; Yannopoulos and Moroz, 2005; Jylhä et al., 2006]. In order to obtain negative index metamaterials, either two interpenetrating lattices of spheres [Holloway et al., 2003; Vendik and Gashinova, 2004; Yannopoulos and Moroz, 2005] or coated spheres [Wheeler et al., 2006] are needed to overlap the resonances in the effective permittivity and permeability. A theoretical report investigated the same principle for designing optical metamaterials using exciton-polaritonic resonances [Yannopoulos and Vitanov, 2006]. Further performance considerations [Ahmadi and Mosallaei, 2008; Popa and Cummer, 2008; Vynck et al., 2009], diamagnetic metamaterials [Hu et al., 2006], cubic resonators [Kim and Gopinath, 2007], inverse structures [Seo et al., 2006], and magnetically tunable metamaterials [Liu et al., 2008b] have since been considered.

The theoretical work has spawned an array of experimental results. The phase velocity in a single layer two-dimensional lattice of garnet spheres was measured [Baker-Jarvis et al., 2006]. Microwave measurements have been reported of a negative index in a two-dimensional array of ferroelectric rods [Peng et al., 2007] and a negative permeability in a simple cubic arrangement of ferroelectric cubes [Zhao et al., 2008b; Ma et al., 2008], which was further refined to be tunable by temperature changes [Zhao et al., 2008a]. Infrared measurements of the magnetic dipole resonance of single isolated SiC whiskers have been performed [Schuller et al., 2007], and the bulk magnetic response of a random powder of SiC micro-particles has been measured [Wheeler et al., 2009a].

### 2.2.3 Plasmonics

A metal nanoparticle can have induced dipole resonances (plasmon-polaritons) which have very intense fields near the surface. These resonances are roughly independent of size, and so a particle which is much smaller than a wavelength can be resonant. These properties have been used to make optical sub-wavelength plasmonic waveguides out of chains of metal nanospheres, where tight coupling can create extreme field localization and prevents diffraction over long distances [Maier et al., 2001; Maier and Atwater, 2005; Sweatlock et al., 2005; Koenderink and Polman, 2006]. Another application of such enhanced localized fields is for sensing or spectroscopy in chemical or biomedical applications [Lal et al., 2007; Maier and Atwater, 2005]. Various arrangements of coupled nanoparticles can create hot spots of great field intensity, which are useful for surface-enhanced Raman scattering [Chien and Szopek, 2008].

There is, however, a close link between plasmonics and optical magnetic and negative index metamaterials. It has been shown that the induced electric dipole resonances present in each plasmonic nanosphere
comprising a ring cluster can couple, creating an artificial resonant loop of displacement current. Therefore a ring cluster of metal nanospheres can have a net optical effective magnetic polarizability [ALÙ ET AL., 2006; ALÙ AND ENGHETA, 2008]. A similar effect can arise in larger spherical clusters [ROCKSTUHL ET AL., 2007; PARK AND WU, 2008]. Higher-order electric multipole moments in a cluster can also interact to form a net magnetic polarizability [SHVETS AND URZHUMOV, 2004, 2005]. The mutual interaction of the plasmon modes generally results in hybridized modes, much like the hybridization of atomic bonds. This effect has been dubbed plasmon “chemistry” [RIIKONEN ET AL., 2005; ROMERO ET AL., 2006; LASSTER ET AL., 2008].

The very same field confinement and enhancement can be obtained from magnetic dipole resonances in sub-wavelength particles. The fields are an exact dual, although the physical mechanism which supports the modes is different. This is much less common because of the comparatively rarer condition required for a magnetic dipole mode in the long-wavelength regime. Nonetheless, magnetic dipole coupling and hybridization can be used to create multi-particle basis units for metamaterials [WHEELER ET AL., 2009b].
Chapter 3

Single Particle Scattering

The scattering properties of single isolated particles form the underlying theory required throughout the remaining chapters. Therefore the essential results of scattering theory will be review in this chapter.

The problem of scattering and absorption by spheres of arbitrary radius and refractive index can be solved exactly. The solution is usually attributed to Mie [1908], and a good reference for the theory is Bohren and Huffman [1983]. The method is also sometimes called Lorenz-Mie theory, since it seems that Lorenz solved the problem first [Mishchenko et al., 2002]. One generalization of the scattering solution for arbitrary particles shapes is the transition matrix (T-matrix) method [Waterman, 1965, 1971; Ström, 1975; Mishchenko et al., 2002; Martin, 2006]. The transition matrix allows for an operator notation for scattering processes, which is particularly convenient when solving systems with multiple scattering, which will be pursued in Chap. 7.

Vector spherical waves will be used as basis functions throughout the work, so they are summarized in Sec. 3.1. The algebraic operator notation of the T-matrix method is outlined in Sec. 3.2. Some particular results for plane wave excitations are given in Sec. 3.3. The polarizabilities of isolated particles can be extracted from the T-matrix, as discussed in Sec. 3.4. The scattering properties of a sphere, coated sphere, and ellipsoid are given in Sec. 3.5, where detailed derivations of the magnetic and electric dipole resonant conditions are also derived. The cross sections of a particle are summarized in Sec. 3.6.

3.1 Vector Spherical Wave Basis Functions

Consider an isolated particle, with an interior of permittivity $\varepsilon_i/\varepsilon_0 = n_i^2$. The particle is embedded in a host medium of permittivity $\varepsilon_h/\varepsilon_0 = n_h^2$. All materials will be assumed to be non-magnetic, so $\mu = \mu_0$ everywhere.

All fields are assumed to be time harmonic with radial frequency $\omega$, such that

$$\mathbf{A}(\mathbf{r}, t) = \text{Re} \left\{ \mathbf{A}(\mathbf{r}) e^{-i\omega t} \right\},$$

(3.1)

where $i^2 = -1$ and $\mathbf{A}(\mathbf{r})$ is a complex vector field.

Both the interior and the exterior regions of the particle are homogeneous and source-free, so the
electric field $\mathbf{E}(\mathbf{r})$ satisfies the vector Helmholtz equation in each region,

$$\nabla^2 \mathbf{E}(\mathbf{r}) + k^2 \mathbf{E}(\mathbf{r}) = 0, \quad (3.2)$$

where $k = k_s = n_s \omega / c$ for the interior region, $k = k_h = n_h \omega / c$ for the exterior host region, and $c$ is the velocity of light in free space. A complete basis of functions which satisfy (3.2) are the vector spherical waves [STOUT et al., 2002; MISHCHENKO et al., 2002; CHEW, 1995],

$$M_{lm}(kr) = -\frac{\xi_l(kr)}{kr} X_{lm}(\hat{\mathbf{r}}), \quad (3.3a)$$

$$N_{lm}(kr) = \sqrt{l(l+1)} \frac{\xi_l(kr)}{(kr)^2} Y_{lm}(\hat{\mathbf{r}}) + \frac{\xi'_l(kr)}{kr} Z_{lm}(\hat{\mathbf{r}}), \quad (3.3b)$$

where $l = 1, 2, \ldots$ and $-l \leq m \leq l$, and $\xi_l(kr)$ are the Riccati-Bessel functions of the third kind (App. A). These basis functions are analogous to atomic orbitals, such that the multipole order $l$ corresponds to the orbital quantum number, and $m$ corresponds to the magnetic quantum number.\(^\ast\) The angular dependencies of these waves are the normalized vector spherical harmonics [STOUT et al., 2002]

$$Y_{lm}(\hat{\mathbf{r}}) = Y_{lm} \sqrt{l(l+1)} P_l^m(\cos \theta) e^{im\phi} \hat{\mathbf{r}}, \quad (3.4a)$$

$$X_{lm}(\hat{\mathbf{r}}) = Y_{lm} \left[ -\frac{im}{\sin \theta} P_l^m(\cos \theta) e^{im\phi} \hat{\theta} + \frac{d}{d\theta} P_l^m(\cos \theta) e^{im\phi} \hat{\phi} \right], \quad (3.4b)$$

$$Z_{lm}(\hat{\mathbf{r}}) = Y_{lm} \left[ \frac{d}{d\theta} P_l^m(\cos \theta) e^{im\phi} \hat{\theta} + \frac{im}{\sin \theta} P_l^m(\cos \theta) e^{im\phi} \hat{\phi} \right], \quad (3.4c)$$

where

$$Y_{lm} = \sqrt{\frac{(2l+1)(l-m)!}{4\pi l(l+1)(l+m)!}}, \quad (3.5)$$

and $P_l^m(x)$ is the associated Legendre function of order $l$ and degree $m$ [ABRAMOWITZ and STEGUN, 1972],

$$P_l^m(x) = (-1)^m(1-x^2)^{m/2} \frac{d^m}{dx^m} P_l(x). \quad (3.6)$$

The basis functions (3.3) are the *irregular* vector spherical waves, and they are appropriate for a region excluding the origin. For a region including the origin, the functions $\xi_l(kr)$ in (3.3) have a singularity and must be replaced by $\psi_l(kr)$. In this case the basis functions are named the *regular* vector spherical waves, $\text{Rg} M_{lm}(kr)$ and $\text{Rg} N_{lm}(kr)$.

\(^\ast\) A third function $L_{lm}(kr)$ is required to represent fields with non-zero divergence.

\(^\ast\) There is no correspondence to an energy quantum number $n$, which is specific to the hydrogen atom where the potential in the Schrödinger equation is $V(r) \propto 1/r$. 
Chapter 3. Single Particle Scattering

The general solution of (3.2) for \( \mathbf{E} \) and \( \mathbf{H} \) in a region excluding the origin is

\[
\mathbf{E}(\mathbf{r}) = E_0 \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left[ a_{lm}^M \mathbf{M}_{lm}(kr) + a_{lm}^N \mathbf{N}_{lm}(kr) \right],
\]
\[
\mathbf{H}(\mathbf{r}) = -\frac{iE_0}{\eta} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left[ a_{lm}^N \mathbf{M}_{lm}(kr) + a_{lm}^M \mathbf{N}_{lm}(kr) \right],
\]

where \( \eta = \sqrt{\mu/e} \). The magnetic field \( \mathbf{H} \) can be derived from \( \mathbf{E} \) by using Faraday’s Law, \( \nabla \times \mathbf{E} = i\omega \mu \mathbf{H} \), along with the curl relationships

\[
\nabla \times \mathbf{M}_{lm}(kr) = k\mathbf{N}_{lm}(kr),
\]
\[
\nabla \times \mathbf{N}_{lm}(kr) = k\mathbf{M}_{lm}(kr).
\]

Since \( \mathbf{H} \) can be derived from \( \mathbf{E} \), only the electric field will be described from hereon. Furthermore, it is sufficient to know only \( a_{lm}^M \) and \( a_{lm}^N \), which are found in both field expansions. The functions \( \mathbf{M}_{lm} \) are transverse to \( r \), since

\[
r \cdot \mathbf{M}_{lm}(kr) = r \cdot \mathbf{X}_{lm}(\hat{r}) = 0.
\]

Conversely, the functions \( \mathbf{N}_{lm} \) have a portion \( \mathbf{Y}_{lm} \) which is longitudinal with \( r \), and may be viewed as “source” fields for the various multipole fields. Therefore the expression for \( \mathbf{E} \) (3.7a) shows that the \( a_{lm}^N \) coefficients are the amplitudes of the electric \( l \)-multipole terms, and the expression for \( \mathbf{H} \) (3.7b) shows that the \( a_{lm}^M \) coefficients are the amplitudes of the magnetic \( l \)-multipole terms.

The expansion of \( \mathbf{E} \) in (3.7a) can be written more concisely using vector notation [CHEW, 1995; TSANG ET AL., 2000]. The expansion coefficients can be grouped into a column vector

\[
a = \begin{bmatrix} a_{lm}^M \\ a_{lm}^N \end{bmatrix},
\]

where \( a_{lm}^M \) and \( a_{lm}^N \) are themselves column vectors containing \( a_{lm}^M \) and \( a_{lm}^N \), respectively. The basis functions can also be grouped into the array

\[
\Psi(kr) = \begin{bmatrix} \mathbf{M}(kr) \\ \mathbf{N}(kr) \end{bmatrix},
\]

where \( \mathbf{M}(kr) \) and \( \mathbf{N}(kr) \) are themselves arrays of the basis functions \( \mathbf{M}_{lm}(kr) \) and \( \mathbf{N}_{lm}(kr) \). The same can be done for \( \mathbf{R}_g\Psi(kr) \). Then the field expansion (3.7a) can be written as

\[
\mathbf{E}(\mathbf{r}) = E_0 \Psi^T(kr) \cdot a,
\]

where the superscript \( ^T \) indicates the vector transpose operation.
3.2 Scattering and the Transition Matrix Method

Consider the isolated particle discussed at the beginning of Sec. 3.1, and let it be placed so that the coordinate origin is in its interior. An arbitrary incident wave is applied, and following (3.12), it can be written as

\[ E^{\text{inc}}(r) = E_0 Rg \Psi^T(k_h r) \cdot a. \] (3.13)

The application of the incident field on the particle results in a scattered field with the expansion

\[ E^{\text{sc}}(r) = E_0 \Psi^T(k_h r) \cdot f. \] (3.14)

An internal field is also supported, having an expansion

\[ E^{\text{int}}(r) = E_0 Rg \Psi^T(k_s r) \cdot g. \] (3.15)

The scattering properties of the particle can be completely specified by the transition matrix \( \mathbf{T} \). Its elements can be calculated by knowing the size, shape, and material composition of the particle and host [MISHCHENKO ET AL., 2002]. It can be evaluated in block form,

\[ \mathbf{T} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix}. \] (3.16)

The compact notation outlined so far leads to a convenient representation of the fields. The incident, scattered, and internal fields are sufficiently represented by the expansion coefficient vectors \( a, f, \) and \( g \), respectively. In addition, the attributes of the particle are completely represented by \( \mathbf{T} \), and its elements are independent of the fields.

By virtue of the T-matrix method, the scattered field can be viewed as the result of operating with \( \mathbf{T} \) on the incident field coefficients,

\[ f = \mathbf{T} \cdot a. \] (3.17)

where the operation \( \cdot \) represents matrix multiplication. The internal field is related to the incident field by

\[ g = \overline{Q}^{-1} \cdot a, \] (3.18)

and the scattered and internal fields are related by

\[ f = -Rg \overline{Q} \cdot g. \] (3.19)

The elements of \( \overline{Q} \) and \( Rg \overline{Q} \) are integrals over the particle surface, as may be found in MISHCHENKO ET AL. [2002]. Substitution of (3.18) into (3.19) and comparing with (3.17) shows that \( \mathbf{T} = - (Rg \overline{Q}) \cdot \overline{Q}^{-1} \).

For numerical calculations the infinite basis of vector spherical waves must be truncated at \( l = l_{\text{max}} \), for which there are \( L_{\text{max}} = 2l_{\text{max}}(l_{\text{max}} + 2) \) basis function “orbitals”. Therefore \( L_{\text{max}} \) is the length of vectors \( a, f, \) and \( g \), and of each dimension of \( \mathbf{T} \).
3.3 Uniform Plane Waves

Although the incident field need not be a uniform plane wave, that is the only case to be considered here. This may be written generally as

\[
\begin{align*}
\mathbf{E}^{\text{inc}}(\mathbf{r}) &= E_0^{\text{inc}} \exp(i\mathbf{k}^{\text{inc}} \cdot \mathbf{r}), \\
\mathbf{H}^{\text{inc}}(\mathbf{r}) &= H_0^{\text{inc}} \exp(i\mathbf{k}^{\text{inc}} \cdot \mathbf{r}),
\end{align*}
\]

where the complex amplitude and polarization of the wave are \( E_0^{\text{inc}} \) and \( H_0^{\text{inc}} \) for the electric and magnetic fields respectively, and \( \mathbf{k}^{\text{inc}} = \mathbf{k}_h \hat{k}^{\text{inc}} \) is the incident wavevector. This incident plane wave can be written in terms of the expansion (3.13), where the coefficients \( a \) are [STOUT ET AL., 2002]

\[
\begin{align*}
a^M_{lm} &= -i \hat{\mathbf{k}}^{\text{inc}} \cdot \hat{\mathbf{E}}^{\text{inc}}, \\
a^N_{lm} &= -i \hat{\mathbf{k}}^{\text{inc}} \cdot \hat{\mathbf{H}}^{\text{inc}}.
\end{align*}
\]

Only one particular plane wave will be needed throughout this work, with complex amplitudes and polarizations \( E_0^{\text{inc}} = E_0 \hat{x}, H_0^{\text{inc}} = H_0 \hat{y} \), and propagation direction \( \hat{k}^{\text{inc}} = \hat{z} \), so that

\[
\begin{align*}
\mathbf{E}^{\text{inc}}(z) &= E_0 \hat{x} \exp(i k_h z), \\
\mathbf{H}^{\text{inc}}(z) &= H_0 \hat{y} \exp(i k_h z),
\end{align*}
\]

where \( H_0 = E_0/\eta_h \) and \( \eta_h = \sqrt{\mu_h/\varepsilon_h} \) is the wave impedance of the host medium. Then the elements of \( a \) for this particular plane wave simplify to

\[
\begin{align*}
a^M_{lm} &= i \hat{\mathbf{k}}^{\text{inc}} \cdot \hat{\mathbf{E}}^{\text{inc}}, \\
a^N_{lm} &= i \hat{\mathbf{k}}^{\text{inc}} \cdot \hat{\mathbf{H}}^{\text{inc}}.
\end{align*}
\]

where \( \delta_{lm} \) is the Kronecker delta.

3.4 Particle Polarizabilities

The electric \( \mathbf{\alpha}_e \) and magnetic \( \mathbf{\alpha}_m \) polarizabilities of a particle are generally tensors which relate the field at the particle origin to induced electric \( \mathbf{p} \) and magnetic \( \mathbf{m} \) dipole moments,

\[
\begin{align*}
\mathbf{p} &= \varepsilon_h \mathbf{\alpha}_e \cdot \mathbf{E}^{\text{inc}}(\mathbf{r} = \mathbf{0}), \\
\mathbf{m} &= \mathbf{\alpha}_m \cdot \mathbf{H}^{\text{inc}}(\mathbf{r} = \mathbf{0}).
\end{align*}
\]

The induced dipole moments may be obtained by examining the dipole portion \( (l = 1) \) of the scattered fields, and comparing them with another known expression for dipole fields. The dipole fields scattered by
an arbitrary particle can be expressed in terms of \( I \), by using the expansion (3.14),

\[
\mathbf{E}_{\text{dipole}}^{\text{calc}}(\mathbf{r}) = E_0 \sum_{m=-1}^{1} \left[ f_{1m}^M \mathbf{M}_{1m}(k_h r) + f_{1m}^N \mathbf{N}_{1m}(k_h r) \right],
\]

(3.25a)

\[
\mathbf{H}_{\text{dipole}}^{\text{calc}}(\mathbf{r}) = \frac{-iE_0}{\eta_h} \sum_{m=-1}^{1} \left[ f_{1m}^N \mathbf{M}_{1m}(k_h r) + f_{1m}^M \mathbf{N}_{1m}(k_h r) \right].
\]

(3.25b)

There are six unknown coefficients: three are \( f_{1m}^M \), and three are \( f_{1m}^N \). One set of three can be identified as electric dipole source amplitudes, and the other set as magnetic dipole source amplitudes. Both sets generally contribute to both the electric and magnetic fields; for example, a radiating electric dipole source creates both an electric and magnetic field. An electric dipole source, however, can be identified by noting that it creates a magnetic field with \( \mathbf{r} \cdot \mathbf{H} = \mathbf{H}_r = 0 \), so its magnetic field is transverse to \( \mathbf{r} \) (TM'). From (3.9), this means that the electric dipole source is responsible for the \( \mathbf{M}_{1m} \) terms of the magnetic field. Therefore, the set of \( f_{1m}^N \) can be attributed to the amplitudes of electric dipole sources, and similarly the set of \( f_{1m}^M \) can be attributed to the amplitudes of magnetic dipole sources.

The magnetic dipole moment \( \mathbf{m} \) can found by comparing the field expansions with the expression for the electric field due to an ideal magnetic dipole [JACKSON, 1999],

\[
\mathbf{E}_{\text{dipole}}^{\text{calc}} = \frac{\eta_h}{4\pi} \left( \mathbf{r} \times \mathbf{m} \right) \frac{\tilde{E}_l(k_h r)}{k_h r} = E_0 \sum_{m=-1}^{1} f_{1m}^M \mathbf{M}_{1m}(k_h r).
\]

(3.26)

In order to evaluate the vector spherical waves, the vector spherical harmonics (3.4b) for \( l = 1 \) are written more conveniently as

\[
\mathbf{X}_{1,\pm 1}(\hat{\mathbf{r}}) = \sqrt{\frac{3}{8\pi}} \hat{\mathbf{r}} \times \left( \frac{\mp \hat{\mathbf{x}} - i\hat{\mathbf{y}}}{\sqrt{2}} \right),
\]

(3.27)

\[
\mathbf{X}_{1,0}(\hat{\mathbf{r}}) = \sqrt{\frac{3}{8\pi}} \hat{\mathbf{r}} \times \hat{\mathbf{z}}.
\]

The result for the magnetic moment is

\[
\mathbf{m} = -E_0 \frac{\sqrt{3\pi}}{\eta_h k_h^3} \left[ \left( f_{1,-1}^M - f_{1,1}^M \right) \hat{\mathbf{x}} - i \left( f_{1,-1}^M + f_{1,1}^M \right) \hat{\mathbf{y}} + \sqrt{2} f_{1,0}^M \hat{\mathbf{z}} \right].
\]

(3.28)

The electric dipole moment can be found in a similar fashion,

\[
\mathbf{p} = E_0 \frac{\varepsilon_h}{\eta_h} \frac{\sqrt{3\pi}}{k_h^3} \left[ \left( f_{1,-1}^N - f_{1,1}^N \right) \hat{\mathbf{x}} - i \left( f_{1,-1}^N + f_{1,1}^N \right) \hat{\mathbf{y}} + \sqrt{2} f_{1,0}^N \hat{\mathbf{z}} \right].
\]

(3.29)

The polarizability tensors can be found from (3.24), and inserting into them the incident plane wave (3.22) and the dipole moments (3.28) and (3.29). The two important elements of the tensors for this work,
due to the specific incident plane wave (3.22), are

\[ \hat{x} \cdot \vec{\alpha} \cdot \hat{x} = \alpha_{r,xx} = \frac{\sqrt{3\pi}}{lk_h^3} (f_{l,0}^N - f_{l,0}^N), \]

\[ \hat{y} \cdot \vec{\alpha} \cdot \hat{y} = \alpha_{m,yy} = \frac{i\sqrt{3\pi}}{lk_h^3} (f_{l,0}^M + f_{l,0}^M). \]

### 3.5 Scattering by Particular Particle Shapes

The mathematical framework of the previous sections has been kept as general as possible, and now specific particle shapes will be considered. The case of spheres will be treated first, and this case is commonly known as Mie theory [Bohren and Huffman, 1983]. Coated spheres will be considered next, and these are another spherically symmetric particle. Finally, a brief summary of some aspects of ellipsoidal particles will be given.

#### 3.5.1 Sphere

A sphere is shown in Fig. 3.1. Its has a radius \( r_s \), is made of permittivity \( \epsilon_s/\epsilon_0 = n_s^2 \), and the permittivity of the host is \( \epsilon_h/\epsilon_0 = n_h^2 \). Due to the spherical symmetry, the T-matrix (3.31) is diagonal [Mishchenko et al., 2002],

\[ T^{11}_{\lambda\mu;l,m} = -b_l \delta_{\lambda1} \delta_{\mu m}, \]

\[ T^{12}_{\lambda\mu;l,m} = 0, \]

\[ T^{21}_{\lambda\mu;l,m} = 0, \]

\[ T^{22}_{\lambda\mu;l,m} = -a_l \delta_{\lambda1} \delta_{\mu m}, \]
and it is independent of \( \mu \) and \( m \). Because of the degeneracy in \( m \), a multipole of level \( l \) is \( 2l + 1 \) times degenerate. The values \( a_l \) and \( b_l \) are the Mie coefficients [Bohren and Huffman, 1983],

\[
\begin{align*}
a_l &= \frac{n_s \psi_l(n_s x) \psi'_l(n_h x) - n_h \psi'_l(n_h x) \psi_l(n_s x)}{n_s \psi_l(n_s x) \xi'_l(n_h x) - n_h \xi'_l(n_h x) \psi_l(n_s x)}, \\
b_l &= \frac{n_h \psi_l(n_s x) \psi'_l(n_h x) - n_s \psi'_l(n_h x) \psi_l(n_s x)}{n_h \psi_l(n_s x) \xi'_l(n_h x) - n_s \xi'_l(n_h x) \psi_l(n_s x)},
\end{align*}
\]

(3.32a) (3.32b)

where \( x = \omega r / c \), \( \psi_l(z) \) and \( \xi_l(z) \) are Riccati-Bessel functions (see App. A), and the primes indicate differentiation with respect to the argument. The expressions of the coefficients (3.32) must be modified slightly when the permeability of either medium differs from \( \mu_0 \) [Bohren and Huffman, 1983].

A physical meaning can be given to the coefficients \( a_l \) and \( b_l \). Using (3.17) and (3.31),

\[
\begin{align*}
-a_l &= \frac{f^N_{lm}}{a^N_{lm}}, \\
-b_l &= \frac{f^M_{lm}}{a^M_{lm}}
\end{align*}
\]

(3.33)

That is, for a fixed excitation, \( a_l \) is proportional to the electric \( l \)-multipole scattered field, and \( b_l \) is proportional to the magnetic \( l \)-multipole scattered field.

The polarizabilities (3.30) of a sphere excited by a plane wave can be simplified by using (3.33) and (3.23), giving

\[
\begin{align*}
\alpha_e &= \alpha_{e,xx} = \frac{6\pi i}{k^3} a_1, \\
\alpha_m &= \alpha_{m,yy} = \frac{6\pi i}{k^3} b_1.
\end{align*}
\]

(3.34a) (3.34b)

Due to the spherical symmetry, the polarizability tensors are diagonal, with \( \alpha_e = \alpha_e \mathbf{I} \) and \( \alpha_m = \alpha_m \mathbf{I} \), where \( \mathbf{I} \) is the identity dyad. The polarizability expressions (3.34) have been derived previously, for instance by Doyle [1989].

Calculations involving the Mie coefficients should include a sufficient number of multipole terms. The choice of cutoff \( l_{\text{max}} \) may be guided by the Wiscombe criterion [Wiscombe, 1980; Bohren and Huffman, 1983],

\[
l_{\text{max}} = (n_h x) + 4.05(n_h x)^{1/3} + 2,
\]

(3.35)

which is an empirical relation based on numerous numerical studies.

Since only sub-wavelength sized particles are of interest, the condition (2.3) can be re-written roughly as

\[
|n_h x| \ll 1.
\]

(3.36)

However, to avoid placing undue restrictions, the wavelength inside the sphere is left unconstrained, so \( n_s x \) can take any value. This implies that the sphere index \( n_s \) is arbitrary. In this sub-wavelength regime,
the dipole amplitudes for \( l = 1 \) are generally dominant, and using some results from App. A, the amplitudes (3.32) reduce to

\[
a_1 \approx -i \frac{2}{3} (n_h x)^3 \frac{\varepsilon_s F(n_s x) - \varepsilon_h}{\varepsilon_s F(n_s x) + 2\varepsilon_h}, \tag{3.37a}
\]

\[
b_1 \approx -i \frac{2}{3} (n_h x)^3 \frac{F(n_s x) - 1}{F(n_s x) + 2}, \tag{3.37b}
\]

where

\[
F(\theta) = \frac{2(\sin \theta - \theta \cos \theta)}{\theta^2 - 1} \sin \theta \cos \theta. \tag{3.38}
\]

This simplification was first derived by LEWIN [1947]. The form of \( b_1 \) would be dual to \( a_1 \) if \( \mu_s \neq \mu_h \).

**Magnetic Dipole Resonances**

The conditions for strong magnetic dipole scattering by a sub-wavelength sphere can be obtained from (3.37b). A resonant condition is found by setting \( 1/b_1 = 0 \),

\[
F(n_s x) = -2. \tag{3.39}
\]

Using (3.38) the resonant condition becomes

\[
\sin(n_s x) = 0, \quad n_s \neq 0. \tag{3.40}
\]

The solutions are the roots

\[
n_s x = \pi q, \quad q = 1, 2, 3, \ldots. \tag{3.41}
\]

The fundamental magnetic dipole resonant frequency is therefore

\[
\omega_m \approx \frac{\pi c}{r_s n_s}. \tag{3.42}
\]

This can be restated as a ratio between the resonant wavelength in the host medium \( \lambda_{h,m} \) and the diameter of the sphere \( 2r_s \),

\[
\frac{\lambda_{h,m}}{2r_s} \approx \frac{n_s}{n_h}. \tag{3.43}
\]

This relationship is useful to determine the material indexes necessary to induce a magnetic dipole resonance in a sub-wavelength sphere. Modifying the approximate long-wavelength condition (2.4) to \( \lambda_h/2r_s \geq 10 \), a magnetic dipole resonance is only possible if

\[
\left| \frac{n_s}{n_h} \right| \geq 10 \quad \text{or} \quad \left| \frac{\varepsilon_s}{\varepsilon_h} \right| \geq 100. \tag{3.44}
\]

This result is not surprising when the sphere is viewed as a dielectric cavity, since the frequency of the particle resonance must be pushed down into the long-wavelength limit of the host medium. The \( H \) field
under the resonant condition is plotted in Fig. 3.2. Ignoring the case of a sphere material with massively large losses, where $\text{Im} \{\epsilon_i\} \gg \text{Re} \{\epsilon_i\}$, then the permittivity inside the sphere $\text{Re} \{\epsilon_i\} > 0$, and from Fig. 3.2 there is a confinement of the internal field at the center of the sphere, this mode will be referred to as a *bulk* magnetic dipole mode. There are nulls in the magnetic field in the equatorial plane ($y = 0$) just inside the sphere surface, which indicate a circulation of maximal electric field within that plane near the surface.

An approximate form of $F(\theta)$ can be obtained for $\theta = n_s x$ near the resonant condition (3.41),

$$F(\theta) \approx \frac{2}{\pi q(\pi q - \theta)} - 1 \quad \text{near} \quad \theta = \pi q.$$  \hspace{1cm} (3.45)

This approximation is plotted for $q = 1$, along with the exact function, in Fig. 3.3. This approximation will be used in later sections.

**Electric Dipole Resonances**

The conditions for strong electric dipole scattering by a sub-wavelength sphere can be obtained from (3.37a). A resonant condition is found by setting $1/a_1 = 0$,

$$F(n_s x) = -2 \frac{\epsilon_h}{\epsilon_s},$$  \hspace{1cm} (3.46)

There are two cases to consider. For the first case the same assumption will be used as for the magnetic dipole resonance, which is that $|\epsilon_s| \gg |\epsilon_h|$. This leads to $F(n_s x) \approx 0$, and using (3.38) the resonant condition

$$\frac{H}{H_0}$$

**Figure 3.2:** The total magnetic dipole field $\mathbf{H}/H_0$ under the bulk magnetic dipole resonant condition (3.42). The incident magnetic field is polarized along $y$ and propagating along $z$, perpendicularly to the page. The arrows are the directions of the components of $\mathbf{H}$ parallel to the page.
Figure 3.3: The function $F(\theta)$. The solid curve is the exact function (3.38), and the dashed is the approximation centered at $\theta = \pi$, given by (3.45).

Figure 3.4: The total electric dipole field $\mathbf{E}/E_0$ under the bulk electric dipole resonant condition (3.48). The incident electric field is polarized along $x$ and propagating along $z$, perpendicularly to the page. The arrows are the directions of the components of $\mathbf{E}$ parallel to the page.
Figure 3.5: The total electric dipole field $E/E_0$ under the surface electric dipole resonant condition (3.50). The incident electric field is polarized along $x$ and propagating along $z$, perpendicularly to the page. The arrows are the directions of the components of $E$ parallel to the page.

becomes

$$\tan n_s x = n_s x. \quad (3.47)$$

The first root is $n_s x = 4.49$. Therefore, the resonant frequency for this case is

$$\omega_e = \frac{4.49c}{n_s r_s}. \quad (3.48)$$

Comparing this frequency with (3.42), it is seen that it is not the electric dipole, but the magnetic dipole which has a lower (fundamental) resonant frequency, since $\omega_m < \omega_e$. The $E$ field under the condition (3.48) is plotted in Fig 3.4. Since the permittivity inside the sphere $\text{Re} \{\varepsilon_s\} > 0$ and since there is a confinement of the internal field at the center of the sphere, this mode will be referred to as a \textit{bulk} electric dipole mode.

The second case for an electric dipole resonance is when the sphere index $n_s$ is not large, but instead comparable with $n_h$. Then $|n_s x| \ll 1$, and from (3.38) where $\theta = n_s x$,

$$\lim_{n_s x \to 0} F(n_s x) = \lim_{\theta \to 0} F(\theta) = 1, \quad (3.49)$$

and the resonant condition (3.46) becomes

$$\varepsilon_s(\omega_e) = -2\varepsilon_h, \quad (3.50)$$

where the frequency dependence of the sphere permittivity has been made explicit, and $\omega_e$ is the resonant frequency. Assuming that $\text{Re} \{\varepsilon_h\} > 0$, then $\text{Re} \{\varepsilon_s(\omega_e)\} < 0$, and for this to be satisfied $\varepsilon_s$ must indeed be
dispersive and a function of frequency. The resonant condition (3.50) can therefore only be solved after the dispersion of \( \varepsilon_s(\omega) \) is specified. Under these first-order approximations, (3.50) shows that the resonant condition is independent of the size of the sphere, as long as the sphere radius is much smaller than a wavelength in the host. A second-order approximation yields [BOHREN AND HUFFMAN, 1983, p. 329]

\[
\varepsilon_s(\omega_c) = -\left[2 + \frac{12}{3} (n_h x)^2\right] \varepsilon_h, \tag{3.51}
\]

so a larger sphere has a resonance at a frequency when the sphere permittivity is more negative. The E field under the conditions (3.50) and \( \lambda_h/2r_s = 10 \) is plotted in Fig. 3.5.

The radial dependence of the radial component of the electric field of this second class of modes can be approximated under the condition \(|n_l x| \ll 1\) using (3.15),

\[
E^{\text{int}}_r(r) \propto \hat{r} \cdot \text{RgN}_l(k_s r)
\]

\[
= \psi_1(k_s r) \kappa_l(k_s r)^2 \kappa_l^{-1}, \tag{3.52}
\]

where (A.8) was used. The case where \( l = 1 \) is depicted in Fig. 3.5, and the internal field is uniform. For the remaining cases \( l \geq 1 \), the field is more intense at the surface, which is why, despite the uniform field inside the sphere in Fig. 3.5, these modes are referred to as surface electric dipole modes.

These surface modes are most commonly found in metal nanoparticles, where they are called plasmon-polariton (or just plasmon) resonances. The scattering amplitude \( a_l \) can be further simplified from (3.37a) by using (3.49), yielding

\[
a_l \approx -i \frac{2}{3} (n_h x)^3 \frac{\varepsilon_s - \varepsilon_h}{\varepsilon_s + 2\varepsilon_h}, \tag{3.53}
\]

where the resonant condition (3.50) can plainly be seen from the denominator. The electric polarizability of the sphere follows from (3.34),

\[
\alpha_e \approx 4\pi r_s^3 \frac{\varepsilon_s - \varepsilon_h}{\varepsilon_s + 2\varepsilon_h}. \tag{3.54}
\]

This can be interpreted as the local field enhancement, since the scattered field is proportional to this factor. In this regime of surface modes where \(|n_h x| \ll 1\) and \(|n_s x| \ll 1\), it is straightforward to derive the resonant conditions for all electric multipole modes terms. Simplifying (3.32a) under these conditions and using results from App. A yields

\[
a_l \approx \frac{-i(l + 1)}{(2l - 1)!!(2l + 1)!!} (n_h x)^{2l+1} \frac{\varepsilon_s - \varepsilon_h}{l \varepsilon_s + (l + 1) \varepsilon_h}, \tag{3.55}
\]

where \( n!! \) is the double factorial function, which is defined in (A.10). Solving for \( 1/a_l = 0 \), the resonant frequency \( \omega_{e,l} \) of electric multipole \( l \) is

\[
\varepsilon_s(\omega_{e,l}) = -\left(\frac{l + 1}{l}\right) \varepsilon_h. \tag{3.56}
\]
There is a sequence of resonances, but the amplitudes also drop off by $(n_h x)^{2l+1}$.

### 3.5.2 Coated Sphere

A coated sphere is shown in Fig. 3.6, with core radius $r_1$ and permittivity $\varepsilon_1/\varepsilon_0 = n_1^2$, coating outer radius $r_2$ and permittivity $\varepsilon_2/\varepsilon_0 = n_2^2$, and the permittivity of the host is $\varepsilon_h/\varepsilon_0 = n_h^2$. Due to the spherical symmetry, the T-matrix is diagonal, as in the case for a solid sphere (3.31), but the coefficients are instead [Bohren and Huffman, 1983],

\[
\begin{align*}
  a_l &= \frac{n_h \psi_l(n_h y) [\psi_l(n_2 y) - A_l \chi_l(n_2 y)] - n_2 \psi_l(n_h y) [\psi_l(n_2 y) - A_l \chi_l(n_2 y)]}{n_h \xi_l(n_h y) [\psi_l(n_2 y) - A_l \chi_l(n_2 y)] - n_2 \psi_l(n_h y) [\psi_l(n_2 y) - A_l \chi_l(n_2 y)]}, \\
  b_l &= \frac{n_2 \psi_l(n_h y) [\psi_l(n_2 y) - B_l \chi_l(n_2 y)] - n_h \psi_l(n_h y) [\psi_l(n_2 y) - B_l \chi_l(n_2 y)]}{n_2 \xi_l(n_h y) [\psi_l(n_2 y) - B_l \chi_l(n_2 y)] - n_h \psi_l(n_h y) [\psi_l(n_2 y) - B_l \chi_l(n_2 y)]},
\end{align*}
\]

(3.57)

which depend on

\[
\begin{align*}
  A_l &= \frac{n_1 \psi_l(n_1 x) \psi_l(n_2 x) - n_2 \psi_l(n_2 x) \psi_l(n_1 x)}{n_1 \psi_l(n_1 x) \chi_l(n_2 x) - n_2 \chi_l(n_2 x) \psi_l(n_1 x)}, \\
  B_l &= \frac{n_2 \psi_l(n_1 x) \psi_l(n_2 x) - n_1 \psi_l(n_2 x) \psi_l(n_1 x)}{n_2 \psi_l(n_1 x) \chi_l(n_2 x) - n_1 \chi_l(n_2 x) \psi_l(n_1 x)},
\end{align*}
\]

(3.58)

where $x = \omega r_1/c$, $y = \omega r_2/c$, and $\psi_l(z)$, $\chi_l(z)$, and $\xi_l(z)$ are Riccati-Bessel functions (App. A). Also similarly to the case of a solid sphere, the scattered fields may be calculated using (3.33), and the polarizabilities with (3.34), each time recalling to using the coefficients (3.57).

Since only sub-wavelength sized particles are of interest, the sub-wavelength condition (3.36) will be
assumed, but it must now be modified to accommodate the outer radius,

\[ |n_h y| \ll 1. \quad (3.59) \]

In addition, the size parameters related to the coating with \( n_2 \) will also be considered to be small, while the size parameter of the core will be kept unrestricted,

\[ |n_2 y| \ll 1, \]
\[ |n_2 x| \ll 1, \quad n_1 x \text{ arbitrary.} \quad (3.60) \]

These imply that the index of the coating \( n_2 \) must be small, but that of the core \( n_1 \) may be arbitrary. Under these conditions the coefficients (3.57) can be approximated as

\[ a_1 \approx -i \frac{2}{3} (n_h y)^3 \frac{\varepsilon_2 F_A - \varepsilon_h}{\varepsilon_2 F_A + 2\varepsilon_h}, \quad (3.61a) \]
\[ b_1 \approx -i \frac{2}{3} (n_h x)^3 \frac{F(n_1 x) - 1}{F(n_1 x) + 2}, \quad (3.61b) \]

where \( F(\theta) \) was defined in (3.38), and

\[ F_A = 1 + 3 \tau \left[ \frac{\varepsilon_1 F(n_1 x) + 2\varepsilon_2}{\varepsilon_1 F(n_1 x) - \varepsilon_2} - \tau \right]^{-1}, \quad (3.62) \]

and

\[ \tau = \left( \frac{r_1}{r_2} \right)^3 = \left( \frac{x}{y} \right)^3. \quad (3.63) \]

**Magnetic Dipole Resonances**

The approximate magnetic dipole coefficient \( b_1 \) from (3.61b) is the same as that for a solid sphere, (3.37b), with the substitution \( n_s \rightarrow n_1 \). Since it has been assumed that \( |n_2| \ll |n_1| \), the coating has a negligible effect on the magnetic dipole resonance supported by the large permittivity core. The magnetic dipole resonance condition is similar to (3.42), but is now written as

\[ \omega_m \approx \frac{\pi c}{r_1 n_1}. \quad (3.64) \]

**Electric Dipole Resonances**

Although in Sec. 3.5.1 it was shown that a solid sphere can support two types of electric dipole modes (bulk and surface), the conditions (3.59) and (3.60) imply that \( |\varepsilon_1| \gg |\varepsilon_2| \), and therefore

\[ F_A \approx \frac{1 + 2\tau}{1 - \tau}. \quad (3.65) \]
The condition for strong electric dipole scattering by a sub-wavelength coated sphere can be obtained from (3.61a). A resonant condition is found by setting $1/a_1 = 0$,

$$F_A = -2\frac{\varepsilon_h}{\varepsilon_2}. \tag{3.66}$$

Equating two previous expressions yields the resonant condition,

$$\varepsilon_2(\omega_e) = -2\varepsilon_h \left( \frac{1 - \tau}{1 + 2\tau} \right), \tag{3.67}$$

where $\omega_e$ is the resonant frequency, which depends on the dispersion of $\varepsilon_2(\omega)$. If $\text{Re} \{ \varepsilon_h \} > 0$, then this implies that $\text{Re} \{ \varepsilon_2 \} < 0$ and therefore these are surface electric dipole modes.

### 3.5.3 Ellipsoid

An ellipsoid has in general three unequal semi-axis lengths $a$, $b$, $c$, as shown in Fig. 3.7. The permittivity of the particle is $\varepsilon_i/\varepsilon_0 = n_i^2$, and the permittivity of the host is $\varepsilon_h/\varepsilon_0 = n_h^2$. The volume of the ellipsoid is

$$V = \frac{4\pi}{3} abc. \tag{3.68}$$

There are no closed-form expressions for the T-matrix elements for ellipsoidal particles, but they can be evaluated numerically [Schneider and Peden, 1988; Mishchenko et al., 2002]. For nearly-spherical ellipsoids, a perturbational approach may suffice [Martin, 1993]. In any case, only the electric polarizabilities in the electrostatic approximation will be needed in this work. In the principle coordinate system of the ellipsoid as shown in Fig. 3.7, the electric polarizability tensor $\alpha_e$ is diagonal, having elements $\alpha_{e,j}$ for $j = 1, 2, 3$.

The analysis of ellipsoids in the electrostatic approximation is performed most conveniently in the ellipsoidal coordinate system [Bohren and Huffman, 1983]. By doing so, a set of geometric factors $L_j$ for that $j = 1, 2, 3$ are obtained. These factors are an alternate way of defining the shape of an ellipsoid. As
Figure 3.8: The domain of geometric factors pairs \((L_1, L_2)\). The large outer triangle is the domain of all possible ellipsoids. Points within one sub-triangle describe the entire range of unique ellipsoidal shapes, so the other sub-triangles represent other orientations.

such, they are functions of the ellipsoidal semi-axis lengths [Bohren and Huffman, 1983],

\[
L_1 = \frac{abc}{2} \int_0^\infty dq \frac{dq}{(a^2 + q)(b^2 + q)(c^2 + q)},
\]

\[
L_2 = \frac{abc}{2} \int_0^\infty dq \frac{dq}{(b^2 + q)(a^2 + q)(c^2 + q)},
\]

\[
L_3 = \frac{abc}{2} \int_0^\infty dq \frac{dq}{(c^2 + q)(b^2 + q)(a^2 + q)}.
\]

Despite the complication of these elliptic integrals, the geometric factors have simple properties:

\[
0 \leq L_j \leq 1,
\]

\[
L_1 + L_2 + L_3 = 1.
\]

Only two of the geometrical factors are independent, so the domain of values \((L_1, L_2)\) can be plotted as shown in the largest triangle in Fig. 3.8. Only one of the six sub-triangles describes all possible unique shapes, and the remaining sub-triangles describe the other possible orientations. The notable shapes of spheres \((L_j = 1/3)\), infinitely-thin needles (one of \(L_j = 0\)), and discs (two of \(L_j = 0\)) are indicated in the figure. The points on the interior lines describe spheroids, which are ellipsoids with two equal semi-axis lengths.

The electric polarizabilities \(\alpha_{e,j}\) in the electrostatic approximation are [Bohren and Huffman, 1983]

\[
\alpha_{e,j} = \frac{V}{\beta + L_j},
\]
where

\[ \beta = \frac{\varepsilon_h}{\varepsilon_s - \varepsilon_h}. \] (3.73)

Due to the electrostatic approximation, these are valid only for surface electric dipole modes. For a sphere \( L_j = 1/3 \), and the polarizability (3.72) reduces to the polarizability of the surface electric dipole modes of a sphere (3.54). The resonant frequency of a surface dipole mode oriented in the direction of principle axis \( j \) is \( \omega_{e,j} \). It can be found from \( 1/\alpha_{e,j} = 0 \), which yields

\[ \frac{\varepsilon_s(\omega_{e,j})}{\varepsilon_h} = 1 - \frac{1}{L_j}. \] (3.74)

The resonant frequencies, to the first order, depend on the material permittivity functions and the shape of the particle, and are independent of the size. For a general ellipsoid with unequal semi-axis lengths, there will be three such resonances.

### 3.6 Cross Sections

In order to describe the scattering \( C_{\text{sca}} \), extinction \( C_{\text{ext}} \), and absorption \( C_{\text{abs}} \) cross sections, it is first convenient to separate the radial and angular dependencies of the scattered field,

\[
\lim_{k_h r \to \infty} E_{\text{sca}}^\hat{r}(r) = \frac{\exp(i k_h r)}{r} E_{\text{sca}}^\hat{r}(\hat{r}), \quad \hat{r} \cdot E_{\text{sca}}^\hat{r}(\hat{r}) = 0. \] (3.75)

The field \( E_{\text{sca}}^\hat{r}(\hat{r}) \) describes the angular dependence of the scattered field in the far field.

The scattering cross section is related to the total power scattered into all directions [MISHCHENKO ET AL., 2002],

\[
C_{\text{sca}} = \frac{1}{|E_0|^2} \iint |E_{\text{sca}}^\hat{r}(\hat{r})|^2 \, d\Omega. \] (3.76)

where \( d\Omega = \sin \theta d\theta d\phi \). The extinction cross section is due to the outgoing power flow of the cross products of the incident and scattered fields. It may also be expressed as [MISHCHENKO ET AL., 2002]

\[
C_{\text{ext}} = \frac{4\pi}{k_h |E_0|^2} \Im \left\{ E_{\text{i}}^\text{sca} (\hat{k}_{\text{inc}}) \cdot E_0^\text{inc*} \right\}. \] (3.77)

The field \( E_{\text{i}}^\text{sca} (\hat{k}_{\text{inc}}) \) is evaluated in the same direction as the propagation of the incident wave, which is the “forward” direction. This relationship between the forward scattering and \( C_{\text{ext}} \) is known as the optical theorem [MISHCHENKO ET AL., 2002; BOHREN AND HUFFMAN, 1983]. Finally, \( C_{\text{ext}} \) is equal to the total of the absorption and scattering all directions [BOHREN AND HUFFMAN, 1983],

\[
C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}}. \] (3.78)

Therefore there are three different physical interpretations of the extinction cross section.

When using the T-matrix formalism, the scattering and extinction cross sections may be evaluated
with [Mishchenko et al., 2002; Stout et al., 2001],

\[
C_{\text{sca}} = \frac{1}{k_h} \mathbf{f}^\dagger \cdot \mathbf{f}, \quad \tag{3.79}
\]
\[
C_{\text{ext}} = -\frac{1}{k_h^2} \text{Re} \left\{ \mathbf{a}^\dagger \cdot \mathbf{T} \cdot \mathbf{a} \right\}, \quad \tag{3.80}
\]

where \( \dagger \) is the Hermitian adjoint operator. The cross sections of a spherically-symmetric particle simplify to the following well-known expressions in Mie theory [Bohren and Huffman, 1983],

\[
C_{\text{sca}} = \frac{2\pi}{k_h^2} \sum_{l=1}^{\infty} (2l + 1) \left( |a_l|^2 + |b_l|^2 \right), \quad \tag{3.81a}
\]
\[
C_{\text{ext}} = \frac{2\pi}{k_h^2} \sum_{l=1}^{\infty} (2l + 1) \text{Re} \left\{ a_l + b_l \right\}. \quad \tag{3.81b}
\]

The \( C_{\text{abs}} \) can be evaluated with (3.78), and for lossless materials \( C_{\text{abs}} = 0 \). The number of terms required in these summations can be estimated with the Wiscombe criterion (3.35).

There are simplified expressions for the cross sections under the electrostatic approximation, where only the electric dipole field is present. For a particle with electric polarizability \( \alpha_e \), then [Bohren and Huffman, 1983]

\[
C_{\text{abs}} = k_h \text{Im} \{ \alpha_e \}, \quad \tag{3.82a}
\]
\[
C_{\text{sca}} = \frac{k_h^4}{6\pi} |\alpha_e|^2, \quad \tag{3.82b}
\]
\[
C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}}. \quad \tag{3.82c}
\]

Note that \( C_{\text{ext}} \) cannot be evaluated directly in the electrostatics approximation, since it would not satisfy the optical theorem [Bohren and Huffman, 1983; Tsang et al., 2000]. This issue may also be framed in a similar way to the electronic radiation reaction [Novotny and Hecht, 2006]. Although the modified cross sections (3.82) can be used for the surface electric dipole modes in spheres and coated spheres, it is particularly useful for ellipsoids, using (3.72).

Now that the basic scattering properties of various particle shapes have been developed, their use in composite metamaterials will be investigated in the next chapter.
The magnetic and electric polarizabilities of several shapes of dielectric particles were discussed in the previous chapter, and the resonant conditions on dipole resonances were also derived. It was shown that sub-wavelength sized dielectric particles can have not only electric dipole resonances, but also magnetic dipole resonances.

In this chapter, a simple yet accurate effective medium model of metamaterials consisting of dielectric particles will be presented in Sec. 4.1. The variety of materials that might be used to construct such metamaterials will be summarized in Sec. 4.2, with particular emphasis on SiC for infrared frequencies. Several design examples of metamaterials having negative permeability, negative permittivity, or negative index will be presented in Sec. 4.3.

### 4.1 Effective Medium Models

The goal of modeling a metamaterial or any composite medium is to obtain the effective media values $\varepsilon_{\text{eff}}$ and $\mu_{\text{eff}}$. Although the modeling of dielectrics is a rich area of research [Scaife, 1998], two predominant methods are usually applied to metamaterials. First, since most metamaterials are periodic structures, the microscopic fields (obtained numerically) can be averaged over a single unit cell [Pendry et al., 1999; Smith and Pendry, 2006]. This is practically impossible for experimental measurements, necessitating the second predominant method, which can be used for both theoretical and experimental work. The complex reflection and transmission coefficients of a slab of metamaterial can be transformed into the effective index $n_{\text{eff}}$ and impedance $z_{\text{eff}}$, and subsequently $\varepsilon_{\text{eff}}$ and $\mu_{\text{eff}}$ [Smith et al., 2002]. However, this algorithm often creates artifacts such as anti-resonances [Koschny et al., 2003; O’Brien and Pendry, 2002; Huang et al., 2004] which seem to indicate gain in passive structures, and the validity and suitability of this method are still open questions [Seetharamdooy et al., 2005; Markel, 2008]. These problems tend only to arise near or within band gap or absorptive regions, so the method otherwise remains generally useful, particularly for inverting experimental measurements into material properties, but it will not be discussed further here. Instead, because the major emphasis is on design, the Clausius-Mossotti model will be used. It is much more robust, since it derives the macroscopic material properties from those of the microscopic constituents, and it is not afflicted with mathematical and physical ambiguities of the parameter inversion algorithm.
4.1.1 The Clausius-Mossotti Model

The Clausius-Mossotti model [Scaife, 1998; Tretyakov, 2003; Jackson, 1999; Collin, 1991; Kittel, 1996; Aspnes, 1982] was developed to describe the macroscopic response of natural bulk dielectrics in terms of the polarizabilities of the atoms which comprise the material. This can be re-used in the analogous situation of modeling a metamaterial in terms of the polarizabilities of the synthesized inclusions which comprise the metamaterial.

Assume that a host medium of electric permittivity $\varepsilon_h$ and magnetic permeability $\mu_h$ is embedded with arbitrary inclusions. The inclusions may be placed in a lattice or randomly. The application of $E$ or $H$ fields will polarize the inclusions. To ensure the validity of the effective media values $\mu_{\text{eff}}$ and $\varepsilon_{\text{eff}}$, it is assumed that the wavelength of the applied fields in the host $\lambda_h$ is much larger than the inclusions or their spacing (2.3). Because of this Bragg diffraction, a common effect in photonic crystals, is generally avoided.

The application of a macroscopic electric field $E$ causes a polarization $P$ due to the cumulative response of the particles in the sample. The relationship between the macroscopic fields is defined by

$$D = \varepsilon_h E + P. \quad (4.1)$$

The polarization is an average of dipole response of the inclusions. If all of the inclusions are the same, it can be related to their dipole moment $p$,

$$P = Np \quad (4.2)$$

where $N$ is the number of inclusion per unit volume. The dipole moment of an inclusion is a response to the local microscopic electric field $E^{\text{loc}}$ present at the site of the inclusion,

$$p = \varepsilon_h \alpha_e E^{\text{loc}}, \quad (4.3)$$

where $\alpha_e$ is the electric polarizability of the inclusion. In general $\alpha_e$ depends on the shape and composition of a particle. In dense solids there are strong fields due to neighbouring particles, which means that the local field $E^{\text{loc}}$ is not equal to the macroscopic field $E$, but instead includes an additional interaction field $E^{\text{int}}$ due to all of the other inclusions,

$$E^{\text{loc}} = E + E^{\text{int}}. \quad (4.4)$$

The determination of $E^{\text{int}}$ is the main concern in the theory of dielectrics [Scaife, 1998]. Although in principle the interaction field could be evaluated by summing the contributions of every other dipole in the sample [Collin, 1991], this is tricky because the sum is not absolutely convergent [Tretyakov, 2003; Vinogradov, 1997]. Another method, which avoids this problem, is to consider a hypothetical spherical partition around the point in question. The particles inside, being finite in number, can be summed, with the result being zero net field for either completely random arrangements or highly symmetric cubic lattices. The particles outside of the sphere can be treated in a macroscopic way, which results in a
polarization over the sphere, with the result that
\[ \mathbf{E}^{\text{loc}} = \mathbf{E} + \frac{1}{3\varepsilon_h} \mathbf{P}, \] (4.5)
which is known as the Lorentz relation [Kittel, 1996]. Combining the above relationships yields the Clausius-Mossotti relation,
\[ \frac{\varepsilon_{\text{eff}}}{\varepsilon_h} = 1 + \frac{3N\alpha_e}{3 - N\alpha_e}. \] (4.6)
Furthermore, the inclusions in general can also have a magnetic polarizability \( \alpha_m \), and so a dual expression of (4.6) can be written for the effective permeability \( \mu_{\text{eff}} \) of the composite. The Clausius-Mossotti relations for both effective parameters can expressed alternatively as
\[ \frac{\varepsilon_{\text{eff}} - \varepsilon_h}{\varepsilon_{\text{eff}} + 2\varepsilon_h} = \frac{N}{3} \alpha_e, \] (4.7a)
\[ \frac{\mu_{\text{eff}} - \mu_h}{\mu_{\text{eff}} + 2\mu_h} = \frac{N}{3} \alpha_m. \] (4.7b)
These relations connect the macroscopic parameters \( \varepsilon_{\text{eff}} \) and \( \mu_{\text{eff}} \) to the microscopic parameters \( \alpha_e \) and \( \alpha_m \).

The polarizability of an inclusion generally includes losses due to scattering. In the long-wavelength regime infinitely periodic lattices should suffer no such losses because diffraction is suppressed. The losses can be corrected with the substitution [Tretyakov, 2003]
\[ \frac{1}{\alpha} \rightarrow \frac{1}{\alpha} + \frac{k_h^3}{6\pi}, \] (4.8)
which should be applied to both \( \alpha_e \) and \( \alpha_m \).

Although (4.7) (and (4.8) for periodic structures) will be used in the remaining chapters, it should be noted that improvements can be made to the Clausius-Mossotti relations. The model of Rayleigh includes higher multipole terms [Scaife, 1998], which provides better results for larger particle densities. Non-spherical particles can also be treated using the T-matrix method [Waterman and Pedersen, 1986]. A more general approach, which reduces to the Clausius-Mossotti relations, is to assume that the forward scattering amplitude of the particles embedded in the hypothetical effective medium should on average be zero [Stroud and Pan, 1978; Niklasson et al., 1981; Luo, 1997; Bohren, 1986]. This method easily incorporates higher multipole moments of the particles, and can treat non-spherical particles and multi-component mixtures as well.

### 4.1.2 Layer Korringa-Kohn-Rostoker Method

The Clausius-Mossotti model specifies the effective media values with only the polarizabilities and density of the inclusions. The actual arrangement of the spheres, particularly in a periodic lattice, should make little difference on the band structure, as long as the homogenized effective (or Bloch) wavelength is much larger than the inclusions or their spacing. An equivalent condition to be satisfied is that the Bloch
wavevectors should be to the region near the centre of the Brillouin zone, where diffraction is not allowed. When this is true, the effective media values are expected to be isotropic.

To confirm both the Clausius-Mossotti calculations and the isotropy of the metamaterial designs, the effective media values will also be calculated using a numerical method which takes into account multiple scattering between the unit cells and higher multipole contributions. The code MULTEM2 [STEFANOU ET AL., 2000, 1998] implements a photonic analogue of the Korringa-Kohn-Rostoker (KKR) [ASHCROFT AND MERMIN, 1976] method. For this work, the MULTEM2 source code was modified to accommodate materials with Lorentzian and Drude dispersion, and to allow for unit cells made of either a sphere or a coated sphere. The Clausius-Mossotti method and the numerical method will be compared with the effective photon dispersion,

\[ k_{\text{eff}}(\omega) = k'_{\text{eff}}(\omega) + ik''_{\text{eff}}(\omega) = \omega \sqrt{\varepsilon_{\text{eff}}(\omega) \mu_{\text{eff}}(\omega)} \quad \text{such that} \quad k''_{\text{eff}}(\omega) \geq 0. \quad (4.9) \]

The MULTEM2 code is particularly suitable for this confirmation since it is a frequency domain method, so modeling dispersive materials is straightforward. In addition, the KKR method tolerates strongly scattering and highly dispersive structures, which may otherwise cause simple analytical effective media models to fail.

The complex band structure of a three-dimensional periodic crystal is calculated in the layer-KKR method as follows. The particle in a unit cell is specified, as is the frequency and the transverse wavevector components. The scattering properties of the particle are calculated using the T-matrix approach using results from Sec. 3.2. The three-dimensional array of unit cells is partitioned into identical two-dimensional slices, where each slice is perpendicular to the direction of wave propagation. The structure is periodic in the plane of a slice, so the fields can be expanded in a Fourier series in terms of the known transverse Bloch wavevector, which is invariant between slices. A scattering matrix approach relates the fields between the slices by the unknown longitudinal Bloch wavevector component \( k_{\text{eff}} \). The solution of an eigenvalue problem yields the dispersion relation \( k_{\text{eff}}(\omega) \). The only approximations are due to a cutoff in the number of spherical harmonics by setting \( l_{\text{max}} \), and the number of reciprocal lattice vectors taken in each two-dimensional slice.

### 4.2 Materials

The magnetic dipole response of a dielectric sphere has two requirements in order to be suitable as a basis in a metamaterial: the sphere must be sub-wavelength in size (2.3), and the magnetic dipole resonant frequency depends on the size and permittivity (3.43). The combination of these requirements necessitates a sphere material with a large magnitude permittivity, \( |\varepsilon_s/\varepsilon_0| \gtrsim 100 \), via (3.44). Such a large permittivity is not particularly common, and it is often limited to specific frequency ranges in select classes of materials. Similarly, the electric dipole response requires either a equivalently large permittivity due to (3.48) or, by (3.50), a negative permittivity. Although materials with a negative permittivity are common, the property is often restricted in frequency as well.

The following subsections will briefly introduce some non-magnetic materials which are appropriate
for use in metamaterial designs. The materials are separated into three classes based on the underlying physical mechanism which contributes to the large permittivity.

4.2.1 Materials with Dipolar Response

Permanent electric dipoles can arise in any non-symmetric molecule. In gases and liquids, molecules with permanent moments are free to change orientation and align with an applied electric field, usually at microwave and longer wavelengths. Sometimes this mechanism is responsible for a very large relative static permittivity. For example, the static relative permittivity of water\(^1\) is 81 at room temperature [BALANIS, 1989]. Since this orientational mechanism rarely applies to solids, it will not be discussed any further.

Ceramics have dipolar relaxation contributions to the electric permittivity. The application of an electric field causes ions to diffuse within the polycrystalline material, and the overdamped response results in a Debye model of dispersion [MOULSON AND HERBERT, 2003]. The slow response of the ions means that this broadband effect usually disappears at frequencies above approximately 10 GHz. In some ceramics this can cause a large isotropic permittivity; a common example is rutile (one of the forms of titania TiO\(_2\)) which has a polycrystalline relative permittivity ranging between 90–170 [MOULSON AND HERBERT, 2003]. One particular ceramic will be used for the microwave experiments in Chap. 7: MgO–CaO–TiO\(_2\), with broadband \(\varepsilon/\varepsilon_0 = 112 + 0.1i\) and \(\mu/\mu_0 = 1\).

Ferroelectric crystals have a spontaneous electric polarization, and are so named because of the comparison to ferromagnetic materials, which can have a spontaneous magnetic polarization. They are non-centrosymmetric crystals, and there are two stable configurations. At low temperatures, the dipole moments of two sublattices do not cancel each other, which creates a spontaneous moment with hysteresis. At temperatures above the Curie temperature, the sublattices can align and the ferroelectric properties are lost. These materials can have huge relative permittivities, on the order of \(10^5\) [KAO, 2004]. The large permittivity can extend up to THz frequencies, although with reduced magnitude [PERRY ET AL., 1964]. Some common examples are perovskite minerals such as BaTiO\(_3\) and SrTiO\(_3\), and a mixture of the two, Barium Strontium Titanate (Ba\(_x\)Sr\(_{1-x}\)TiO\(_3\)) (BST). Another ferroelectric material is LiTaO\(_3\) [BARKER ET AL., 1970; SCHALL ET AL., 1999], which is often used for its large electro-optic and non-linear optical effects [XU, 1991]. The extremely large permittivity of ferroelectric materials is most often exploited to make very compact microwave devices such as phase shifters and capacitors [DE FLAVIIS ET AL., 1997]. Ferroelectric materials are attractive candidates for use in microwave metamaterials, but since their peculiar properties disappear above far-infrared frequencies, they will not be considered further.

4.2.2 Materials with Ionic Vibrations

Vibrations alter the relative positions of differently charged ions which comprise a material or molecule, causing a net electric polarization. In molecular gases and liquids, there can be many resonant vibrations due to the many modes of stretching, bending, and rotation of the bonds between the nuclei. Similarly, in crystalline solids consisting of two or more atomic species there can be many vibrations depending

\(^1\)See van de Hulst [1981, pp. 281–284] for magnetic dipole scattering from water droplets.
on the symmetries of the crystal lattice. This response can be modeled as a linear superposition of harmonic oscillators, where in each case the ions act effectively as masses bound elastically by a spring. The permittivity follows the Lorentz dispersion model \cite{Kittel,1996},

\[
e(\omega) = \epsilon_\infty \left(1 + \frac{\omega_L^2 - \omega_T^2}{\omega_T^2 - \omega^2 - i\omega\gamma}\right),
\]

where \(\omega_T\) and \(\omega_L\) are the transverse and longitudinal frequencies, \(\epsilon_\infty\) is the permittivity for \(\omega \gg \omega_T\), and \(\gamma\) is a damping constant. The permittivity at frequencies much lower than the resonance \(\omega \ll \omega_T\) is \(\epsilon_0\), which is related to the other constants by the Lyddane-Sachs-Teller (LST) relation,

\[
\frac{\omega_L^2}{\omega_T^2} = \frac{\epsilon_0}{\epsilon_\infty}.
\]

The transverse frequency \(\omega_T\) is approximately the center frequency of the resonance where \(1/e(\omega_T) \approx 0\), and the longitudinal frequency \(\omega_L\) is when \(e(\omega_L) \approx 0\), as long as \(\gamma \ll \omega_T\). For \(\omega_T < \omega < \omega_L\), the permittivity is negative, \(\text{Re}\{e(\omega)\} < 0\).

The normal modes of the interaction of light (comprised of photons) and ionic vibrations (comprised of phonons) are known as phonon-polaritons. Near the resonant frequency \(\omega_T\) this can be a very strong interaction, and as a result some materials will have a very large permittivity at nearby frequencies. The large dielectric constant, and not necessarily the resonant response, makes such materials a suitable choice for constructing magnetic metamaterials. The larger the permittivity, the easier it is to create a negative effective permeability. The resonant frequencies of phonon-polaritonic modes are found at far-to mid-infrared frequencies.

Silicon carbide (SiC) has one of the highest phonon-polaritonic resonant frequencies \(\omega_T\), and a moderately large \(\epsilon_0\). This combination makes it an attractive candidate for dielectric-based infrared
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Metamaterials. Although there are many crystallographic types of SiC (see Sec. 5.1), the permittivity of all of them are very similar, even for the uniaxial types [Spitzer et al., 1959a,b]. Therefore, the exact morphological form of SiC will be ignored in the theoretical models of this chapter, and the permittivity can be fit to the Lorentzian dispersion model (4.10), where [Spitzer et al., 1959a,b; Kittel, 1996]

\[
\begin{align*}
\omega_T &= 790 \text{ cm}^{-1}, \\
\omega_L &= 966 \text{ cm}^{-1}, \\
\gamma &= 5 \text{ cm}^{-1}, \\
\epsilon_\infty &= 6.7.
\end{align*}
\]

(4.12)

An inverse centimetre (cm\(^{-1}\)) is a unit of frequency, commonly used in infrared spectroscopy. The conversion to an SI unit is

\[
1 \text{ cm}^{-1} = 0.03 \text{ THz}.
\]

(4.13)

The relative permittivity of SiC is plotted in Fig. 4.1.

4.2.3 Materials with Electronic Vibrations

The electronic contribution to the permittivity is similar to the ionic response, in that the distortion or displacement of electrons relative to the nuclei causes a net electric polarization. In general the permittivity can be fit, to a first approximation, to the Lorentz dispersion model (4.10). In metals, however, electrons are not bound to particular ions; they are free carriers of charge. The same is true for doped semiconductor crystals. In the harmonic oscillator model, free carriers have no restoring force, which implies that \(\omega_T = 0\) in (4.10). This leads to the Drude dispersion model [Kittel, 1996],

\[
\epsilon(\omega) = \epsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}\right),
\]

(4.14)

where \(\omega_p = \omega_L\) is the plasma frequency. The plasma frequency is related to the density of free carriers \(N_c\) by [Yu and Cardona, 2001]

\[
\omega_p^2 = \frac{N_ce^2}{m^*\epsilon_\infty},
\]

(4.15)

where \(e = 1.6 \times 10^{-19} \text{ C}\) is the fundamental charge and \(m^*\) is the effective mass of the carriers. The free carriers are screened by the dielectric background \(\epsilon_\infty\). Metals typically have a large concentration of free electrons, therefore \(\omega_p\) is usually in the ultra-violet range of frequencies.

Doped semiconductors can be designed to have \(\omega_p\) in the infrared frequency range. For \(n\)-type silicon, \(m^* = 0.27m_0\) [Spitzer and Fan, 1957], where \(m_0 = 9.1 \times 10^{-31} \text{ kg}\) is the mass of a free electron, and \(\epsilon_\infty/\epsilon_0 = 11.7\) [Kittel, 1996]. Then from (4.15),

\[
\omega_p = 31.7\sqrt{N_c},
\]

(4.16)

where \(N_c\) has units of \(\text{m}^{-3}\). The range the range of frequencies \(\omega < \omega_p\) where \(\text{Re} \{\epsilon\} < 0\) is controllable by
choosing the doping concentration.

4.3 Metamaterials made of Non-Magnetic Inclusions

The electromagnetic response of a metamaterial is due to the response of its constituent inclusions. The polarizabilities $\alpha_e$ and $\alpha_m$ of spherically symmetric inclusions are found in (3.34). For solid spheres the scattering coefficients $a_1$ and $b_1$ are the Mie coefficients (3.32), and for coated spheres the coefficients are (3.57). These quantities can be substituted into the Clausius-Mossotti relations (4.6) to yield the effective permittivity $\epsilon_{\text{eff}}$ and permeability $\mu_{\text{eff}}$ of the metamaterial,

\[
\frac{\epsilon_{\text{eff}}}{\epsilon_h} = \frac{k_h^3 + 4\pi i N a_1}{k_h^3 - 2\pi i N a_1},
\]

\[
\frac{\mu_{\text{eff}}}{\mu_h} = \frac{k_h^3 + 4\pi i N b_1}{k_h^3 - 2\pi i N b_1}.
\]

An alternate form follows from (4.7),

\[
\frac{\epsilon_{\text{eff}}}{\epsilon_h} = 1 + N \left[ \frac{k_h^3}{6\pi i a_1} - \frac{N}{3} \right]^{-1},
\]

\[
\frac{\mu_{\text{eff}}}{\mu_h} = 1 + N \left[ \frac{k_h^3}{6\pi i b_1} - \frac{N}{3} \right]^{-1}.
\]

The equivalent forms (4.17) and (4.18) are valid for random mixtures having particle volume density $N$. For periodic lattices, the scattering correction (4.8) should be applied. Substituting (3.34) for spherically-symmetric particles into (4.8) results in the transformations

\[
\frac{1}{a_1} \rightarrow \frac{1}{a_1} - 1 \quad \text{and} \quad \frac{1}{b_1} \rightarrow \frac{1}{b_1} - 1.
\]

This correction for periodic structures leads to the effective media values

\[
\frac{\epsilon_{\text{eff}}}{\epsilon_h} = 1 + N \left[ \frac{k_h^3}{6\pi i a_1} - \frac{N}{3} \right]^{-1},
\]

\[
\frac{\mu_{\text{eff}}}{\mu_h} = 1 + N \left[ \frac{k_h^3}{6\pi i b_1} - \frac{N}{3} \right]^{-1}.
\]

These equations determine the effective electromagnetic parameters of the metamaterial composite in the long-wavelength limit. They depend on the frequency of the excitation, as well as the radius, density, and material composition of the spheres. The form (4.17) has also been derived by DOYLE [1989]; GRIMES AND GRIMES [1991]; RUPPIN [2000]. These expressions are sometimes referred to as the extended Maxwell-Garnet model. The effective refractive index $n_{\text{eff}}$ can be calculated using (2.6).

The concentration of the inclusions can be expressed either by the number per unit volume $N$, or as a
volume filling fraction $f$, which are related by

$$f = Nv,$$  \hspace{1cm} (4.21)

where $v$ is the volume of the inclusions. For periodic structures this can be expressed in terms of the unit cell dimensions. The only lattice that will be considered here is the simple cubic lattice, for which the unit cell is a cube. The edge length of the cube is the lattice constant $a$, and the volume is $a^3$, so

$$N = \frac{1}{a^3}. \hspace{1cm} (4.22)$$

The general model of metamaterials made from spherically symmetric dielectric particles is complete. The remaining subsections develop specific results for designs using either solid spheres or coated spheres as the lattice basis. Some design examples with numerical verification will also be presented.

### 4.3.1 Basis of Solid Spheres

A good approximation to the effective media values of a metamaterial made from dielectric spheres is obtained by substituting the approximate Mie coefficients (3.37) into the Clausius-Mossotti relations (4.18),

$$\frac{\varepsilon_{eff}}{\varepsilon_h} = 1 + \frac{3f}{\frac{\varepsilon_s F(n_s x) + 2\varepsilon_h}{\varepsilon_s F(n_s x) - \varepsilon_h} - f}^{-1}, \hspace{1cm} (4.23a)$$

$$\frac{\mu_{eff}}{\mu_0} = 1 + \frac{3f}{\frac{F(n_s x) + 2}{F(n_s x) - 1} - f}^{-1}, \hspace{1cm} (4.23b)$$

where the filling fraction $f$ is the volume fraction of the spheres,

$$f = \frac{4\pi}{3} N r_s^3. \hspace{1cm} (4.24)$$

These approximate forms were first derived by Lewin [1947]. Applying the radiation correction (4.19) yields

$$\frac{\varepsilon_{eff}}{\varepsilon_h} = 1 + \frac{3f}{\frac{\varepsilon_s F(n_s x) + 2\varepsilon_h}{\varepsilon_s F(n_s x) - \varepsilon_h} - f + i \frac{2}{3} (n_h x)^3}^{-1}, \hspace{1cm} (4.25a)$$

$$\frac{\mu_{eff}}{\mu_0} = 1 + \frac{3f}{\frac{F(n_s x) + 2}{F(n_s x) - 1} - f + i \frac{2}{3} (n_h x)^3}^{-1}. \hspace{1cm} (4.25b)$$

The radiation correction has added the last term in the square brackets, but since $n_h x \ll 1$, it provides negligible improvement over (4.23). Even so, (4.23) will only be used to analytically estimate the resonant properties of $\varepsilon_{eff}$ and $\mu_{eff}$; all other calculations will be done using the original form, either (4.18) or (4.20). Therefore, the radiation-corrected approximate form (4.25) will not be considered further.

When a metamaterial is formed from a random or periodic collection of dielectric spheres, the bulk responses $\varepsilon_{eff}$ and $\mu_{eff}$ will differ somewhat from the properties of an isolated sphere. That is, the electric or
magnetic dipole resonances of the isolated spheres will be altered due to interactions among neighbouring spheres. The metamaterial properties can be engineered by estimating the resonant frequencies.

**Permeability Resonances**

The resonant frequency $\omega_\mu$ of the effective permeability $\mu_{\text{eff}}$ of a metamaterial can be estimated from $1/\mu_{\text{eff}} = 0$ and using (4.23b). The resonant condition is

$$F(n_sX) = \frac{f + 2}{f - 1} = -2 + \frac{3f}{f - 1}. \quad (4.26)$$

Since $f$ should be at most moderately smaller than unity, this resonant condition is not greatly different than that for the isolated magnetic dipole mode, (3.39). Therefore, the approximation of $F(n_sX)$ from (3.45) can be used, which yields the approximate resonant condition of the $q$-th harmonic of the permeability resonance,

$$n_sX \approx \pi q - \frac{3}{\pi q} \left( \frac{f}{f + 2} \right). \quad (4.27)$$

By comparing this with the same condition for an isolated sphere (3.41), it can be seen that the second term on the right-hand side contains the loading effect of the composite through the filling fraction $f$.

The loading will tend to decrease the resonant frequency. For spheres made of a material with Lorentz dispersion, the resonant frequency $\omega_\mu$ can be estimated by assuming $\gamma \approx 0$ in (4.10) and substituting this into the resonant condition (4.27),

$$\omega_\mu^2 \approx \frac{1}{2} \left[ \left( \omega_L^2 + \Omega^2 \right) - \sqrt{\left( \omega_L^2 + \Omega^2 \right)^2 - 4\Omega^2 \omega_L^2} \right],$$

where

$$\Omega = \frac{\pi c}{r_s \sqrt{\epsilon_\infty}} \left[ q - \frac{3}{\pi^2 q} \left( \frac{f}{f + 2} \right) \right]. \quad (4.28)$$

The second term in the square brackets of $\Omega$ indicates that an increased loading $f$ lowers the resonant frequency.

**Permittivity Resonances**

The resonant frequency $\omega_\varepsilon$ of the effective permittivity $\varepsilon_{\text{eff}}$ of a metamaterial can be estimated from $1/\varepsilon_{\text{eff}} = 0$ and using (4.23a). The resonant condition is

$$F(n_sX) = \frac{\varepsilon_b}{\varepsilon_i} \left( \frac{f + 2}{f - 1} \right). \quad (4.29)$$

Again, comparing with (3.46), the loading of the composite is manifested through $f$.

Two classes of electric dipole modes were investigated in Sec. 3.5.1. Bulk modes may arise if $|\varepsilon_b| \gg |\varepsilon_i|$, in which case (4.29) simplifies to $F(n_sX) \approx 0$. This effectively nullifies the loading effect of the composite, and the resonant condition is the same as that for an isolated sphere, (3.48). For spheres made of a material with Lorentz dispersion, the resonant frequency $\omega_\varepsilon$ can be estimated by assuming $\gamma \approx 0$ in (4.10) and
substituting this into the resonant condition (3.48),

\[
\omega_\varepsilon^2 = \frac{1}{2} \left( \omega_L^2 + \Omega^2 \right) - \sqrt{\left( \omega_L^2 + \Omega^2 \right)^2 - 4 \Omega^2 \omega_T^2},
\]

where \( \Omega = \frac{4.49c}{r_s \sqrt{\varepsilon_\infty}} \).

Surface modes may arise if \( \text{Re} \{ \varepsilon_s \} < 0 \). Using (3.49), the resonant condition (4.29) simplifies to

\[
\varepsilon_s(\omega_\varepsilon) = \varepsilon_h \left( \frac{f + 2}{f - 1} \right),
\]

This condition is independent of the absolute size of the spheres \( r_s \). For spheres made of a material with Lorentzian dispersion, the resonant frequency is

\[
\omega_\varepsilon \approx \frac{\sqrt{\varepsilon_\infty \omega_L^2 - \varepsilon_h \omega_T^2}}{\frac{f + 2}{f - 1}}.
\]

A metamaterial made of a single set of identical spheres can have resonances in both the permittivity and permeability, but not simultaneously. Two cases have been considered: on one hand, when \( |\varepsilon_s| \gg |\varepsilon_h| \), the resonant frequencies of \( \mu_{\text{eff}} \) (4.28) and \( \varepsilon_{\text{eff}} \) (4.30) cannot be equal. On the other hand, when \( \text{Re} \{ \varepsilon_s \} < 0 \), only there can be a resonance in \( \varepsilon_{\text{eff}} \) only, at the frequency such that (4.31) is satisfied. In either case, such metamaterials cannot be designed to have a negative index, but instead either a negative permeability or permittivity metamaterials can be produced. The next two subsections will present two design examples.

4.3.2 Design Example: SiC Spheres

Silicon carbide has frequency ranges where \( |\varepsilon_s| \gg |\varepsilon_h| \) and \( \text{Re} \{ \varepsilon_s \} < 0 \), because of its phonon-polariton resonance, as shown in Fig. 4.1. Therefore, a metamaterial composed with a SiC sphere as its basis can be designed to have frequency ranges with negative permeability or negative permittivity.

Consider a single SiC sphere having a diameter \( 2r_s = 2 \mu \text{m} \). The intent is to use this sphere as the periodic inclusion for a metamaterial, but first the scattering properties of this single sphere can be studied. Resonant frequencies of the electric \( a_1 \) and magnetic \( b_1 \) dipole scattering coefficients can be estimated from (3.42), (3.48), and (3.50). This leads to the following predictions:

1. Resonant bulk magnetic dipole mode at 754 cm\(^{-1} \) (first harmonic; \( q = 1 \)).
2. Resonant bulk electric dipole mode at 773 cm\(^{-1} \).
3. Resonant bulk magnetic dipole mode at 782 cm\(^{-1} \) (second harmonic; \( q = 2 \)).
4. Resonant surface electric dipole mode at 928 cm\(^{-1} \).
Figure 4.2: Magnitudes of the Mie scattering coefficients of a SiC sphere, having diameter $2r_s = 2 \mu m$. The curves are: $|a_1|$ electric dipole, $|b_1|$ magnetic dipole, $|a_2|$ electric quadrupole, and $|b_2|$ magnetic quadrupole. The arrows denote analytically-approximated resonant frequencies of $a_1$ and $b_1$.

The magnitudes of the exact dipole and quadrupole scattering coefficients are shown in Fig. 4.2, along with arrows denoting the approximate resonant frequencies listed above. The estimated resonances are generally quite accurate. The electric and magnetic dipole terms are dominant over the entire frequency range shown, so it is acceptable to conveniently simplify the calculations by neglecting the quadrupole and all other higher-order multipole terms. The most important feature of the curves in Fig. 4.2 is that the magnetic dipole term is dominant around its resonance at $754 \text{ cm}^{-1}$, making the sphere to a good approximation an ideal magnetic dipole scatterer at that frequency, and thus it may be used as an inclusion for a magnetic metamaterial.

Assume now that many of these SiC spheres are arranged into a composite having filling fraction $f = 26.8\%$. If it is a periodic arrangement in a simple cubic lattice, this corresponds to a lattice constant $a = 2.5 \mu m$. This is sufficient information to estimate the resonant frequencies in $\mu_{\text{eff}}$ and $\varepsilon_{\text{eff}}$. From the results of Sec. 4.3.1, the following resonances can be predicted:

1. Resonant $\mu_{\text{eff}}$ due to bulk magnetic dipole mode at $751 \text{ cm}^{-1}$ (first harmonic; $q = 1$).
2. Resonant $\varepsilon_{\text{eff}}$ due to bulk electric dipole mode at $773 \text{ cm}^{-1}$.
3. Resonant $\mu_{\text{eff}}$ due to bulk magnetic dipole mode at $781 \text{ cm}^{-1}$ (second harmonic; $q = 2$).
4. Resonant $\varepsilon_{\text{eff}}$ due to surface electric dipole mode at $914 \text{ cm}^{-1}$.

The effective media values for this design are plotted in Fig. 4.3. These were calculated using the radiation-corrected Clausius-Mossotti equations (4.20). All four of the predicted resonances are denoted by arrows. The resonance in $\mu_{\text{eff}}$ around $751 \text{ cm}^{-1}$ is excited strongly enough that the permeability is negative for frequencies above the resonance. The resonances in $\varepsilon_{\text{eff}}$ around $773 \text{ cm}^{-1}$ and $\mu_{\text{eff}}$ around $782 \text{ cm}^{-1}$ are
Figure 4.3: The real (solid) and imaginary (dashed) effective medium values of a metamaterial consisting of SiC spheres, with filling fraction 26.8%. Each sphere diameter is 2 μm. The arrows denote the analytically-approximated resonant frequencies.
also seen, but they are both only weakly excited. The strong resonance in \( \varepsilon_{\text{eff}} \) around 900 cm\(^{-1} \) is indeed due to the surface electric dipole modes, although this is a noticeably different frequency than the simple estimate of 914 cm\(^{-1} \). The frequency is reduced by the finite size of the sphere, which would be revealed if the resonant condition (4.31) were derived with a more accurate approximation akin to (3.51). Nonetheless, this strongly excited resonance causes the permittivity to be negative.

The effective media values shown in Fig. 4.3 demonstrate quite clearly that this metamaterial no longer has the properties of the constituent material, SiC. Indeed, looking back to the permittivity of SiC in Fig. 4.1, what is a single strong and broad resonance in the permittivity become a set of various different resonances in \( \varepsilon_{\text{eff}} \) and \( \mu_{\text{eff}} \). Particularly striking is that bulk SiC is almost completely reflective at \( \omega = \omega_T \), since the relative power reflected from an infinite slab [BALANIS, 1989] would be

\[
\lim_{\omega \to \omega_T} |\Gamma'(\omega)|^2 = \left| \frac{\eta_{\text{SiC}}(\omega) - \eta_h}{\eta_{\text{SiC}}(\omega) + \eta_h} \right|^2 \to 1, \tag{4.33}
\]

where \( \eta_{\text{SiC}} = \sqrt{\mu_0/\varepsilon_{\text{SiC}}} \). In contrast, this metamaterial is essentially transparent at the same frequency. Around \( \omega = \omega_T \), \( \varepsilon_{\text{eff}}/\varepsilon_0 \approx 2.22 + i0.05 \), \( \mu_{\text{eff}}/\mu_0 \approx 0.73 + i0.06 \), and \( \eta_{\text{eff}} = \sqrt{\mu_{\text{eff}}/\varepsilon_{\text{eff}}} \approx 0.57 \). Therefore the relative power reflected from an infinite slab of this metamaterial is

\[
\lim_{\omega \to \omega_T} |\Gamma'(\omega)|^2 = \left| \frac{\eta_{\text{eff}}(\omega) - \eta_h}{\eta_{\text{eff}}(\omega) + \eta_h} \right|^2 \approx 0.08. \tag{4.34}
\]

The effective media values can be compared with results using the layer-KKR method described in Sec. 4.1.2. The Bloch wavevector was calculated along the \( \Gamma X \), \( \Gamma M \), and \( \Gamma R \) directions. The complex dispersion relation \( k_{\text{eff}}(\omega) \) is compared via (4.9), and the results are shown in Fig. 4.4. Although the layer-KKR method does not converge well in the regions of high loss, it is clear that there are frequency bands of anomalous dispersion due to the permeability resonance around 750 cm\(^{-1} \) and the permittivity resonance around 900 cm\(^{-1} \). In the anomalous dispersion regions, the phase velocity \( v_p = \omega/k > 0 \) but the group velocity \( v_g = \partial \omega/\partial k < 0 \). That is, they are regions of negative group velocity.\(^2\) All of the curves generally match closely, particularly for frequencies away from the regions of anomalous dispersion and far from the Brillouin zone edges. That is, \( \mu_{\text{eff}} \) and \( \varepsilon_{\text{eff}} \) are isotropic except when the losses are large or the effective values are so large as to induce Bragg scattering near the Brillouin zone edges. When either \( \text{Re}\{\mu_{\text{eff}}\} \) or \( \text{Re}\{\varepsilon_{\text{eff}}\} \) are negative, the dispersion relation bends to the left of the light line, but even then the metamaterial remains isotropic.

The resonances in \( \mu_{\text{eff}} \) and \( \varepsilon_{\text{eff}} \) are due to the localized dipole resonances in each sphere comprising the metamaterial. In the long-wavelength regime they are independent of the lattice structure or unit cell size \( a \). When the resonances are very strong, however, \( \text{Re}\{n_{\text{eff}}\} \) becomes very large, and the Bloch wavevector \( \lambda_{\text{eff}} = 2\pi/\text{Re}\{k_{\text{eff}}\} \) decreases to be on the order of the lattice size \( \lambda_{\text{eff}} \sim a \). This results in Bragg scattering, which is an important effect in photonic crystals, and occurs when \( \text{Re}\{k_{\text{eff}}\} \) is close to the Brillouin zone.

\(^2\)A negative group velocity means that the group delay of a pulse traveling through the structure is negative. That is, if a pulse in this frequency range were applied to a slab of this material, the peak of the output would precede the peak of the input [WOODY AND MOJAHEDI, 2004]. This does not violate causality, since attenuation accompanies the anomalous dispersion [MOJAHEDI ET AL., 2000; SIDDQUI ET AL., 2003].
boundaries. When this happens, the moments in neighboring particles are oppositely directed. Before the advent of photonic crystals, this same breakdown of the macroscopic effective medium description caused by strongly resonant inclusions was studied, and named an antiferromagnetic-like phenomenon [Sipe and Kranendonk, 1974]. Although this effect is not captured in the effective medium model, it can in principle be captured in the layer-kkr method, although it happens to coincide with the lossy regions where the solutions have been discarded in Fig. 4.4. This Bragg scattering occurs in this example around 745 cm\(^{-1}\) and 900 cm\(^{-1}\).

### 4.3.3 Design Example: Doped Si Spheres

Silicon is a semiconductor that can be doped with an \(n\)-type impurity to obtain a Drude model dispersion (4.14). Then it will have frequencies such that \(\text{Re} \{\epsilon_s\} < 0\), and sub-wavelength spheres made of such material can support only surface electric dipole modes. Therefore, a metamaterial consisting of such spheres as its basis can be designed to have a frequency range with negative permittivity.

Consider a design where spheres are made of \(n\)-type Si, which is doped to a concentration \(N_c = 2 \times 10^{19}\) cm\(^{-3}\). Using (4.16) the plasma frequency is \(\omega_p = 761\) cm\(^{-1}\), and assume that \(\gamma \approx 1\) cm\(^{-1}\). Each sphere has diameter \(2r_s = 2.1\) \(\mu\)m, and the filling fraction is \(f = 31.0\%\). If the spheres are arranged in a simple cubic lattice, this corresponds to a lattice constant \(a = 2.5\) \(\mu\)m.

Since the Drude dispersion model is a special case of the Lorentz dispersion model such that \(\omega_T = 0\)
and \( \omega_L = \omega_p \), the resonant frequency of \( \epsilon_{\text{eff}} \) can be estimated from (4.32),

\[
\omega_c = \omega_p \left[ 1 - \frac{\epsilon_h}{\epsilon_\infty} \left( \frac{f + 2}{f - 1} \right) \right]^{-1/2}.
\]  

(4.35)

For the given design parameters, the resonant frequency is \( \omega_c \approx 671 \, \text{cm}^{-1} \).

The effective media values for this design are plotted in Fig. 4.5. These were calculated using the radiation-corrected Clausius-Mossotti equations (4.20). The predicted resonance in \( \epsilon_{\text{eff}} \) can be seen centered around 650 cm\(^{-1}\), which is reasonably close to the estimated resonant frequency. It is a very strong resonance with large negative permittivity at frequencies above the resonance. The values for \( \mu_{\text{eff}} \) do not vary significantly from unity, varying from slightly diamagnetic to slightly paramagnetic across the range shown in the figure.

The effective media values shown in Fig. 4.5 demonstrate quite clearly that this metamaterial no longer has the properties of the constituent material, \( n\)-Si. Indeed, because of the \( n\)-type free carriers, the constituent semiconductor is highly reflective for \( \omega < \omega_p \), where \( \text{Re} \{ \epsilon_i \} < 0 \). In contrast, the metamaterial composite is highly reflective only in the comparatively narrow bandwidth between 650 cm\(^{-1}\) and 730 cm\(^{-1}\) where \( \text{Re} \{ \epsilon_{\text{eff}} \} < 0 \).
Figure 4.6: The real (left side) and imaginary (right side) parts of the dispersion relation of a simple cubic lattice of doped Si spheres. The lattice constant is \( a = 2.5 \mu m \), and the diameter of the spheres is \( 2r_s = 2.1 \mu m \). The light line is the dispersion in vacuum.

The effective media values can be compared with results using the layer-k \textit{krr} method described in Sec. 4.1.2. The Bloch wavevector was calculated along the \( \Gamma X, \Gamma M, \) and \( \Gamma R \) directions. The complex dispersion relation \( k_{\text{eff}}(\omega) \) is compared via (4.9), and the results are shown in Fig. 4.6. Although the layer-k \textit{krr} method does not converge well in the regions of high loss, it is clear that there this band of anomalous dispersion due to the permittivity resonance between 650 cm\(^{-1}\) to 725 cm\(^{-1}\). All of the curves generally match closely, particularly for frequencies away from the regions of anomalous dispersion and far from the Brillouin zone edges. That is, as long as \( \varepsilon_{\text{eff}} \) is not too large or too lossy, then the numerical results confirm that the metamaterial is isotropic.

### 4.3.4 Basis of Coated Spheres

A good approximation to the effective media values of a metamaterial made from coated dielectric spheres is obtained by substituting the approximated scattering coefficients (3.61) into the Clausius-Mossotti relations (4.18),

\[
\frac{\varepsilon_{\text{eff}}}{\varepsilon_h} = 1 + 3f \left[ \frac{\varepsilon_F + 2\varepsilon_h}{\varepsilon_F - \varepsilon_h} - f \right]^{-1}, \quad (4.36a)
\]

\[
\frac{\mu_{\text{eff}}}{\mu_0} = 1 + 3f \left[ \frac{1}{\tau} \left( \frac{F(n_1x)}{F(n_1x) - 1} - f \right) \right]^{-1}, \quad (4.36b)
\]
where the filling fraction $f$ is the volume fraction of the coated spheres,

$$f = \frac{4\pi}{3} Nr^3. \quad (4.37)$$

Applying the radiation correction (4.19) yields

$$\frac{\varepsilon_{\text{eff}}}{\varepsilon_h} = 1 + 3f \left[ \frac{\varepsilon_2 F_A + 2\varepsilon_h}{\varepsilon_2 F_A - \varepsilon_h} - f + i\frac{2}{3} (n_h y)^3 \right]^{-1}, \quad (4.38a)$$

$$\frac{\mu_{\text{eff}}}{\mu_0} = 1 + 3f \left[ \frac{1}{\tau} \cdot \frac{F(n_1 x) + 2}{F(n_1 x) - 1} - f + i\frac{2}{3} (n_h y)^3 \right]^{-1}. \quad (4.38b)$$

The radiation correction has added the last term in the square brackets, but since $n_h y \ll 1$, it provides negligible improvement over (4.36). Even so, (4.36) will only be used to analytically estimate the resonant properties of $\varepsilon_{\text{eff}}$ and $\mu_{\text{eff}}$; all other calculations will be done using the exact form, either (4.18) or (4.20). Therefore, the radiation-corrected approximate form (4.38) will not be considered further.

When a metamaterial is formed from a random or periodic collection of coated dielectric spheres, the bulk responses $\varepsilon_{\text{eff}}$ and $\mu_{\text{eff}}$ will differ somewhat from the properties of an isolated coated sphere. That is, any electric or magnetic dipole resonances of the isolated coated spheres will be altered due to interactions among neighbouring coated spheres. In order to design the metamaterial properties, the resonant frequencies will be estimated, for the case where $|\varepsilon_1| \gg |\varepsilon_2|$.

**Permeability Resonances**

By comparing (4.23b) and (4.36b), it can be seen that the coating does not affect the resonant condition. That is, the resonant condition from (4.36b) is

$$F(n_1 x) = \frac{f \tau + 2}{f \tau - 1}, \quad (4.39)$$

where $f \tau = f_{\text{core}} = 4\pi Nr_1^3/3$ is the filling fraction of the core only, and $\tau$ is defined in (3.63). This resonant condition is only true because of the design restriction that $|\varepsilon_1| \gg |\varepsilon_2|$, or (3.60), either of which imply that the shell is of negligible electrical thickness and has no effect on the bulk magnetic dipole resonance supported within the core. Therefore the resonances in $\mu_{\text{eff}}$ can be found by applying the substitutions $r_s \rightarrow r_1$ and $\varepsilon_s \rightarrow \varepsilon_1$, $n_s \rightarrow n_1$, and $f \rightarrow f_{\text{core}}$ to the results of Sec. 4.3.1.

**Permittivity Resonances**

Unlike with the permeability, both the core and the shell contribute to the electric dipole response of a coated sphere, making the design more complicated. Although both bulk and surface modes can be supported, only the surface mode will be considered here. The resonant frequency $\omega_e$ of the effective
permittivity $\varepsilon_{\text{eff}}$ of a metamaterial can be estimated from $1/\varepsilon_{\text{eff}}$ and using (4.36a) and (3.65).

$$\varepsilon_2(\omega) = \varepsilon_\mu \left( \frac{f + 2}{f - 1} \right) \left( \frac{1 - \tau}{1 + 2\tau} \right).$$  \hspace{1cm} (4.40)

For a coating made of a material with Drude dispersion, the resonant frequency $\omega_r$ can be estimated by assuming $\gamma \approx 0$ in (4.14) and substituting this into the resonant condition (4.40),

$$\omega_r = \omega_p \left[ 1 - \frac{\varepsilon_\mu}{\varepsilon_\infty} \left( \frac{f + 2}{f - 1} \right) \left( \frac{1 - \tau}{1 + 2\tau} \right) \right]^{-1/2}. \hspace{1cm} (4.41)$$

The term in the square brackets is smaller than the corresponding term for a solid sphere in (4.35). Equivalently, for a coated core $\tau \neq 0$, and the square-bracketed term is smaller than the case without a core, $\tau = 0$. Therefore, the resonant frequency is raised because of the thickness of the coating.

### 4.3.5 Design Example: SiC Spheres Coated with Doped Si

A negative index metamaterial can be designed using a coated dielectric sphere as the basis. The design of the core can be tuned to provide $\mu_{\text{eff}} < 0$, and then the coating can be designed to provide a simultaneous $\varepsilon_{\text{eff}} < 0$. The design example of the metamaterial consisting of a solid SiC spheres in Sec. 4.3.2 has a band with $\text{Re} \{ \mu_{\text{eff}} \} < 0$, so it may be used as a core. Applying a coating with $|\varepsilon_2| \ll |\varepsilon_1| = |\varepsilon_{\text{SiC}}|$ at the same frequencies will not affect the response of the core. Therefore, the core diameter will be $2r_1 = 2 \mu$ m. Keeping the same core volume filling fraction $f_{\text{core}} = 26.8\%$, the resonant frequency of $\mu_{\text{eff}}$ is $\omega_\mu \approx 751 \text{ cm}^{-1}$.

The doped Si spheres, from the example in Sec. 4.3.3, can be hollowed out to make a thin coating. The outer diameter is $2r_2 = 2.1 \mu$m. Using (3.63), $\tau = 0.86$. The lattice constant will be $a = 2.5 \mu$m as before. Using (4.37) and (4.22), the volume filling fraction of the coated sphere is $f = 31.0\%$. The doped Si shell provides a surface electric dipole response which causes a resonance in $\varepsilon_{\text{eff}}$ at $\omega_r \approx 755 \text{ cm}^{-1}$, as predicted by (4.41).

The effective media values for this design are plotted in Fig. 4.7. These were calculated using the radiation-corrected Clausius-Mossotti equations (4.20). There are resonances in both $\varepsilon_{\text{eff}}$ and $\mu_{\text{eff}}$, with resonant frequencies very close to the predicted values, which are denoted by arrows. The overlap in the resonances has caused a bandwidth of $\text{Re} \{ n_{\text{eff}} \} < 0$. Note that there is a frequency where $\text{Re} \{ n_{\text{eff}} \} = -1$, which is an important criterion for sub-wavelength focusing [PENDRY, 2000]. The attenuation is quite moderate at these frequencies. The presence of loss is an inevitable consequence of the underlying resonances, but the losses are smaller at frequencies away from the center of the resonances. This is why it is better, as shown in Fig. 4.7, that the resonances in $\varepsilon_{\text{eff}}$ and $\mu_{\text{eff}}$ are staggered so that the two resonances do not directly overlap, and the losses in the bandwidth of $\text{Re} \{ n_{\text{eff}} \} < 0$ are reduced.

The figure of merit of a metamaterial is usually defined as $|\text{Re} \{ n_{\text{eff}} \}| / \text{Im} \{ n_{\text{eff}} \}$, and this is plotted in Fig. 4.8. Large values are associated with small losses. The value at the frequency for which $\text{Re} \{ n_{\text{eff}} \} = -1$ is quoted most often, since this is the condition most sought for imaging applications. For this design this condition occurs at $756 \text{ cm}^{-1}$, and the figure of merit is 1.11. Although larger figures of merit have been reported for other classes of metamaterials [VALENTINE ET AL., 2008], this is an example design only;
Figure 4.7: The real (solid) and imaginary (dashed) effective medium values of a metamaterial consisting of SiC spheres coated with doped Si, with filling fraction 31.0%. Each core diameter is $2r_1 = 2.0 \mu m$, and the coating diameter is $2r_2 = 2.1 \mu m$. The arrows denote the analytically-approximated resonant frequencies.

Figure 4.8: Figure of merit for the metamaterial described in the caption of Fig. 4.7.
other designs could have a larger figure of merit.

The effective media values can be compared with results using the layer-KKR method described in Sec. 4.1.2. The Bloch wavevector was calculated along the ΓX, ΓM, and ΓR directions. The complex dispersion relation $k_{\text{eff}}(\omega)$ is compared via (4.9), and the results are shown in Fig. 4.9. Although the layer-KKR method does not converge well in the regions of high loss, it is clear that there are frequency bands of anomalous dispersion due to the resonances in $\varepsilon_{\text{eff}}$ and $\varepsilon_{\text{eff}}$. The curves generally match closely, for frequencies away from the regions of anomalous dispersion and far from the Brillouin zone edges. They match particularly well for $\omega > 755$ cm$^{-1}$. In these ranges numerical results confirm that the metamaterial is isotropic.

The metamaterial has Re $\{n_{\text{eff}}\} < 0$ in the band $754$ cm$^{-1} < \omega < 759$ cm$^{-1}$. The layer-KKR method shows that this region is isotropic. The dispersion relation shows the transition between negative and positive index is around $\omega > 759$ cm$^{-1}$, where the branches of the dispersion relation cross each other and through $k'_{\text{eff}} = 0$. At the frequencies below this, the branch where $k'_{\text{eff}} < 0$ contains the valid solutions, since the losses are low or moderate, and therefore the group velocity $v_g = \partial \omega/\partial k$ must be positive. Since $v_p < 0$ in this range, these are backward wave solutions (2.7), which confirms that this is a negative index metamaterial.

In this section several design examples of metamaterials have been given, predominately based on spheres made of SiC. More detailed properties of SiC, the methods of its fabrication, and the fabrication and characterization of SiC-based metamaterials will be the content of the next chapter.
Chapter 5

Fabrication of Silicon Carbide Spheres

Silicon carbide was shown to be a good material with which to make infrared metamaterials in the previous chapter. This chapter presents the results of some attempts to fabricate such SiC metamaterials in collaboration with Jennifer Chen and Prof. Geoffrey Ozin of the Department of Chemistry at the University of Toronto. A short history of SiC and a summary of its basic properties are presented in Sec. 5.1. A templating method was developed using a polymer precursor to SiC; the fabrication method is summarized in Sec. 5.2, and the results are presented in Sec. 5.3. A discussion of the results concludes the chapter in Sec. 5.4.

5.1 History and Properties of Silicon Carbide

Silicon carbide is a very hard ceramic similar to diamond, although much less precious. It may take on many colours including black, grey, green, blue, and yellow, depending on the impurities. It is mostly used for its high strength and hardness, which are maintained even at high temperatures. It is most commonly used in abrasives, refractory materials, crucibles, and furnace elements.

Although SiC is not as commonly used for its electrical properties, it is an interesting high-power semiconductor. Harrison discovered that SiC is a semiconductor in 1907, and used it as a radio detector [Lee, 2004, p. 298]. The first observation of electroluminescence1 was by Round while using SiC in his search for rectifiers to replace vacuum tubes [Schubert, 2006]. It has a wide bandgap (2.3 eV for the cubic structure, ~ 3.0 eV for the hexagonal structures), which was for a time exploited to make (inefficient) blue light-emitting diodes [Moulson and Herbert, 2003, p. 136]. Its nonlinear resistivity is used to absorb surges in power lines and to suppress sparking in electrical relays [Moulson and Herbert, 2003, p. 150].

There are over 200 polytypes of SiC [Moraes, 2000, pp. 27–28]. They are usually classified into two basic groups: \( \alpha \)-SiC and \( \beta \)-SiC [Nakashima and Harima, 1997]. The \( \alpha \)-SiC are uniaxial types, either hexagonal or rhombohedral, based on the wurtzite structure. There many polytypes in this group which differ in the period of the stacking of the (111) planes. The \( \beta \)-SiC type has the cubic zincblende structure.

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1 Even in the samples prepared from this research, the same weak yellow electroluminescence was observed by the author using needle contacts and a source voltage of approximately 11 V.
SiC can be found in nature only as the rare mineral moissanite [NASSAU, 1999]. Due to its rarity, industrial applications must rely on synthetic versions. In 1891, Acheson accidentally created SiC while attempting to make synthetic diamonds. The first useful manufacturing process to synthesize SiC is named the Acheson method, and it involves heating sand (silica) and coke in a graphite furnace to temperatures up to 2500 °C. This process is, with minor modifications, is still common today [MOULSON AND HERBERT, 2003, p. 136]. It is also now common to produce powders or films of either crystalline or polycrystalline SiC by chemical vapor deposition [NISHINO ET AL., 1983]. Nanoparticles have been fabricated using laser pyrolysis [HUISKEN ET AL., 1999]. Monodisperse microspheres can be produced by a sol-gel process [HATAKEYAMA AND KANZAKI, 1990; SEOG AND KIM, 1993]. Carbo-thermal reduction has been used to convert resin powders into polydisperse SiC microspheres [JUNG ET AL., 2002].

5.2 Fabrication by the Templating Method

A templating method for fabricating SiC microspheres was adapted from a procedure for synthesizing large-scale photonic crystals, whereby an opal template is formed around close-packed sacrificial microspheres. The spheres are then etched, leaving behind an inverse opal photonic crystal with air voids [BLANCO ET AL., 2000; LÓPEZ, 2003]. This inexpensive method is successful at creating a long-range ordered lattice of monodisperse (< 5% diameter variation) air voids (spheres). This method was used as a starting point for fabricating monodisperse micron-sized spheres. The inverse opal can be used as a mould, and infiltrated with a liquid precursor and eventually processed to form spheres of the desired material, which in this case is SiC.

The process by which organic precursors can be converted to SiC was first developed by YAJIMA [1980]. There is only one SiC precursor product on the market, SMP–10 (Starfire Systems Inc., Malta, NY, USA). It is a clear, viscous liquid made of allyhydridopolycarbosilane [MORAES, 2000]. Pyrolysis crosslinks the polymer to form a glassy material, and with further pyrolysis hydrogen gas is lost, leaving amorphous SiC [MORAES, 2000]. With sufficiently high temperatures the SiC will crystallize to β-SiC. The Starfire polymer precursor has been used to make a monolithic microstructure of SiC with a lattice of air micropores, which was fabricated for fuel cell applications [SUNG ET AL., 2005].

The templating process for fabricating the SiC spheres was modified as necessary from the process of BLANCO ET AL. [2000] to accommodate the SMP–10 SiC precursor. The fabrication process is summarized in Fig. 5.1, and the steps are as follows:

(1) Monodispersed polystyrene microspheres [OZIN AND ARSENAULT, 2005] of 2.7 μm diameter are deposited onto a silicon substrate by evaporation, whereby they self-assemble into a close-packed lattice. Sintering helps to bond the lattice of spheres for mechanical stability.

(2) A silica template is formed around the microspheres by chemical vapor deposition (CVD) using H₂O and SiCl₄. This is repeated up to seven times to ensure that all of the interstices between the

---

4It is, however, common in other parts of the universe where it is formed in carbon-rich stars [PAPOUŁAR ET AL., 1998; MUTSCHEK ET AL., 1999]. Those stars are the original source of the SiC found on earth; it has all been carried here in meteorites.

3Pyrolysis is the heat-induced chemical decomposition of an organic material.

4Sintering is the joining of solids by diffusion at high temperature.
microspheres are infiltrated. After every few round of CVD, reactive ion etching (RIE) was performed to remove any excessive build-up of silica which might prevent the subsequent CVD vapors from penetrating to the interior.

(iii) The polystyrene spheres are etched with an oxygen plasma, leaving only the silica inverse template.

(iv) The template is infiltrated with SiC precursor. A vacuum aids the capillary infiltration. Optimal results are attained when template is completely infiltrated, but no excess polymer has built up on the outer surface of the template.

(v) The sample is pyrolyzed in a tube furnace 950 °C in an N₂ environment to convert the polymer to amorphous SiC.

(vi) The silica template is etched away in HF. The lattice of bonded spheres is broken in an ultrasonic bath. The spheres are transferred to a glassy carbon substrate, and put in a glassy carbon crucible (glassy carbon is non-porous and very inert at extremely high temperatures). The samples are calcined⁵ at 1600 °C for 240 minutes under vacuum in a graphite furnace. This crystallizes the SiC. A collateral effect is that the spheres are also sintered in the high temperature.

(vii) The sample is sonicated to break the bonds between the spheres. The sample is etched in oxygen

⁵Calcination is a heat treatment for the purpose of thermal decomposition or phase transition.
plasma to remove excess carbon. A combination of sonication and centrifugation helps to separate the free-standing spheres from any larger debris.

The omitted details on the above procedures may be found in the nanochemistry literature [Ozim and Arsenault, 2005] and the Starfire Systems SMP–10 product datasheet and process guide.

5.3 Results

Scanning electron microscopy (SEM) images were taken of the samples. The results for a sample after calcination to 950 °C are shown in Fig. 5.2. The top left image shows that the SiC has indeed infiltrated the spherical voids of the template. The lattice of spheres is connected by a series of necks, which when broken leave a small scar on the surfaces. The top right image displays an overview of the sample, after having been broken in the ultrasonic bath. There are plenty of spheres, but also much debris formed within the interstices of the template. The bottom left image shows a close-up view of two isolated spheres, which are roughly 2 μm in diameter; the pyrolysis has reduced the diameter of the spheres by 25%. A fractured sphere is shown in the bottom right image, demonstrating that the precursor completely filled the template to form solid SiC, since no voids are visible at this scale. Although the infiltration seems to
be successful, the SiC is still amorphous at this stage, since the processing temperature has so far been insufficiently high to order the atoms into a crystalline lattice.

Some SEM images of a sample after calcination to 1400 °C are shown in Fig. 5.3. The SiC is now polycrystalline, but these images prove that the spheres are no longer solid SiC. The surface has been badly pitted and scarred, and it is unclear how deep the degradation is. The image on the right shows significant sintering between spheres and with other interstitial debris. In addition, the image on the left shows that the spheres have a diameter of about 1.5 µm; the calcination stage has reduced the diameter by 25%.

Some SEM images of another sample after calcination to 1600 °C are shown in Fig. 5.4. The polycrystalline SiC spheres are damaged further by the increased temperature. The damaged surfaces suggest that the spheres are hollow. An even greater degree of sintering has occurred between spheres and other debris. The sphere diameters are roughly 1.2 µm, which is a 20% decrease from the samples treated to 1400 °C, and a 40% decrease overall. This may be due to material contraction or other mechanical changes, or possibly a portion of the SiC is oxidized to SiO or SiO₂ and lost as vapor.
Figure 5.5: XRD patterns of SiC samples calcined to 1400 °C and 1600 °C.

Powder x-ray diffraction (XRD) measurements were performed on samples calcined to 1400 °C and 1600 °C. The pattern data are shown in Fig. 5.5. The Miller indices of the diffraction planes are also displayed in the figure, and follow the pattern expected for β-SiC, which has a face-centered cubic structure. Analysis of the data using the Rietveld method [WILL, 2006] suggests that the mean crystallite size is 12.5 nm at 1400 °C, and 16.5 nm at 1600 °C. Raising the calcination temperature to 1600 °C has made a great improvement in the sharpness of the peaks and the crystallite size. These data are similar to other published XRD results, including the indication of stacking faults [YANG ET AL., 2004].

Raman spectra taken of the SiC samples calcined to 1400 °C and 1600 °C are shown in Fig. 5.6. Confocal Raman microscopy [BARBILLAT ET AL., 1994] was performed on some of the larger chunks of SiC debris, since it was difficult to focus the laser spot on isolated spheres. All of the results shown in Fig. 5.6, regardless of whether oxygen plasma treatment was performed or not, display two sharp peaks at 792 cm⁻¹ and 965 cm⁻¹, which correspond to β-SiC [NAKASHIMA AND HARIMA, 1997]. These lines have also been observed in the Starfire SiC polymer precursor [MORAES, 2000, p. 66] as well as SiC produced by other polymer precursors [SASAKI ET AL., 1987]. Since the Raman shift is due to inelastic scattering by the phonons in the structure, these two lines are confirmation of the transverse ωₜ and longitudinal ωₖ oscillator frequencies in the Lorentz dispersion model (4.12). The samples calcined to 1600 °C display somewhat sharper SiC lines, particularly at ωₖ ≈ 965 cm⁻¹. The results prior to the oxygen plasma treatment also have two strong yet broad peaks around 1340 cm⁻¹ and 1580 cm⁻¹. Both correspond to graphite; the latter to a crystalline form, and the former to other forms such as charcoal, lampblack,
vitreous carbon [Tuinstra and Koenig, 1970]. Excess carbon is a common impurity in SiC, regardless of production method [Moraes, 2000; Sasaki et al., 1987; Charpentier et al., 1999]. The O₂ plasma treatment in fabrication step (vii) was introduced to remove this excess carbon. The curves in Fig. 5.6 corresponding to plasma-treated samples verify that not only are the graphitic lines greatly reduced, but the SiC lines remain prominent and unaltered.

The metamaterial properties of the SiC spheres can be measured using Fourier transform infrared (FTIR) spectroscopy. Since the samples are SiC spheres of $2r_s \approx 1.2 \mu m$, such measurements might verify metamaterial properties similar to the design of a negative permeability metamaterial made of SiC spheres, as was presented in Sec. 4.3.2.

Transmission measurements were conducted with an FTIR spectrometer and two different sampling methods. First, a sample of SiC spheres was mixed with KBr powder and pressed into a pellet. Section B.1 outlines the experimental method and two theoretical models of the KBr pellet sampling method. The theoretical transmittance $T$ of the pellet can be calculated using either (B.3) and (B.4), or (B.5). The experimental and calculated results are shown in Fig. 5.7. The SiC spheres were calcined to 1600 °C, so the diameters of the spheres is roughly $2r_s = 1.2 \mu m$, as measured from Fig. 5.4. It is difficult to accurately measure the density of the spheres $N$, so in the calculations it is assumed that $NL = 1.5 \times 10^{10} \, m^{-2}$, where $L$ is the KBr pellet thickness. This provides a comparable transmission magnitude. The discrepancy between the calculations and experiment is quite large. The calculations predicts a magnetic dipole resonance around 780 cm⁻¹, and an electric dipole resonance around 885 cm⁻¹, which is qualitatively very similar.
Figure 5.7: Experimental (solid) and calculated (dashed) transmission through a dilute sample of SiC spheres pressed into a KBr pellet. The spheres were calcined to 1600 °C.

to the resonances predicted in Fig. 4.3. In contrast, the experimental results have a broad feature over the bandwidth 790 cm\(^{-1}\) to 970 cm\(^{-1}\). This broad feature might be suggestive of the reflectance of a SiC film [SPIZTER ET AL., 1959a], which would suggest that the SiC spheres have formed a continuous or dense network within the pellet, thus resembling such a film. To eliminate this possibility, much effort was made to thoroughly sonicate the spheres to minimize the number of interconnections among the spheres and other remaining debris. Still, similar results were always obtained. Instead, the likely explanation is that the degradation of the SiC sphere surfaces and interior structure (or lack thereof) greatly affect the response of the composite. Such shape-dependent effects are the subject of Chap. 6.

The second sampling method is diffuse reflectance. The experimental and theoretical model of the method are outlined in Sec. B.2. A comparison of the results is shown in Fig. 5.8. The calculations predicts a magnetic dipole resonance around 780 cm\(^{-1}\), and an electric dipole resonance around 885 cm\(^{-1}\). The calculated diffuse reflectance in Fig. 5.8 is qualitatively very similar to the calculated transmittance in Fig. 5.7, although the weaker features are accentuated, such as the magnetic dipole resonance and an electric quadrupole resonance around 910 cm\(^{-1}\). The experimental curve does not match the calculations at all. The experimental curve is similar to that of the KBr pellet method (Fig. 5.7); there is a broad over the bandwidth 790 cm\(^{-1}\) to 970 cm\(^{-1}\).

There are some ripples is the experimental diffuse reflectance over the range 700 cm\(^{-1}\) to 800 cm\(^{-1}\), but it is unlikely that they are in any way suggestive of a magnetic dipole response. Indeed, they were eventually identified as signatures of various polymers, and are likely related to the contamination of the sample during preparation. At the time, a standard procedure was being followed whereby samples were
thoroughly mixed in plastic sample vials with a “Wig-L-Bug” grinding mill. The results showed, throughout a wide spectral range, many distinct bands which were eventually traced to various polymer substances. It is likely that the extremely hard SiC microparticles themselves ground small amount of plastic from the vial walls, contaminating the sample. This was only discovered much after the last samples were fabricated, and by that time the results of Chap. 6 had been obtained, which explain all of the shortcomings of these results, and effectively negate the efforts made to fabricate these spheres.

5.4 Discussion

Although the XRD patterns, Raman spectra, and SEM images of the amorphous spheres seem quite promising, the FTIR measurements fail to adequately match the theoretical model of SiC spheres as derived in Chap. 4. The following are some conclusions that have been drawn on the fabrication process.

It seems that the extremely high temperatures in during calcination ultimately ruined the morphology of the spheres too much, and reduced their size significantly. Indeed, the sacrificial polystyrene spheres were originally 2.7 µm in diameter, but by the end of the process the SiC spheres were between 1.2 µm to 1.5 µm in diameter. In addition, the many stages of sintering and sonication decreases the yield of SiC spheres and creates much misshapen debris.

The density of SiC in the spheres might be increased by carrying out multiple infiltrations of the precursor. This should help to reduce the loss of SiC mass and prevent surface degradation. This was attempted by re-infiltrating the SiC precursor by repeating stages (iv) and (v) after the initial pyrolysis.
Unfortunately the high temperature during pyrolysis warps the silica template. Since the template is crucial for maintaining the spherical surfaces, it seems impossible to reliably re-infiltrate the template as long as it is made of silica. Possibly another template material could be found which is compatible with the remainder of the process, and which could withstand the pyrolysis temperature.

It may also be possible, although unlikely, that the degree of crystallinity of the SiC obtained after pyrolysis to 950 °C after stage (v) is sufficient to drive a weak magnetic response. That is, the extreme and morphologically-detrimentsal calcination stage could possibly be unnecessary, and that a lower degree of crystallinity than sought here might have been acceptable. This would allow the spheres to remain spherical and solid throughout, as in Fig. 5.2. However, it would be expected that the SiC phonon-polariton damping factor would increase significantly. This would dramatically reduce the resonance in the permittivity function [MUTSCHKE et al., 1999] to moderate or small values, whereas the large values of crystalline SiC near its resonance (Fig. 4.1) are sought. Therefore the effective magnetic metamaterial properties might vanish. In addition, studies of amorphous SiC derived from polymer precursors indicate that below at least 1000 °C, spectral fingerprints of organic matter, which cause many absorption lines, remain present [MUTSCHKE et al., 1999; MORAES, 2000], which might corrupt the metamaterial.

Two serious issues are apparent in the failure of the fabricated SiC spheres to match the effective media model. First, the fabricated spheres are porous, and can be interpreted as effective media themselves. Indeed, each microsphere is a mixture of SiC and air, with an effective permittivity an intermediate of the two [SPANIER AND HERMAN, 2000]. The corresponding reduction in the permittivity is likely insufficient to excite the magnetic dipole modes of the spheres. The second issue is that the surfaces of the spheres are ruined, and the spheres lose their solid spherical shape throughout the fabrication process. This can drastically change the response of the particles and of the metamaterial composite as a whole. This second issue will be investigated in the next chapter.

Finally, some other promising research has led to other methods for fabricating SiC microspheres: These include sol-gel processing [HATAKEYAMA and KANZAKI, 1990; SEO AND KIM, 1993] for monodisperse spheres, and carbo-thermal reduction [JUNG et al., 2002] for polydisperse spheres. These methods may be of interest in any future attempts to fabricate SiC metamaterials.
Chapter 6

Silicon Carbide Micro-Powder

The previous chapter presented results of attempts to fabricate a metamaterial comprised of monodisperse SiC microspheres. It was found that the infrared transmission spectra of SiC sphere samples differed greatly than the theoretical calculations. The foremost conclusion was that the discrepancy is likely due to the deterioration of the surfaces and the loss of internal density of the spheres. In order to investigate these issues further, a micropowder sample of SiC were studied. This powder differs greatly from the meticulously-fabricated SiC microspheres: the powder is polydisperse both in particles size and in particle shape. It is a crystalline $\alpha$-SiC sample, mechanically milled to a fine micropowder. It was purchased from Alfa-Aesar (Ward Hill, MA, USA, item #40155). An SEM image of the powder is shown in Fig. 6.1. Its likely intended use was either as an abrasive, or for the manufacture of refractories or heating elements; the powder would be put in a form and sintered at 2500 °C to form a monolith [Moulson and Herbert, 2003, p. 138].

The contents of this chapter present a model of the magnetic and electric response of this SiC powder. The size dispersion of the powder will be discussed in Sec. 6.1. A study of shape dispersion in spheroidal particles is presented in Sec. 6.2. The size and shape dispersions are incorporated into the models of the magnetic and electric dipole responses of the powder in Sec. 6.3 and Sec. 6.4. The model is compared with infrared measurements in Sec. 6.5.

6.1 Particle Size Dispersion

The SiC powder shown in Fig. 6.1 is polydisperse; there is a wide range of particle sizes. Since the micropowder was formed by mechanical milling, the size dispersion can be modeled by a log-normal distribution [Allen, 1999]. The normalized log-normal distribution is [Allen, 1999; Kokhanovsky, 2004; Mishchenko et al., 2002]

$$
\frac{d\phi}{dx} = \frac{1}{x \ln x} = \frac{1}{x \ln \sigma_g \sqrt{2\pi}} \exp \left[ -\frac{(\ln x - \ln x_g)^2}{2\ln^2 \sigma_g} \right],
$$

(6.1)
where $x_g$ is the geometric mean size (arithmetic mean of the logarithms), which is equal to the median size. The geometric standard deviation is $\sigma_g$. The distribution is normalized so that
\[
\int_0^\infty \frac{df}{dx} \, dx = \int_{-\infty}^\infty \frac{df}{d\ln x} \, d\ln x = 1. \tag{6.2}
\]
Thus the average of any quantity $f(x)$ over all particle sizes is
\[
\langle f(x) \rangle = \int_0^\infty f(x) \frac{df}{dx} \, dx = \int_{-\infty}^\infty f(x) \frac{df}{d\ln x} \, d\ln x. \tag{6.3}
\]
The $k$-th moment is
\[
\langle x^k \rangle = x_g^k \exp \left( \frac{k^2}{2} \ln^2 \sigma_g \right). \tag{6.4}
\]
For example, the volume of a sphere is $V = 4\pi r^3/3 = \pi d^3/6$, so
\[
\langle V \rangle = \frac{\pi}{6} \langle d^3 \rangle, \tag{6.5}
\]
\[
\langle V^2 \rangle = \left( \frac{\pi}{6} \right)^2 \langle d^6 \rangle. \tag{6.6}
\]

For the sample shown in Fig. 6.1 the median particle size (diameter) is roughly $d_g = 0.7 \mu m$ and the geometric standard deviation is roughly $\sigma_g = 1.5$. The probability density of this distribution is plotted in Fig. 6.2. The maximum particle size is roughly 2 $\mu m$. Particles of all sizes support electric dipole resonances, while only particles larger than roughly 0.5 $\mu m$ support magnetic dipole resonances. To support these claims, the extinction cross sections are plotted in Fig. 6.3 for a variety of sphere diameters. The resonances are labeled by the particular type of multipole scattering by the coefficients as defined in (3.32). It is indeed true that the surface mode electric dipole scattering $a_1$ is present for all sphere sizes (and furthermore its resonant frequency is weakly independent of size). The magnetic dipole resonances only become apparent for $2r_s > 0.5 \mu m$, which proves the assertion on the magnetic dipole contributions labeled in Fig. 6.2. The
magnetic dipole resonant frequencies are only weakly dependent on size. This is due to the confined frequency range of the large permittivity values of SiC below $\omega_T$ (See Fig. 4.1), which in turn tends to restrict the spread of the resonant frequencies over the size distribution. Lastly, the electric quadrupole mode $a_2$, the bulk electric dipole mode $a_1$, and the second harmonic of $b_1$ only arise for larger particle sizes ($2r_s \gtrsim 2 \mu$m) which are effectively absent from the sample, so it is valid neglect such contributions.

### 6.2 Particle Shape Dispersion

The powder of irregularly shaped particles cannot be modeled in general as spheres using the effective medium approach based on Mie theory from Chap. 4. As a first step towards generalizing the model, the scattering properties of SiC spheroidal particles will be considered. Spheroids are a subset of ellipsoids in which the lengths of two of the three principle axes are equal, as shown in Fig. 6.4. The vertical-to-rotational axis ratio $a/b$ determines the class of spheroid: prolate (cigar-shaped) spheroids have $a/b < 1$, and oblate (pancake-shaped) spheroids have $a/b > 1$. The orientation-averaged, volume-normalized extinction cross sections $C_{ext}/V$ for various spheroidal particles was calculated numerically using a T-matrix code [MISHCHENKO AND TRAVIS, 1998]. The results for SiC particles in a KBr host are shown in Fig. 6.5. The largest dimension of each spheroidal particle is 0.7 $\mu$m (which corresponds to the median size $x_g$ of the SiC powder sample).

The cross sections of the set of spheroidal particles all contain both magnetic dipole and electric dipole scattering. The magnetic dipole resonances all occur at roughly the same frequency, just below $\omega_T = 790$ cm$^{-1}$. The resonant frequencies are roughly independent of the particle shape, and therefore satisfy the magnetic dipole resonant condition of the dielectric sphere (3.42). The only difference between the resonant peaks in the cross sections is the magnitude; the intensity of the magnetic dipole scattering from the prolate ($a/b < 1$) spheroids is less than that of the oblate spheroids ($a/b > 1$). This is not
Figure 6.3: The extinction of various diameters of SiC spheres.
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Prolate ($a/b < 1$)

Oblate ($a/b > 1$)

Figure 6.4: Schematic of prolate and oblate spheroids.

Figure 6.5: Volume-normalized and orientation-averaged extinction cross sections of various spheroidal SiC particles. The host medium is KBr. The maximum size of each spheroid is 0.7 µm.
unreasonable, since the volume of a prolate spheroid shown in Fig. 6.5 is less than that of the equivalent oblate spheroid. Indeed, consider the corresponding pair of spheroids with the most extreme axis ratios in the figure. The prolate case has \((a/b)_{\text{pro}} = 0.2\) and \(b_{\text{pro}} = 0.7\ \mu\text{m}\), and the oblate case has \((a/b)_{\text{obl}} = 5\) and \(a_{\text{obl}} = 0.7\ \mu\text{m}\). The ratio of their volumes, using (3.68), is

\[
\frac{V_{\text{prolate}}}{V_{\text{oblate}}} = \frac{(a/b)_{\text{pro}}^2 b_{\text{pro}}^3}{(b/a)_{\text{obl}} a_{\text{obl}}^3} = \left(\frac{a}{b}\right)_{\text{pro}}^2 \left(\frac{a}{b}\right)_{\text{obl}} = \left(\frac{a}{b}\right)_{\text{pro}} \left(\frac{b}{a}\right)_{\text{obl}} < 1,
\]

where the last equality is true for cases with complementary axis ratios, \((a/b)_{\text{pro}} = 1/(a/b)_{\text{obl}}\). The axis ratio is a factor in the reduced volume of the prolate particles. These results indicate that the resonant strength is roughly proportional to the particle volume, as should be expected for bulk modes. The most important conclusion on the magnetic dipole resonances is that their resonances are roughly independent of particle shape, and may be modeled adequately as equivalently-sized spheres.

In contrast to the magnetic dipole resonance, the deformation of a sphere into spheroids splits the electric dipole resonance from 895 cm\(^{-1}\) (the heavy curve in Fig. 6.5) into two peaks at other frequencies within the range where \(\text{Re}\{\varepsilon_s\} < 0\). This indicates that the splitting is due to the surface mode nature of the resonances. Two peaks are expected for spheroids, which have only two unique semi-axis lengths; three peaks would be expected for ellipsoidal particles for which all three semi-axis lengths are unequal. These conclusions are supported by the resonant condition for small ellipsoids, (3.74). This dramatic effect of resonance splitting must be captured in a model of the powder.

### 6.3 Model of Powder Magnetic Dipole Response

All cases of extinction by SiC spheroidal particles in Fig. 6.5 have a magnetic dipole resonance near 785 cm\(^{-1}\), indicating weak dependencies on particle shape. This is because the resonant magnetic dipole field is a bulk mode, and the field is contained within the volume of the particle (Fig. 3.2). The magnetic response can therefore be approximated by the magnetic dipole scattering Mie coefficient (3.32b), even though the particles are not spheres. Hence, the shape- and orientation-averaged magnetic dipole scattering coefficient \(\overline{b_1}\) is

\[
\overline{b_1} \approx b_1^{\text{Mie}}.
\]

The superscript "Mie" indicates that \(b_1\) should be evaluated assuming a sphere of equivalent size, using (3.32b). The extinction \(C_{\text{ext}}\), scattering \(C_{\text{sca}}\), and absorption \(C_{\text{abs}}\) cross sections will be required later in
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this chapter, so the magnetic dipole contributions to them, including both size and shape dispersion, are

\[
\langle C_{\text{mag}}^{\text{ext}} \rangle \approx \frac{6\pi}{k_i^2} \left( \text{Re} \left\{ B_1^{\text{Mie}} \right\} \right),
\]

(6.9a)

\[
\langle C_{\text{sca}}^{\text{mag}} \rangle \approx \frac{6\pi}{k_i^2} \left( \left| B_1^{\text{Mie}} \right|^2 \right),
\]

(6.9b)

\[
\langle C_{\text{abs}}^{\text{mag}} \rangle = \langle C_{\text{ext}}^{\text{mag}} \rangle - \langle C_{\text{sca}}^{\text{mag}} \rangle,
\]

(6.9c)

where (3.81) and (3.78) have been used. These cross sections are sufficient to model the magnetic contributions to the electromagnetic response of the SiC powder. However, the effective permeability \( \mu_{\text{eff}} \) of the powder may be generalized to include the size and shape dispersion of the particles. From (4.7),

\[
\frac{\mu_{\text{eff}} - \mu_h}{\mu_{\text{eff}} + 2\mu_h} = \frac{N}{3} \langle \alpha_\text{m} \rangle,
\]

(6.10)

where, using (3.34b),

\[
\langle \alpha_\text{m} \rangle = \frac{6\pi i}{k_i^2} \left( b_1^{\text{Mie}} \right),
\]

(6.11)

### 6.4 Model of Powder Electric Dipole Response

The sample is comprised of a wide variety of particle shapes, and it is clear from Fig. 6.5 that the surface electric dipole resonances of a particle are strongly dependent on its shape. Although the curves in that figure were calculated for various spheroidal particles, it will prove to be easier and more general to model the powder as a continuous distribution of ellipsoids (cde) [Bohren and Huffman, 1983]. In fact, this model has been used to analyze interstellar spectra for identifying SiC crystallites [Mutschke et al., 1999]. The cde model is particularly simple when the particles are sub-wavelength sized ellipsoids. In that case the electrostatic approximation of the electric polarizability (3.72) can be used. For each possible ellipsoidal shape, there will be in general three surface electric dipole resonances in \( \alpha_{e,j} \) with frequencies satisfying (3.74). A dispersion of shapes will cause the resonances to form a broad continuum of extinction within the range of frequencies where \( \text{Re} \{ \epsilon_j \} < 0 \).

All possible shapes of ellipsoids can be labeled by \((L_1, L_2)\) within the domain shown in Fig. 3.8. Assume that the probability density of ellipsoidal particles is \( p(L_1, L_2) \). The shape and orientation average of a quantity \( f(L_1, L_2) \) can evaluated with

\[
\bar{f} = \int \int_{\Delta} f(L_1, L_2) \ p(L_1, L_2) \ dL_1 dL_2,
\]

(6.12)

where the region \( \Delta \) is the largest triangle shown in Fig. 3.8. This region incorporates all possible ellipsoidal
shapes and orientations. The probability density \( p(L_1, L_2) \) is normalized such that

\[
\int_{\Delta} p(L_1, L_2) \, dL_1 dL_2 = 1. \tag{6.13}
\]

A general expression for \( p(L_1, L_2) \) which is useful for the current work is

\[
p_{p1,p2,C_p}(L_1, L_2) \propto (L_1 L_2 L_3)^{p_1} \left[ \sum_{j=1}^{3} \left( L_j - \frac{1}{3} \right)^{p_2} + C_p \right]. \tag{6.14}
\]

An important feature of this general density is that it is symmetric in all \( L_j \). However, it is only a function of \((L_1, L_2)\), since \( L_3 \) is linearly dependent by \((3.71)\).

There are three interesting cases of (6.14) to consider. The simplest case is a uniform distribution [Bohren and Huffman, 1983],

\[
p(L_1, L_2) = 2, \tag{6.15}
\]

which can be reduced from (6.14) by using \((p_1, p_2) = (0, 0)\). Although this distribution is conveniently simple, it over-estimates the presence of extremely eccentric particles (thin disks and needles). Osenkopf et al. [1992] proposed a modified distribution,

\[
p(L_1, L_2) = 120L_1L_2L_3, \tag{6.16}
\]

which can be reduced from (6.14) by using \((p_1, p_2) = (1, 0)\). The contours of the probability density are shown on the left in Fig. 6.6, where it can be seen that this distribution eliminates the probability of infinitely eccentric particles for which at least one \( L_j = 0 \). In this work a further refinement will be made. To account for the relative lack of spheres in the powder sample (Fig. 6.1),

\[
p(L_1, L_2) \propto L_1 L_2 L_3 \left[ \sum_{j=1}^{3} \left( L_j - \frac{1}{3} \right)^2 + C_p \right] \quad \text{where} \quad C_p = 0.05, \tag{6.17}
\]

which can be reduced from (6.14) by using \((p_1, p_2) = (1, 2)\). The value of \( C_p \) is used to lower the probability of sphere-like particles, as long as \( C_p < \frac{21}{50} \). The contours of the probability density are shown on the right in Fig. 6.6, where it can be seen that this distribution has a decreased probability of sphere-like shapes, and instead favors moderately eccentric ellipsoids.

Having laid out some probability distributions to model the shape dispersion of the powder, the electric dipole contributions to the various cross sections can be integrated over all sizes, shapes, and orientations,

\[
\langle C_{ext}^{\text{elec}} \rangle = \langle C_{\text{sca}}^{\text{elec}} \rangle + \langle C_{\text{abs}}^{\text{elec}} \rangle, \tag{6.18a}
\]

\[
\langle C_{\text{sca}}^{\text{elec}} \rangle \approx \frac{k^4}{6\pi} \frac{\mu_0}{|\alpha_e|^2}, \tag{6.18b}
\]

\[
\langle C_{\text{abs}}^{\text{elec}} \rangle \approx k_0 \text{Im} \{\langle \alpha_e \rangle \}. \tag{6.18c}
\]
These are generalizations of (3.82), and are valid for the electrostatic polarizability $\alpha_e$ outlined in Sec. 3.5.3.

To see how to evaluate $\langle \alpha_e \rangle$ and $|\langle \alpha_e \rangle|^2$, first consider a collection of identical ellipsoids having no shape dispersion. Then the orientation-only averages are [Bohren and Huffman, 1983]

\[
\langle \alpha_e \rangle = \frac{1}{3} \sum_{j=1}^{3} \alpha_{e,j},
\]

\[
|\langle \alpha_e \rangle|^2 = \frac{1}{3} \sum_{j=1}^{3} |\alpha_{e,j}|^2,
\]

where $\alpha_{e,j}$ comes from (3.72). Generalizing these expressions to include shape dispersion,

\[
\langle \alpha_e \rangle = \frac{1}{3} \sum_{j=1}^{3} \alpha_{e,j},
\]

\[
|\langle \alpha_e \rangle|^2 = \frac{1}{3} \sum_{j=1}^{3} |\alpha_{e,j}|^2.
\]
Figure 6.7: Comparison of the shape-averaged electric polarizability integrals for three shape probability distributions. The short-dashed line is for \((p_1, p_2) = (0, 0)\); the long-dashed line is for \((p_1, p_2) = (1, 0)\); the solid line is for \((p_1, p_2) = (1, 2)\) and \(C_p = 0.05\). The solid curves are used in the results of this chapter.

Substituting (3.72) yields

\[
\bar{\alpha}_e \in \frac{1}{3} \sum_{j=1}^{3} \left( \frac{V}{\beta + L_j} \right) \\
= \frac{V}{3} \sum_{j=1}^{3} \left( \frac{1}{\beta + L_j} \right) \\
= V \left( \frac{1}{\beta + L_1} \right) \\
= V I^{(1)}
\]

\[
|\bar{\alpha}_e|^2 \in \frac{1}{3} \sum_{j=1}^{3} \left( \frac{V}{\beta + L_j} \right)^2 \\
= \frac{V^2}{3} \sum_{j=1}^{3} \left( \frac{1}{\beta + L_j} \right)^2 \\
= V^2 I^{(2)}.
\]

In these expressions each term in the sum over \(j\) is identical. It has been assumed that there is no correlation between particle shape and volume; this generous assumption keeps the model simple and is adequate in the absence of such correlation data.
The shape averaging in (6.21) requires the evaluation of two integrals,

\[ I^{(1)} = \iint_{\Delta} \frac{p(L_1, L_2)}{\beta + L_1} \, dL_1 dL_2, \]

\[ I^{(2)} = \iint_{\Delta} \left| \frac{p(L_1, L_2)}{\beta + L_1} \right|^2 \, dL_1 dL_2. \]

(6.22)

These integrals can be evaluated in closed form for the general shape probability distribution (6.14) and the three special cases (6.15), (6.16), (6.17). This is another reason for the choice of such distributions. The results, however, are too lengthy to write out explicitly. Instead, the two integrals are evaluated for the three different shape distributions. The results are plotted in Fig. 6.7 for SiC particles using (4.10) and (4.12).

The electric dipole contributions to the various cross sections (6.18) become, after including size, shape, and orientation averaging:

\[ \langle C_{\text{elec}}^{\text{ext}} \rangle = \langle C_{\text{elec}}^{\text{sca}} \rangle + \langle C_{\text{elec}}^{\text{abs}} \rangle, \]

\[ \langle C_{\text{sca}}^{\text{elec}} \rangle \approx \frac{k^4}{6\pi} \langle V^2 \rangle I^{(2)}, \]

\[ \langle C_{\text{abs}}^{\text{elec}} \rangle \approx k_h \langle V \rangle \text{Im} \left\{ I^{(1)} \right\}. \]

(6.23)

These cross sections are sufficient to model the electric contributions to the electromagnetic response of the SiC powder. The factors involving the size-averaged volume can be evaluated using (6.5) and (6.6). However, the effective permittivity \( \epsilon_{\text{eff}} \) of the powder may be generalized to include the size and shape dispersion of the particles. From (4.7) and using (6.21),

\[ \frac{\epsilon_{\text{eff}} - \epsilon_h}{\epsilon_{\text{eff}} + 2\epsilon_h} = \frac{N}{3} \langle \epsilon_e \rangle, \]

\[ \frac{N}{3} \langle V \rangle I^{(1)}. \]

(6.24)

6.5 Infrared Spectroscopy Results

The response of the SiC powder can be characterized using infrared spectroscopy. The KBr pellet method for infrared transmission measurements is summarized in Sec. B.1. This method was used on the SiC powder, both experimentally and theoretically using (B.5). The results are plotted in Fig. 6.8. The shape distribution (6.17) was used in the calculated results. The experimental and calculated curves match very closely between 800 cm\(^{-1}\) and 900 cm\(^{-1}\). This dominant and broad feature is due to the shape broadening of the surface electric dipole modes. This is supported by the similarity to the integrals over the shape distributions, as shown in Fig. 6.7. However, there are features around 780 cm\(^{-1}\) and 945 cm\(^{-1}\) in the experimental transmittance that are not captured in the model. The pronounced shoulder around 780 cm\(^{-1}\) suggests a magnetic response, because of the magnetic dipole frequencies of the particles predicted by Fig. 6.5. Yet the magnetic dipole response is almost absent in the calculations because the powder particles
are almost too small, providing only a negligible effect; the sample was not optimized to enhance the magnetic dipole response. The feature around 945 cm\(^{-1}\) is likely due to the surface electric dipole modes. Both of these features might have been augmented beyond the calculated predictions due to mechanisms peculiar to the KBr pellet method, such as particle aggregation at the grain boundaries between the fused KBr crystallites [Pecharromán and Iglesias, 1996].

The response of the SiC powder sample was also characterized by the diffuse reflectance technique. An overview of the method is presented in Sec. B.2. The comparison of the experimental and calculated diffuse reflectance of the SiC powder is shown in Fig. 6.9. The density of SiC powder is \(N = 3 \times 10^{13} \text{ m}^{-3}\). The broad peak from 800 cm\(^{-1}\) to 960 cm\(^{-1}\) is due to the shape-broadened electric dipole resonances. This may be verified by comparing with the similarly broad integrals plotted in Fig. 6.7; the dependency on them is given in (6.23). The peak around 785 cm\(^{-1}\) is due to the magnetic dipole response of the dielectric particles. The calculations agree well with the measurement, except for a small overall shift in frequency, and for slightly unequal magnetic-to-electric resonant strength ratio, which is quite likely due to the approximate statistics used to generalize the model to random particles. Nevertheless, the powder model captures all of the essential features of the crude and random mixture. The constant \(C_p\) of (6.17) only affects the match of the shoulder in the electric resonance from 870 cm\(^{-1}\) to 930 cm\(^{-1}\) (this effect can be seen in the shape distribution integrals in Fig. 6.7). The value \(C_p = 0.05\) was chosen to match the shoulder around 920 cm\(^{-1}\) in the experimental results.

The magnetic dipole response and the shape-broadened electric dipole response of the SiC powder are confirmed by the KBr pellet transmittance results in Fig. 6.8 and the diffuse reflectance results in Fig. 6.9.
In Chap. 5 it was hypothesized that the deformation of the shapes of the spheres had caused the broad experimental results shown in Fig. 5.7, which did not match the calculations at all. Now that a model of particle shape dispersion has been developed, the theoretical results can be re-calculated. From Fig. 5.3 and Fig. 5.4, it is seen that the particles are roughly monodisperse, so for simplicity a size dispersion will not be applied in the model. A shape distribution, however, clearly must be applied. The theoretical infrared transmittance and diffuse reflectance can now be re-calculated using the shape dispersion model, which was presented in Sec. 6.4. The results of the re-calculation are compared with the experimental results in Fig. 6.10. Results were calculated for two CDE models, both of which match the experimental results reasonable well. These results confirm that the deterioration of the shapes of the SiC spheres during processing is a major cause of the broad transmission result.

A magnetic dipole response has been verified in the SiC random powder sample only. There are otherwise only superficial differences between the results for the random powder, Fig. 6.8 and Fig. 6.9, and those for the fabricated spheres, Fig. 6.10. Unless the fabrication method can be altered to yield non-hollow spheres (in contrast to Fig. 5.3 and Fig. 5.4) which might support magnetic dipole modes, the random powder metamaterial is superior and is much easier to obtain.

Figure 6.9: The experimental (solid) and calculated (dashed) diffuse reflectance of a dilute mixture of the SiC powder sample in a KBr host.
Figure 6.10: Experimental (solid) and calculated (dashed) characterization of a dilute sample of SiC spheres. The experimental results are reproduced from Fig. 5.7 and Fig. 5.8. The different dash lengths indicate different CDE models. Long dashes: \((p_1, p_2) = (1, 0)\); short dashes: \((p_1, p_2) = (1, 2)\).
Chapter 7

Coupled Magnetic Dipoles

It was shown in Sec. 3.5.1 that a sphere of sub-wavelength size can support an induced magnetic dipole resonance if $\varepsilon_s \geq 100\varepsilon_h$. In this chapter the near-field coupling among small clusters of such magnetic dipoles will be studied. The interactions cause mode hybridization; the sphere clusters act as photonic *metamolecules*. Even though clusters increase the complexity over single spheres, they have more degrees of freedom, allowing for greater engineering control over the design of metamaterial inclusions.

Various cluster geometries are studied, all comprised of identical spheres. The spheres were manufactured by Countis Laboratories (Grass Valley, CA, USA), from a mixture of MgO–CaO–TiO$_2$. Each sphere has the properties

$$r_s = 1.07 \text{ mm}, \quad \varepsilon_s/\varepsilon_0 = 112 + 0.1i, \quad \mu_s/\mu_0 = 1.$$ (7.1)

Using (3.42), the resonant frequency of the induced magnetic dipole $f_m \approx 13.2$ GHz, which corresponds to a free-space host wavelength $\lambda_h = 2.3$ cm. The host wavelength is about 10 times larger than the diameter of the sphere $2r_s$, thus they are reasonably sub-wavelength sized. To further confirm that this sphere is a good approximation to a magnetic dipole, the scattering coefficients (3.32) are plotted in Fig. 7.1. The magnetic dipole term $|b_1|$ is dominant from 12.5 GHz to 13.5 GHz, so in this bandwidth the sphere may be assumed to be a magnetic dipole.

The remainder of the contents of this chapter will present both theoretical and experimental investigations of the near-field coupling by such ideal magnetic dipoles at microwave frequencies. An approximate coupled dipole model (CDM) will be presented in Sec. 7.1. An exact multiple scattering solution using the T-matrix method will be summarized in Sec. 7.2. A microwave Gaussian beam transmission experiment will be outlined in Sec. 7.3. The calculations and experimental results for spheres arranged in pairs, chains, and rings will be given in Sec. 7.4.

### 7.1 Coupled Dipole Model

The spheres specified by (7.1) act approximately as pure ideal magnetic dipoles, as confirmed by the magnetic dipole scattering amplitude in Fig. 7.1. A cluster of such spheres can be modeled by a system of linear equations. These equations will be used primarily to estimate the resonant frequencies and eigenmodes of the system. Various CDMs have been used before, most notably for plasmonic coupling [Webber and
Figure 7.1: Magnitudes of the Mie scattering coefficients of a dielectric sphere, having radius \( r_s = 1.07 \) mm, permittivity \( \varepsilon_r/\varepsilon_0 = 112 + 0.1i \), and unit permeability. The curves are: \(|a_1|\) electric dipole, \(|b_1|\) magnetic dipole, \(|a_2|\) electric quadrupole, and \(|b_2|\) magnetic quadrupole. The magnetic dipole is dominant around 13.2 GHz.

Ford, 2004; Fung and Chan, 2008. An overview of the CDM will be presented in this section; specific examples will be given in Sec. 7.4.

The magnetic field radiated by a magnetic dipole is [Jackson, 1999]

\[
H(r) = \frac{e^{ik_hr}}{4\pi r^3} \left[ \left( \mathbf{I} - \hat{r} \hat{r} \right) (k_hr)^2 + (3\hat{r} \hat{r} - \mathbf{I}) (1 - ik_hr) \right] \cdot \mathbf{m},
\]

\[= \mathbf{G}(r) \cdot \mathbf{m}, \tag{7.2}\]

where \( \mathbf{G}(r) \) is the Green's dyadic and \( \mathbf{I} \) is the identity dyad. The coordinate origin is the site of \( \mathbf{m} \). For a system of \( N_s \) spheres, located at \( \mathbf{x}_j \) \((1 \leq j \leq N_s)\), the local field at particle \( j \) is

\[
H_{\text{loc}}(\mathbf{x}_j) = H_{\text{inc}}(\mathbf{x}_j) + \sum_{k \neq j}^{N_s} H_k(\mathbf{x}_j - \mathbf{x}_k), \tag{7.3}\]

where \( H_k(\mathbf{r}) = \mathbf{G}(\mathbf{r}) \cdot \mathbf{m}_k \) is the magnetic field due to the moment \( \mathbf{m}_k \) of particle \( k \). The local field at sphere \( j \) induces a moment \( \mathbf{m}_j = \alpha_m H_{\text{loc}}(\mathbf{x}_j) \), where \( \alpha_m \) is given approximately by (3.34b). For a cluster of identical spheres (7.3) becomes

\[
\frac{1}{\alpha_m} \mathbf{m}_j - \sum_{k \neq j}^{N_s} \mathbf{G}(\mathbf{x}_j - \mathbf{x}_k) \cdot \mathbf{m}_k = H_{\text{inc}}(\mathbf{x}_j). \tag{7.4}\]

This set of equations models the system of coupled magnetic dipoles.

The extinction cross section can be calculated from the optical extinction theorem [Markel, 1995;
Mishchenko et al., 2002]. To do so, the vector scattering amplitude is required,  

\[ \mathbf{F}(\hat{\mathbf{r}}) = r e^{-i k_h r} \mathbf{H}^{\text{sca}}, \]

\[ = \frac{k_h^2}{4\pi} \sum_{j=1}^{N_s} \left[ \mathbf{m}_j - (\mathbf{m}_j \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} \right] \exp \left( -i k_h \hat{\mathbf{r}} \cdot \mathbf{x}_j \right), \tag{7.5} \]

where \( \mathbf{m}_j \) are the solutions of the forced coupled system (7.4), and \( \mathbf{H}^{\text{sca}} \) is the total scattered magnetic field in the far-field approximation, which may be found from (7.2) for \( k_h r \gg 1 \) for each \( \mathbf{m}_j \). Then the extinction cross section for a plane wave excitation is

\[ C_{\text{ext}} = \frac{4\pi}{k_h |\mathbf{H}_0^{\text{inc}}|^2} \text{Im} \left\{ \mathbf{F} \left( \hat{\mathbf{k}}_{\text{inc}} \right) \cdot \mathbf{H}_0^{\text{inc}} \right\}, \tag{7.6} \]

where \( \mathbf{H}_0^{\text{inc}} \) and \( \hat{\mathbf{k}}_{\text{inc}} \) are defined in (3.20).

The system of equations (7.4) can be written as

\[ A \mathbf{v} = \mathbf{h}, \tag{7.7} \]

where \( \mathbf{v} \) is a column vector comprised of each component of \( \mathbf{m}_j \) for all \( N_s \) spheres. Similarly, the corresponding incident wave terms are collected in \( \mathbf{h} \). The resonant modes of the system are the solutions in the absence of an excitation, when \( \mathbf{h} = 0 \). Therefore the resonant modes are the eigenmodes of the homogeneous system

\[ A \mathbf{v} = 0. \tag{7.8} \]

When the matrix elements of \( A \) are evaluated using (7.4), the coupling between the spheres is accounted for by the terms in the summation. That is, the elements are evaluated in the basis of isolated ideal magnetic dipole moments at each sphere site. This basis can be changed to hybridized cluster modes \( \mathbf{v}' \) by diagonalizing \( A \) such that \( A = \mathbf{PDP}^{-1} \), where \( D \) is a matrix with the eigenvalues on the diagonal, and \( \mathbf{P} \) is a matrix comprised of columns of the corresponding eigenvectors. The hybridized modes are given by \( \mathbf{v}' = P^{-1} \mathbf{v} \). The hybridized modes account for interactions between the spheres, so in this basis the summation in (7.4) is zero, and thus the eigenvalues are

\[ \lambda = \frac{1}{\alpha_{cl}} = \frac{\alpha_{cl}^*}{|\alpha_{cl}|^2}, \tag{7.9} \]

where \( \alpha_{cl} \) is the multipole polarizability of a hybridized cluster mode.

The complex polarizability \( \alpha_{cl} \) is never exactly zero, since there will always be at least non-zero scattering losses included in the imaginary part. However, the real part passes approximately linearly through zero. Therefore a hybridized mode resonates when

\[ \text{Re} \{ \lambda \} = \text{Re} \{ \alpha_{cl} \} = 0, \tag{7.10} \]

and \( A \) is nearly singular. Since \( A \) is frequency dependent, a straightforward way to find these resonances is
to sweep the frequency, each time diagonalizing $A$. When a resonance is found via (7.10), the hybridized mode pattern of magnetic dipole vectors induced in each sphere is given by the associated eigenvector.

Not all eigenmodes can be excited by a given incident wave. The degree to which a mode can be excited can be determined by writing the excitation $\mathbf{h}$ in the basis of the hybridized modes,

$$
\mathbf{h}' = P^{-1}\mathbf{h}.
$$

Since each element of this vector represents a hybridized mode, any zero entry means that the corresponding eigenmode cannot be excited. At least for the cases considered in this chapter, it is approximately true that the eigenvector basis is orthogonal\(^1\), so (7.11) simplifies to

$$
\mathbf{h}' \approx P^1\mathbf{h},
$$

where $^\dagger$ is the Hermitian adjoint operator. Since $P^\dagger$ is a matrix comprised of rows of the complex conjugate eigenvectors of $A$, the incident wave can excite an eigenmode $\mathbf{v}$ if

$$
\mathbf{v}^\dagger \cdot \mathbf{h} \neq 0.
$$

### 7.2 Solution Using the Transition Matrix Method

In contrast to the approximate coupled dipole model, the T-matrix approach is exact in principle; the only limitation is set by the upper limit on the number of multipoles $l_{\text{max}}$ for practical implementation. This method improves upon the coupled dipole method of the previous section because all multipole terms can be included. The improvement, however, will only be apparent for very closely spaced spheres, since the magnetic dipole scattering dominates all other higher-order multipoles for the particles considered here (Fig. 7.1). A further benefit of this approach is that it is generally flexible enough to handle clusters of particles with arbitrary geometry, material composition, and particle shape. Indeed, the method has been used to study multiple scattering in systems of particles comparable in size to the wavelength [Chew, 1995; Stout et al., 2002; Bruning and Lo, 1971a,b; Mackowski and Mishchenko, 1996; García de Abajo, 1999; Mishchenko et al., 2002], as well as in plasmonic clusters and chains [Quinten and Kreibig, 1993; Chern et al., 2007; Chi et al., 2008; Stout et al., 2008]. The solution of multiple scattering using the T-matrix approach will be outlined in this section. The notation required for this method may be found in Sec.3.2.

A cluster of $N_s$ spheres, where sphere $j$ is located at $\mathbf{x}_j$, is shown in Fig. 7.2. The incident wave has vector spherical wave expansion coefficients $\mathbf{a}$, and it is assumed to be a plane wave according to (3.22), and the elements of $\mathbf{a}$ are (3.23). The scattering properties of particle $j$ in isolation are described by $\mathbf{T}_1^{(j)}$, where the subscript indicates that the matrix includes only single scattering effects. The total scattered field is represented by expansion coefficients $\mathbf{f}$. The entire cluster, including all mutual coupling, is represented

\(^1\)The basis is only nearly orthogonal since $A$ is not unitary. A good approximation to $A$ for the cases considered in this chapter requires only the near-field terms since $k_0r \ll 1$, and the other terms are small perturbations. Then $A$ is unitary, and $P^{-1} \approx P^\dagger$.\]
Figure 7.2: A cluster of $N_s$ spheres, bounded by a dashed sphere. Particle $j$, in isolation, is modeled by $T^{(j)}$, and after calculating the multiple scattering solution the cluster within the dashed boundary is modeled by $T_{\text{clust}}$. The incident wave is represented by $a$, and $f$ is the total scattered field.

by $T_{\text{clust}}$; the calculation of this is the goal of this section.

If particle $j$ were in isolation, the single scattering process could be written following (3.17). To generalize to the multiple scattering case, it will no longer be true that the field exciting the particle is the incident wave $a$; it is instead a general excitation field,

$$ E_j^{\text{exc}}(r) = E_0 R_g \Psi^T(k_h r_j) \cdot e^{(j)}. $$  \hfill (7.14)

Therefore, the generalization of (3.17) becomes

$$ f^{(j)} = T^{(j)}_1 \cdot e^{(j)}. $$ \hfill (7.15)

The expression of the multiple scattering problem will be developed with expressions of the $E$ field, since this is more convenient when using the T-matrix method. Similarly to (7.3), the total field exciting sphere $j$ due to the scattered fields from the other $N_s - 1$ particles and the incident wave is

$$ E_j^{\text{exc}}(r) = E_0 \Psi^T(k_h r_j) \cdot e^{(j)} + \sum_{k \neq j} E_k^{\text{scat}}(r), $$ \hfill (7.16)

where $E_k^{\text{scat}}(r)$ is the field scattered by particle $k$. Each term in this equation can be expanded in vector spherical waves,

$$ R_g \Psi^T(k_h r_j) \cdot e^{(j)} = R_g \Psi^T(k_h r_j) \cdot a + \sum_{k \neq j} \Psi^T(k_h r_k) \cdot f^{(k)} $$ \hfill (7.17)

where $r_k = r - x_k$ is the position vector relative to particle $k$. The basis functions for each particle are centered at their own local coordinate system, but they can all be translated to a common coordinate
system at particle $j$ by using the vector translation-addition theorem [CHEW, 1995],

$$\Psi^T(k_h r_k) = Rg \Psi^T(k_h r_j) \cdot \mathbf{H}^{(j,k)}, \quad r_j < d_{jk}, \quad (7.18a)$$

$$\Psi^T(k_h r_k) = \Psi^T(k_h r_j) \cdot J^{(j,k)}, \quad r_j > d_{jk}, \quad (7.18b)$$

$$Rg \Psi^T(k_h r_k) = Rg \Psi^T(k_h r_j) \cdot J^{(j,k)}, \quad \forall r_j, \quad (7.18c)$$

where $d_{ij} = |x_j - x_k|$, and the irregular and regular translation-addition matrices are $\mathbf{H}^{(j,k)} = \mathbf{H}(k_h (r_j - r_k))$ and $J^{(j,k)} = J(k_h (r_j - r_k))$ respectively, and $\bar{J}^{(j,k)} = Rg \mathbf{H}^{(j,k)}$. The translation-addition matrices are fairly complicated to write down, and so are omitted here. They are also time consuming to evaluate numerically; the best algorithms are recursive [CHEW, 1992, 1993; STOUT ET AL., 2002]\textsuperscript{2}. Armed with the translation matrices, (7.17) can be written in a single coordinate system,

$$Rg \Psi^T(k_h r_j) \cdot e^{(j)} = Rg \Psi^T(k_h r_j) \cdot J^{(j,0)} \cdot a + \sum_{k \neq j} N_r Rg \Psi^T(k_h r_j) \cdot \mathbf{H}^{(j,k)} \cdot f^{(k)}. \quad (7.20)$$

The basis functions are all the same, so

$$e^{(j)} = J^{(j,0)} \cdot a + \sum_{k \neq j} \mathbf{H}^{(j,k)} \cdot f^{(k)}. \quad (7.21)$$

Using (7.15), this simplifies to

$$e^{(j)} = J^{(j,0)} \cdot a + \sum_{k \neq j} \mathbf{H}^{(j,k)} \cdot \mathbf{T}^{(k)} \cdot e^{(k)}. \quad (7.22)$$

This constitutes a set of $N_r$ equations running over the index $j$, which can in principle be solved for the set of $e^{(j)}$.

Although the set of equations (7.22) can be solved as written [MACKOWSKI AND MISHCHENKO, 1996], the solutions are numerically unstable [STOUT ET AL., 2002]. Recursive methods [CHEW, 1995; STOUT ET AL., 2002] are more stable and tend to be more efficient. A particularly stable recursive method [STOUT ET AL., 2002] uses a definition of scatterer-centered matrices $\mathbf{T}^{(j,k)}_{N_r}$ [MACKOWSKI, 1994], resulting in the

\textsuperscript{2}The expressions for evaluating the scalar translation coefficients for $m < 0$ in $(C_4)$ of [STOUT ET AL., 2002] are unclear and contain typos. For a lossless host, where $kr$ is a real number, these elements can be found from

$$\beta_{\nu,\mu,\eta,m}(kr, \theta, \phi) = (-1)^{\mu-\nu} \beta_{\nu,-\mu,\eta,-m}(kr, \theta, \phi) e^{-i(\mu-\nu)\phi}, \quad (7.19)$$

and similarly for $s_{\nu,\mu,\eta,m}$. Also, it should be stressed that in order to calculate the desired values for $0 \leq \nu \leq n_{\text{max}}$ and $-\nu \leq \mu \leq \nu$, the extra terms with $n_{\text{max}} < \nu \leq 2n_{\text{max}}$ are necessary.
algorithm [STOUT ET AL., 2002],

\[ T^{(N_i,N_i)}_{N_i} = \left[ I - T_1^{(N_i)} \cdot \sum_{k=1}^{N_i-1} H^{(N_i,k)} \cdot \sum_{j=1}^{N_i-1} T^{(j,N_i)}_{N_i-1} \cdot H^{(j,N_i)} \right]^{-1} \cdot T_1^{(N_i)}, \]  
(7.23a)

\[ T^{(N_i,N_i)}_{N_i} = T^{(N_i,N_i)}_{N_i} \cdot \sum_{j=1}^{N_i-1} H^{(N_i,j)} \cdot T^{(j,N_i)}_{N_i-1}, \quad k \neq N_i, \]  
(7.23b)

\[ T^{(j,N_i)}_{N_i} = \sum_{k=1}^{N_i-1} T^{(j,k)}_{N_i-1} \cdot H^{(k,N_i)} \cdot T^{(N_i,N_i)}_{N_i-1} \cdot T^{(j,N_i)}_{N_i-1} \cdot T^{(N_i,k)}_{N_i}, \quad j \neq N_i, \]  
(7.23c)

\[ T^{(j,k)}_{N_i} = T^{(j,k)}_{N_i-1} + \sum_{l=1}^{N_i-1} T^{(j,l)}_{N_i-1} \cdot H^{(l,N_i)} \cdot T^{(N_i,k)}_{N_i}, \quad j, k \neq N_i. \]  
(7.23d)

The recursion is initiated with a single particle: \( N_i = 1, T_1^{(1)} \), and \( x_1 \). On each iteration another particle is added to the system, and \( N_i \rightarrow N_i + 1 \). When all particles have been added, the set of \( T^{(j,k)}_{N_i} \) for \( j, k = 1 \ldots N_i \) contains the solution to the multiple scattering problem. The solution can be written as a single matrix \( T_{\text{clus}} \) by shifting all of the \( T^{(j,k)}_{N_i} \) to the origin,

\[ T_{\text{clus}} = \sum_{j=1}^{N_i} \sum_{k=1}^{N_i} j^{(j,k)} \cdot T^{(j,k)}_{N_i} \cdot j^{(k,0)} . \]  
(7.24)

The total field scattered by the cluster is \( f = T_{\text{clus}} \cdot a \), analogously to the single scattering solution (3.17). This simple abstraction of the solution is depicted in Fig. 7.2 by the dashed bounding sphere.

The extinction cross section \( C_{\text{ext}} \) of the cluster may be evaluated with \( T_{\text{clus}} \) in (3.80). For the case of the incident plane wave propagating in the \( z \) direction with \( x \)-polarized electric field, whose expansion coefficients \( a \) are (3.23), it is both more efficient and more accurate to evaluate \( C_{\text{ext}} \) using [STOUT ET AL., 2002]

\[ C_{\text{ext}} = -\frac{1}{k_h} \sum_{j=1}^{N_i} \sum_{k=1}^{N_i} \text{Re} \left\{ \exp \left[ ik_h \hat{z} \cdot (x_k - x_j) \right] \right\} a^+ \cdot T^{(j,k)}_{N_i} \cdot a . \]  
(7.25)

### 7.3 Experimental Setup

The incident uniform plane wave defined by (3.22) can be approximated experimentally at microwave frequencies with a pyramidal horn source and a dielectric lens for focusing, as shown in Fig. 7.3. A mirror image of the system captures the transmitted power. The frequency range will be restricted to within the Ku band (12 to 18 GHz), and the centre wavelength is \( \lambda_h = 2 \) cm.

The biconvex lens is approximately \( d_L = 7.5 \) cm thick along its axis, and is made of Rexolite ( \( n_L = 1.59 \) ). The surface facing the horn has a focal length \( f_1 = 18.68 \) cm corresponding to a radius \( R_1 = 11 \) cm, and the surface facing the sample has a focal length \( f_2 = 29.00 \) cm corresponding to a radius \( R_2 = -17.1 \) cm.

The shape of a pyramidal horn is sufficient information to map it into Gaussian optics [GOLDSMITH, 1998]. The horn aperture dimensions are \( w_{H} = 4.29 \) cm in the H-plane and \( w_{E} = 3.30 \) cm in the E-plane, which provide an approximate average beam width at the aperture \( w_a = (0.35w_H + 0.5w_E)/2 \). The
pyramidal slant lengths in each plane are $S_H = 10.13 \text{ cm}$ and $S_E = 8.36 \text{ cm}$, which result in an approximate average wavefront radius $R_a = (S_H + S_E)/2$ in the aperture plane.

The beam must be focused to a waist where the samples are placed. To approximate a plane wave, there are two requirements. First, to ensure that the field amplitude is uniform over the samples, the beam waist at the sample $w_{0,s}$ must be much larger than the transverse extent of the samples. Second, to ensure that the wavefronts are planar, the Rayleigh range $z_{0,s}$ must be much larger than the longitudinal extent of the samples. The distance from the horn aperture to the front of the lens is chosen to be $d_1 = 15 \text{ cm}$. The remaining dimensions can be calculated using Gaussian beam principles, as derived in App. C. The results are that the space between the back of the lens and the sample is $d_2 = 30 \text{ cm}$, the beam waist at the sample plane is $w_{0,s} = 2.7 \text{ cm}$, and the Rayleigh range at the sample is $z_{0,s} = 11.7 \text{ cm}$. A good approximation to a plane wave is ensured because the latter two dimensions are indeed much larger than the samples that will be studied in Sec. 7.4.

A sample placed at the focused beam waist will either scatter power in all directions, or absorb some power which will be lost as heat (although this is nearly absent in the samples). The total of these effects, by (7.78), is proportional to the extinction cross section $C_{\text{ext}}$, which can be calculated using (7.6) for the coupled dipole model, or (7.25) for the T-matrix approach. The normalized transmittance through the system $T_{\text{calc}}$ is the ratio of the intensity measured with the sample in place $I_t$ to that with no sample $I_0$, which is approximately

$$T_{\text{calc}} = \frac{I_t}{I_0} \approx 1 - \frac{C_{\text{ext}}}{A_b},$$

where $A_b = \pi w_{0,s}^2 / 0.86$ is the transverse area of the beam at the sample plane, and $w_{0,s}$ is the beam waist.\(^3\)

The factor $1/0.86$ is due to the definition of the beam width as the $1/e$ distance, so only 86% of the power in the beam is contained within the cylinder defined by the waist.

A sample holder was made from polystyrene foam, which is essentially transparent to microwaves.

\(^3\)The measurement of $|S_{\|}|^2$ would yield a result proportional to the backscattering cross section $C_b$ or the radar cross section $\sigma_b$. 
The horns were connected to an HP 8722C vector network analyzer, allowing for the measurement of the transmission magnitude \( |S_{21}| \). The system was calibrated by first saving a measurement of the transmitted power density \( I_0 \propto |S_{21}|^2 \) without a sample in place. Then a sample was inserted and another measurement was taken \( I_t \propto |S_{21}|^2 \). The ratio of these measurements yields the normalized transmittance \( T_{\text{meas}} = I_t/I_0 \), which may be compared with (7.26). This process removes the effects of the horns, lenses, and sample holder. Furthermore, 0.2% smoothing and 16 sample averages were used to minimize the noise in these sensitive measurements. The resulting measurements continue to display small ripples, which are likely due to Fabry-Perot reflections between combinations of the lenses and horns. Since the rough extent of the apparatus is on the order of \( \Delta d \sim 1 \) m, the ripples have a frequency separation [Saleh and Teich, 1991] on the order of \( \Delta f = c/(2\Delta d) \sim 0.15 \) GHz.

### 7.4 Results

Three classes of clusters will be presented. First, a pair of spheres will be studied for two polarizations and for various coupling distances. The dipole hybridization will be quite apparent in the model and the results. Second, a chain of touching spheres will be presented briefly, since it is an extension of the pair of spheres. Third, a ring of spheres will be investigated, and the hybrid modes will be connected to effective cluster moments and effective polarizabilities for metamaterial structures.

The orbital momentum cutoff in the T-matrix calculations is \( l_{\text{max}} = 5 \). This is chosen based on a measure of uniform convergence, which may be defined as

\[
\Delta_l = \frac{1}{N_f} \sum_{i=1}^{N_f} \left| \frac{C^l_{\text{ext}}(f_i) - C^{l-1}_{\text{ext}}(f_i)}{C^{l-1}_{\text{ext}}(f_i)} \right|
\]

where \( N_f \) frequency points are evaluated in the range \( f_{\min} \leq f \leq f_{\max} \), so that each frequency is \( f_i = f_{\min} + (i-1)\Delta f \), and the frequency step is \( \Delta f = (f_{\max} - f_{\min})/(N_f - 1) \). This definition provides a notion of convergence over the entire bandwidth of interest. The choice \( l = l_{\text{max}} = 5 \) guarantees that \( \Delta_l \leq 10^{-3} \) for all of the results presented here. Note that this value of \( l_{\text{max}} \) is significantly smaller than would be expected for the dual case of strongly coupled plasmonic spheres. For example, for only a pair of nearly touching silver nanospheres, a value \( l_{\text{max}} > 14 \) is required to ensure a similar measure of convergence of \( \sim 10^{-2} \) [Chern et al., 2007], but this is still a factor of 10 weaker than the case presented here. The reason for this difference is that metal spheres have higher-order multipole resonances, as a consequence of the Drude-like dispersion, which satisfy the condition (3.56). This creates many multipole resonances within a bandwidth adjacent to the dipole resonance, which complicate the strong coupling spectrum.

#### 7.4.1 Pair of Spheres

A pair of spheres, where \( N_s = 2 \), is shown for two orientations in Fig. 7.4. Since the incident magnetic field is \( y \)-polarized, as seen from (3.22), magnetic dipoles will be induced in that direction, so \( \mathbf{m}_j = m_j \hat{y} \).
Chapter 7. Coupled Magnetic Dipoles

Figure 7.4: Schematic of a pair of spheres excited by a plane wave for two orientations. Each sphere supports an induced magnetic dipole which will be parallel to the excitation $\mathbf{H}^{\text{inc}}$. When the induced dipole moments are parallel to the axis of the spheres, longitudinal modes are excited. When the induced dipole moments are perpendicular to the axis of the spheres, transverse modes are excited.

Dotting (7.4) on the left with $\hat{y}$ gives the matrix elements for the system (7.8),

$$A_{jk} = \begin{cases} \frac{1}{\alpha_m} & j = k \\ -\hat{y} \cdot \overline{\mathbf{G}}(\mathbf{x}_j - \mathbf{x}_k) \cdot \hat{y} & j \neq k, \end{cases}$$

where $j, k = 1, 2$. Two cases will be examined, longitudinal and transverse modes.

**Longitudinal Modes**

The orientation in which longitudinal modes can arise is shown on the left in Fig. 7.4. This case is denoted longitudinal since the axis of the pair is parallel to $\mathbf{H}^{\text{inc}}$. In general, $|\mathbf{x}_j - \mathbf{x}_k| = d|j - k|$, and the system matrix from (7.28) becomes

$$A_{jk} = \begin{cases} \frac{1}{\alpha_m} & j = k \\ \frac{-\exp(ik_h(j - k)d)}{2\pi|(j - k)d|^3} (1 - ik_h|j - k|d) & j \neq k. \end{cases}$$

This valid for any number of equally spaced spheres, but the analysis of a pair of spheres where $j, k = 1, 2$ will be continued in more detail.

To extract the essential physics of the pair of coupled spheres, the system matrix (7.29) can be simplified by keeping only the near-field terms. Since $k_h d \ll 1$,

$$A \approx \frac{1}{2\pi d^3 \alpha_m} \begin{bmatrix} 2\pi d^3 & -\alpha_m \\ -\alpha_m & 2\pi d^3 \end{bmatrix}.$$  \hspace{1cm} (7.30)

One eigenvalue is $\lambda_a = 2\pi d^3 + \alpha_m$, and the associated eigenvector is $\mathbf{v}_a = (1, -1)/\sqrt{2}$. This anti-symmetric
mode will be labeled in the hybridized basis as \( \mathbf{v}_s' = \begin{bmatrix} 1 & 0 \end{bmatrix}^T \). The other eigenvalue is \( \lambda_s = 2\pi d^3 - \alpha_m \), and the associated eigenvector is \( \mathbf{v}_s = (1,1)/\sqrt{2} \). This symmetric mode will be labeled in the hybridized basis as \( \mathbf{v}_s' = \begin{bmatrix} 0 & 1 \end{bmatrix}^T \). Solving for \( \text{Re} \{ \lambda_{a,s} \} = 0 \) and using (3.34b), (3.37b), and (3.45), the resonant frequencies of the pair are

\[
 f = \frac{c}{2n_s r_s} \left[ 1 - \frac{3}{\pi^2} \left( \frac{1}{1 + (d/r_s)^3} \right) \right]. \tag{7.31}
\]

The minus sign applies for the anti-symmetric mode, and the plus sign for the symmetric mode. For the case of touching spheres, \( d = 2r_s \), so the resonant frequency for the spheres with properties (7.1) is 12.80 GHz for the symmetric mode and 13.82 GHz for the anti-symmetric mode. The numerical solution using all terms in the dipole dyadic from (7.29) yields 12.63 GHz and 13.72 GHz for the respective modes. The near-field terms provide a very good approximation, with roughly only a 1% error.

To determine which modes are excited, the forcing term in (7.7) must be included,

\[
 \mathbf{h} = \begin{bmatrix} \mathbf{h} \cdot \mathbf{H}^{\text{inc}}(\mathbf{x}_1) \\ \mathbf{h} \cdot \mathbf{H}^{\text{inc}}(\mathbf{x}_2) \end{bmatrix} = H_0 \begin{bmatrix} 1 \\ 1 \end{bmatrix}. \tag{7.32}
\]

Using (7.11), the excitation in the hybridized mode basis is

\[
 \mathbf{h}' = P^{-1} \mathbf{h} = \frac{H_0}{\sqrt{2}} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \propto \mathbf{v}_s', \tag{7.33}
\]

so only the symmetric mode can be excited. This may also be verified using (7.13). This can be understood physically since the spheres are both placed in a plane of uniform phase.

The complete results of all three methods (experimental, coupled dipole model, and T-matrix method) are plotted in Fig. 7.5 for various spacings of the spheres. The case of a single sphere is equivalent to two spheres with infinite spacing. As the spheres are brought together, the splitting of the resonant frequency increases. The resonant frequency of the anti-symmetric mode is shown by the empty arrowhead, indicating that it is uncoupled by the incident wave. These results are similar to the bonding of two atomic \( 2p_y \) orbitals, where the hybridization creates bonding \( \sigma_{2p_y} \) and anti-bonding \( \sigma^*_{2p_y} \) molecular orbitals [Oxtoby and Nachtrieb, 1996].

**Transverse Modes**

The orientation in which transverse modes can arise is shown on the right in Fig. 7.4. This case is denoted transverse since the axis of the pair is perpendicular to \( \mathbf{H}^{\text{inc}} \). In general, \( |\mathbf{x}_j - \mathbf{x}_k| = d|j - k| \), and the system matrix from (7.28) becomes

\[
 A_{jk} = \begin{cases} 1/\alpha_m & j = k, \\ \exp \left( \frac{ik_h j - k|d|}{4\pi(|j - k|d)^3} \left[ 1 - \frac{ik_h j - k|d| - (k_h j - k|d|^2) |j - k|}{\pi|j - k|^3} \right] \right) & j \neq k. \end{cases} \tag{7.34}
\]
Figure 7.5: Experimental measurement (solid), coupled dipole model calculation (dotted), and T-matrix calculation (dashed) of the normalized transmittance through various spacings of a pair of spheres, for longitudinal modes, as sketched on the left in Fig. 7.4. The arrows denote the resonant frequencies calculated with the coupled dipole model, and empty arrowheads indicate uncoupled modes. The “s” and “a” denote symmetric and anti-symmetric coupling.
This valid for any number of equally spaced spheres, but the analysis of a pair of spheres where \( j, k = 1, 2 \) will be continued in more detail.

To extract the essential physics of the pair of coupled spheres, the system matrix (7.34) can be simplified by keeping only the near-field terms. Since \( k_h d \ll 1 \),

\[
A \approx \frac{1}{4\pi d^3 \alpha_m} \begin{bmatrix} 4\pi d^3 & \alpha_m \\ \alpha_m & 4\pi d^3 \end{bmatrix}.
\] (7.35)

One eigenvalue is \( \lambda_a = 4\pi d^3 - \alpha_m \), and the associated eigenvector is \( v_a = (1, -1)/\sqrt{2} \). This anti-symmetric mode will be labeled in the hybridized basis as \( v'_a = \begin{bmatrix} 1 \\ 0 \end{bmatrix}^T \). The other eigenvalue is \( \lambda_s = 4\pi d^3 + \alpha_m \), and the associated eigenvector is \( v_s = (1, 1)/\sqrt{2} \). This symmetric mode will be labeled in the hybridized basis as \( v'_s = \begin{bmatrix} 0 \\ 1 \end{bmatrix}^T \). Solving for \( \lambda_{a,x} \) = 0 and using (3.34b), (3.37b), and (3.45), the resonant frequencies of the pair are

\[
f \approx \frac{c}{2n_r r_s} \left[ 1 - \frac{3}{\pi^2} \left( \frac{1}{1 \pm 2(d/r_s)^3} \right) \right].
\] (7.36)

The plus sign applies for the anti-symmetric mode, and the minus sign for the symmetric mode. For the case of touching spheres, \( d = 2r_s \), so the resonant frequency for the spheres with properties (7.1) is 13.51 GHz for the symmetric mode and 13.01 GHz for the anti-symmetric mode. The numerical solution using all terms in the dipole dyadic from (7.29) yields 13.35 GHz and 12.94 GHz for the respective modes. The near-field terms provide a very good approximation, with roughly only a 1% error.

To determine which modes are excited, the forcing term in (7.7) must be included,

\[
h = \begin{bmatrix} \hat{y} \cdot \mathbf{H}^{inc}(x_1) \\ \hat{y} \cdot \mathbf{H}^{inc}(x_2) \end{bmatrix} = H_0 \begin{bmatrix} \exp(ikhd/2) \\ \exp(-ikhd/2) \end{bmatrix}.
\] (7.37)

The approximation \( k_h d \ll 1 \) will not be applied here, to keep the excitation general. Using (7.11), the excitation in the hybridized mode basis is

\[
h' = P^{-1}h = i\sqrt{2}H_0 \sin(k_h d/2)v'_a + \sqrt{2}H_0 \cos(k_h d/2)v'_s,
\] (7.38)

so the plane wave excites both the symmetric and anti-symmetric mode. This may also be verified using (7.13). This can be understood physically since the phase of the incident wave is generally unequal at each sphere.

The complete results of all three methods (experimental, coupled dipole model, and T-matrix method) are plotted in Fig. 7.6 for various spacings of the spheres. The case of a single sphere is equivalent to two spheres with infinite spacing. As the spheres are brought together, the splitting of the resonant frequency increases. These results are similar to the bonding of two atomic \( 2p_y \) orbitals, where the hybridization creates bonding \( \pi_{2p_y} \) and anti-bonding \( \pi^*_{2p_y} \) molecular orbitals [OXToby AND NACHTRIEB, 1996].
Figure 7.6: Experimental measurement (solid), coupled dipole model calculation (dotted), and T-matrix calculation (dashed) of the normalized transmittance through various spacings of a pair of spheres, for transverse modes, as sketched on the right in Fig. 7.4. The arrows denote the resonant frequencies calculated with the coupled dipole model. The “s” and “a” denote symmetric and anti-symmetric coupling.
**Figure 7.7:** The eigenmode patterns and resonant frequencies of a chain of eight touching spheres, calculated with the coupled dipole model.

### 7.4.2 Linear Chain of Spheres

A chain of spheres is simply a generalization of the pair of spheres depicted in Fig. 7.4. Only the case of \( N_s = 8 \) touching spheres will be considered. Since the spacing between the spheres is equal, the system matrices in the coupled dipole approximation are (7.29) for longitudinal modes, and (7.34) for transverse modes. The eigenmode analysis follows the process described in Sec. 7.4.1, and the results are displayed in Fig. 7.7. There are \( N_s = 8 \) eigenmodes for each polarization, and the mode patterns are essentially the same in both cases. The patterns alternate between even and odd symmetry with respect to the center of the chain. The resonant frequencies are ordered oppositely in the two cases.

The complete results of all three methods (experimental, coupled dipole model, and T-matrix method) are plotted in Fig. 7.8. In the case of the longitudinal modes, only four of the eight modes are excited. As with the pair of spheres under longitudinal excitation, only even (symmetric) modes are coupled, since the spheres are all located in a plane of uniform phase of the incident wave. In the case of the transverse modes, both the even and odd modes can be excited, although some are so weakly coupled that they cannot be distinguished in the transmittance results. Since the spheres are placed along the direction of phase propagation, the incident wave is a frequency-dependent mixture of even and odd modes. In addition, the frequency spread of the resonances is much smaller, so the modes resonances merge into each other and are not isolated and distinguishable as in the longitudinal case.
Figure 7.8: Experimental measurement (solid), coupled dipole model calculation (dotted), and T-matrix calculation (dashed) of the normalized transmittance through a chain of eight touching dielectric spheres. The arrows denote the resonant frequencies calculated with the coupled dipole model, and empty arrowheads indicate uncoupled modes.

7.4.3 Ring of Spheres

A system of \( N_s = 4 \) spheres which forms a ring of radius \( R \) excited by a plane wave is shown in Fig. 7.9. Magnetic dipoles will be induced in the \( yz \) plane in each sphere, so (7.4) consists of \( 2N_s = 8 \) equations. Writing the system in the form (7.8), the vector of unknown dipole moments can be arranged as

\[
\mathbf{v}^T = \begin{bmatrix} m_{1,y} & m_{1,z} & m_{2,y} & m_{2,z} & m_{3,y} & m_{3,z} & m_{4,y} & m_{4,z} \end{bmatrix}.
\]  

(7.39)

Figure 7.9: Schematic of a ring of spheres excited by a plane wave.
Chapter 7. Coupled Magnetic Dipoles

The system matrix $A$, after many simplifications due to the symmetries in the structure and the dipole field, is

$$
A = \begin{bmatrix}
0 & 0 & \zeta_1 & 0 & \zeta_3 & \zeta_4 & \zeta_2 & 0 \\
0 & 0 & 0 & \zeta_2 & \zeta_4 & \zeta_3 & 0 & \zeta_1 \\
\zeta_1 & 0 & 0 & 0 & \zeta_2 & 0 & \zeta_3 & -\zeta_4 \\
0 & \zeta_2 & 0 & 0 & 0 & \zeta_1 & -\zeta_4 & \zeta_3 \\
\zeta_3 & \zeta_4 & \zeta_2 & 0 & 0 & 0 & \zeta_1 & 0 \\
\zeta_4 & \zeta_3 & 0 & \zeta_1 & 0 & 0 & 0 & \zeta_2 \\
\zeta_2 & 0 & \zeta_3 & -\zeta_4 & \zeta_1 & 0 & 0 & 0 \\
0 & \zeta_1 & -\zeta_4 & \zeta_3 & 0 & \zeta_2 & 0 & 0 \\
\end{bmatrix} - \frac{1}{\alpha_m} I_{8 \times 8}, \tag{7.40}
$$

where $I_{n \times n}$ is the identity matrix of dimension $n$. All of the entries can be related through various symmetries to the Green's function of a z-directed dipole, and only eight unique entries are required, four of which are non-zero:

$$
\begin{align*}
\zeta_1 &= G_{zz}(d\hat{z}) = \frac{\exp(i k_h d)}{4 \pi d^3} \frac{1}{2}(1 - i k_h d), \\
G_{yz}(d\hat{z}) &= 0, \\
\zeta_2 &= G_{zz}(d\hat{y}) = \frac{\exp(i k_h d)}{4 \pi d^3} [(k_h d)^2 - (1 - i k_h d)], \\
G_{yz}(d\hat{y}) &= 0, \\
\zeta_3 &= G_{zz}(d\hat{y} + d\hat{z}) = \frac{\exp(i k_h \sqrt{2} d)}{8 \pi \sqrt{2} d^3} \left[ (k_h d)^2 + \frac{1}{2} (1 - i k_h \sqrt{2} d) \right], \\
\zeta_4 &= G_{yz}(d\hat{y} + d\hat{z}) = \frac{\exp(i k_h \sqrt{2} d)}{8 \pi \sqrt{2} d^3} \left[ -(k_h d)^2 + \frac{3}{2} (1 - i k_h \sqrt{2} d) \right], \\
G_{zz}(d\hat{y} - d\hat{z}) &= \zeta_3, \\
G_{yz}(d\hat{y} - d\hat{z}) &= -\zeta_4,
\end{align*}
$$

where $d = \sqrt{2} R$. The results of the eigenmode analysis of $A$ are shown in Fig. 7.10, for touching spheres ($d = 2 r_s$). There are doubly-degenerate modes at 12.72 GHz and 13.45 GHz.

The complete results of all three methods (experimental, coupled dipole model, and T-matrix method) are shown in the top two panels in Fig. 7.11. Two cases are shown, which differ only in the relative direction of the incident plane wave, as shown in the insets. The results for the two cases are almost the same, with two exceptions: the resonance near 12.63 GHz is uncoupled in the upper configuration, and the resonance near 13.87 GHz is uncoupled in the lower configuration. The coupling of the incident wave to the eigenmodes can be analyzed using (7.11). It is, however, easier to use (7.13) and inspecting the mode patterns in Fig. 7.10. If the inner product of $H^{inc}$ evaluated at each sphere and an eigenmode patterns is zero, the mode cannot be excited by the incident wave. In addition, it can be shown using (7.13) that the 14.21 GHz mode is uncoupled not only for both cases shown in Fig. 7.11, but for any plane wave with $k_0$ in the $yz$ plane and $E^{inc} \propto \hat{x}$ if $k_0 r_s \ll 1$.

The eigenmode analysis also allows for easy evaluation of the dipole moments of the ring. The net
<table>
<thead>
<tr>
<th>Mode Pattern</th>
<th>Frequency</th>
<th>( m_{\text{net}} )</th>
<th>( p_{\text{net}} )</th>
</tr>
</thead>
<tbody>
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<td><img src="image1" alt="Pattern" /></td>
<td>12.38 GHz</td>
<td>○</td>
<td>×</td>
</tr>
<tr>
<td><img src="image2" alt="Pattern" /></td>
<td>12.63 GHz</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td><img src="image3" alt="Pattern" /></td>
<td>12.72 GHz</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td><img src="image4" alt="Pattern" /></td>
<td>13.45 GHz</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td><img src="image5" alt="Pattern" /></td>
<td>13.87 GHz</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td><img src="image6" alt="Pattern" /></td>
<td>14.21 GHz</td>
<td>○</td>
<td>○</td>
</tr>
</tbody>
</table>

Figure 7.10: The eigenmode patterns and resonant frequencies of a ring of four touching spheres excited by a plane wave as shown in Fig. 7.9, calculated with the coupled dipole model. The arrows denote the induced magnetic dipole moments. The net dipole moments of the ring for each eigenmode are also shown, with × indicating any non-zero value.
Figure 7.11: Top two panels: Experimental measurement (solid), coupled dipole model calculation (dotted), and T-matrix calculation (dashed) of the normalized transmittance through a ring of touching dielectric spheres, for two orientations. The arrows denote the resonant frequencies calculated with the coupled dipole model, double arrows denote doubly-degenerate modes, and empty arrowheads indicate uncoupled modes. Bottom two panels: calculated effective permittivity and permeability, extracted from the T-matrix calculations, of a periodic metamaterial having the ring as the basis unit. The results correspond to both orientations shown in the top two panels.
magnetic dipole moment $\mathbf{m}_{\text{net}}$ of the cluster is simply the vector sum of the induced moments,

$$
\mathbf{m}_{\text{net}} = \sum_{j=1}^{N_s} \mathbf{m}_j.
$$

(7.42)

Just as $\mathbf{m}$ can be evaluated when the electric current density $\mathbf{J}$ is known [JACKSON, 1999, p. 413], the net electric dipole moment $\mathbf{p}_{\text{net}}$ of the cluster can be evaluated in terms of the magnetic current density $J_m$,

$$
\mathbf{p}_{\text{net}} \propto \int \mathbf{x}' \times J_m(\mathbf{x}') \, d\mathbf{x}'.
$$

(7.43)

The magnetic current density is related to the point dipole moments by

$$
J_m(\mathbf{x}) = -i\omega \sum_{j=1}^{N_s} \mathbf{m}_j \delta(\mathbf{x} - \mathbf{x}_j),
$$

(7.44)

where $\delta(\mathbf{x})$ is the Dirac delta function. Therefore (7.43) simplifies to

$$
\mathbf{p}_{\text{net}} \propto \sum_{j=1}^{N_s} \mathbf{x}_j \times \mathbf{m}_j.
$$

(7.45)

Whether or not either net dipole moment is zero for each eigenmode is displayed in Fig. 7.10.

The non-zero net dipole moments of certain eigenmodes indicates that the ring cluster might be used as a basis unit in a periodic metamaterial. The ring (Fig. 7.9) may be interpreted as a cluster "molecule", as illustrated by the enclosing spherical boundary in Fig. 7.2. The electric and magnetic polarizabilities $\alpha_{e,xx}$ and $\alpha_{m,yy}$ may be evaluated from (3.30). This requires the total scattered field $\mathbf{f}$, which may be calculated by inserting $\mathbf{T}_{\text{clust}}$ into (3.17). The effective permittivity $\varepsilon_{\text{eff},xx}$ and permeability $\mu_{\text{eff},yy}$ of a periodic composite with cluster density $N$ can be found using the Clausius-Mossotti relations (4.7). For a periodic structure, the radiation correction (4.8) can be applied. The resulting effective media values are shown in the lower two panels in Fig. 7.11, which were calculated using data from the T-matrix solution shown in the top two panels. A cubic lattice of rings is assumed, with unit cell density $N = (6 \text{ mm})^{-3}$.

The lowest frequency hybridized mode around 12.38 GHz has a net electric dipole moment parallel to the ring axis, which is due to the circulation of magnetic displacement current (Fig. 7.10). This results in the resonance in $\varepsilon_{\text{eff},xx}$. The doubly-degenerate modes near 12.72 GHz and 13.45 GHz both have a net magnetic dipole moments, and so contribute to resonances in $\mu_{\text{eff},yy}$. The degeneracy of both these modes explains why the effective media values are the same for any rotation of the incident wave in the $yz$ plane. The remainder of the modes have no net dipole moments, and although such higher-moment modes may contribute very slightly to the true effective media values, they do not enter the first-order Clausius-Mossotti model.

The ring structure examined in this section has demonstrated that the strong near-field coupling of dipoles can lead to interesting physics and possibly new and more flexible metamaterial designs. Most notably, the lowest frequency eigenmode of coupled circulating magnetic dipoles acts like an effective electric dipole. This indeed is an interesting metamaterial concept, whereby the response of the cluster
Figure 7.12: Comparison of the magnitude of the effective electric polarizabilities of the ring, as arranged in the top panel of Fig. 7.11, and a single sphere of volume equal to the four spheres comprising the ring.

is quite different from the response of its constituent particles. It might therefore be considered a *meta-molecule*. Metamaterials comprised of inclusions made from similar clusters of a large number of particles has been named *meta-metamaterials* [Rockstuhl et al., 2007]. The ring of dielectric spheres studied here is a dual case of the report on a metamaterial made with a ring of plasmonic spheres as a basis, whose individual electric dipole resonances form a circulating electric displacement current and therefore, as a cluster, acts as a magnetic dipole which contributes to an effective permeability [Alù et al., 2006; Alù and Engheta, 2008]. Although there are resonances in both the effective permittivity and permeability, they do not overlap in frequency, but it might be possible to optimize the design to overlap the resonances and create a negative index metamaterial.

Finally, it is interesting to compare the effective electric polarizability \( \alpha_{e,xx} \) induced by the coupled circulation of magnetic dipoles in the ring to that of a similar single sphere, having the same permittivity as the spheres in the ring, but with a volume equal to the total volume of ring spheres. Thus, the comparison sphere has a radius 1.70 mm. The result is shown in Fig. 7.12, where it is seen that the polarizabilities are comparable, and the hybridized mode does not suffer any noticeable coupling loss or broadening. Therefore, such engineered hybridized modes should be useful to create designer molecular-like responses. It is stressed, however, that this comparison is only similar for the effective electric dipole mode of the ring; comparisons of other quantities, such as the cross sections, share few or no similarities.
Chapter 8

Conclusions

It has been shown that a wide variety of metamaterial properties is possible by using inclusions of dielectric particles. The very simple structure of the spherical inclusions makes them an attractive alternative to srr-based magnetic metamaterials, particularly for optical frequencies. They may also be used more generally for negative permittivity or negative refractive index metamaterials. Although there are materials restrictions on the implementation, a wide array of materials may be chosen, depending on the frequency range of an application.

A model was developed of the scattering and effective medium properties of randomly shaped SiC micro-particles. The model approximates the magnetic dipole scattering as though the particles were spheres using Mie theory, but uses a model of a continuous distribution of ellipsoids for the electric dipole scattering. Infrared spectroscopic measurements and calculations indicate both magnetic and electric dipole responses in a purely dielectric sample. This demonstrates that magnetic metamaterials need not require sophisticated fabrication techniques, although one fabrication technique using nanochemistry was developed. The magnetic metamaterial verified here is also an isotropic, bulk three-dimensional structure, which are further properties that are difficult to obtain in srr-based metamaterial structures. The concepts and results presented here should greatly simplify the implementation and application of optical metamaterials.

The mutual coupling of ideal magnetic dipoles in small clusters of dielectric spheres was also studied. An approximate coupled dipole model and an exact multiple scattering method were used to confirm microwave Gaussian beam measurements. Three types of sphere clusters were studied: pairs, chains, and rings. Due to mutual coupling, the magnetic dipoles induced in each sphere hybridize, just like atomic orbitals. Most notably, a coupled circulation of magnetic dipoles was shown to cause an effective electric polarizability. This metamolecule concept should prove useful in broadening the engineering possibilities in future metamaterials.

8.1 Future Work

There are several immediate paths for improvement and application of the material presented in this dissertation. The preliminary results of the magnetic response in the random SiC micropowder presented here might be improved upon by additional processing. By controlling the size distribution through many
filtering stages, a more monodisperse size distribution should be obtained. It would likely be more difficult
to narrow the shape distribution, but at least in the interest of magnetic materials it plays little part.

Improved measurements on the SiC powder sample would attempt to obtain phase information. Indeed,
such information is necessary to retrieve the complex $\mu_{\text{eff}}$ and $\epsilon_{\text{eff}}$ [Padilla et al., 2006]. In addition,
more advanced measurements should be able to characterize with samples with larger particle densities.
The particle densities were required to be very small, to be compatible with the simple spectroscopic
techniques used here. Despite the validation of the magnetic response of the SiC powder, the low particle
density limits the effective magnetic and electric susceptibilities such that the $\mu_{\text{eff}}$ and $\epsilon_{\text{eff}}$ corresponding
to the results found here were roughly 1% different from the host values, $\mu_h = \mu_0$ and $\epsilon_h$. Thus a larger
density is necessary to obtain a negative permeability metamaterial.

The use of coupled particle clusters should allow for more engineering flexibility in the design of
metamaterials. This true for optical frequencies, particularly in the design of inclusions which rely less
heavily on large permittivity materials, which are somewhat uncommon or difficult to accommodate.
The use of cluster inclusions might in fact be even more pertinent to microwave metamaterials, where
arranging clusters can be done at a larger size scale.

\section*{8.2 Other Future Directions}

Looking beyond the scope of metamaterials, the metamolecule concept, the coupled dipole model and
analysis, and the T-matrix method should prove useful in the study of either the phonon-polaritonic
resonances of dielectric crystal particles at infrared frequencies, or the plasmon-polaritonic resonances
of metal particles at visible frequencies. The latter case of plasmonics has been much studied by other
researchers [Novotny and Hecht, 2006]. In both cases, it is the surface electric dipole resonances which
are most likely useful towards applications in requiring local field enhancements or strong coupling, such as
optical (or infrared) antennas, near field spectroscopy and sensors, and waveguides. This is due particularly
to the accumulation of many spectrally-adjacent multipole resonances, as seen by (3.56), which contribute
to the enhanced near-field intensities [Chern et al., 2007]. That phononic resonances may be useful
for such enhancement has been noted before: the local field enhancement relative to the incident field
$E_{\text{loc}}/E_{\text{inc}} \propto \alpha_e$ for the phononic resonance of a SiC particle is stronger and narrower in bandwidth than
that of the plasmonic resonance of Ag by a factor of over 2; both effects are due to the smaller imaginary
part of the dielectric function of SiC over silver, at their respective resonant frequencies [Rockstuhl
et al., 2005; Hillenbrand et al., 2002]. By using the results of this dissertation, the optimization of
field enhancement and bandwidth might be improved with the control of particle sizes, shapes, materials,
and also by using coupled interactions among particle clusters.

Recent research has noted the ability of metal nanoparticles to increase the power conversion efficiency
of solar cells [Catchpole and Polman, 2008b; Derkacs et al., 2008; Nakayama et al., 2008; Kim
et al., 2008]. This effect can be understood in terms of enhanced scattering cross sections of plasmon
resonances. The particles can often scatter power as if they were over 10 larger than their physical cross
section. This enhancement increases the fields that are transmitted into the photovoltaic cell, which can
increase the photocurrent [Catchpole and Polman, 2008b]. However, much of the work in this area has been done without much regard to possible improvements through particle distributions, particle shape effects, and interactions among the particles. Since these issues played a large role in this dissertation, it is plausible that the tools and insights revealed here may be useful in the improvement of photovoltaics. A launching point for this path of research might be a preliminary study of particle shapes for in the context of solar cells [Catchpole and Polman, 2008a], and the integration of the T-matrix method with planar interfaces [Kristensson and Ström, 1982].

8.3 Publications

Portions of the content of this dissertation have been presented in the following publications:


Additional work accomplished during the pursuit of research has not been included in this dissertation, but can be found in the following publications:


Appendix A

Riccati-Bessel Functions

The Riccati-Bessel functions $\psi_l$, $\chi_l$, and $\xi_l$ are related to the spherical Bessel functions $j_l$, $y_l$, and $h_l^{(1)} = j_l + iy_l$, as well as the cylindrical Bessel functions $J_l$, $Y_l$, and $H_l^{(1)} = J_l + iY_l$, by [Abramowitz and Stegun, 1972],

\[
\psi_l(z) = z j_l(z) = \sqrt{\frac{\pi z}{2}} J_{l+1/2}(z), \tag{A.1}
\]
\[
\chi_l(z) = -z y_l(z) = -\sqrt{\frac{\pi z}{2}} Y_{l+1/2}(z), \tag{A.2}
\]
\[
\xi_l(z) = z h_l^{(1)}(z) = \sqrt{\frac{\pi z}{2}} H_{l+1/2}^{(1)}(z). \tag{A.3}
\]

and

\[
\xi_l(z) = \psi_l(z) - i\chi_l(z). \tag{A.4}
\]

The integer orders of the spherical Bessel functions and Riccati-Bessel functions can be written in terms of trigonometric functions. For $l = 1$,

\[
\psi_1(z) = \frac{\sin(z)}{z} - \cos(z), \quad \psi_1(z) = \frac{-\sin(z)}{z^2} + \frac{\cos(z)}{z} + \sin(z), \tag{A.5}
\]
\[
\chi_1(z) = \frac{\cos(z)}{z} + \sin(z), \quad \chi_1(z) = \frac{-\cos(z)}{z^2} - \frac{\sin(z)}{z} + \cos(z), \tag{A.6}
\]
\[
\xi_1(z) = \left(\frac{-i}{z} - 1\right) e^{iz}, \quad \xi_1(z) = \left(\frac{i}{z^2} + \frac{1}{z} - i\right) e^{iz}. \tag{A.7}
\]

For a small argument $|z| \ll 1$, these are approximately [Abramowitz and Stegun, 1972]

\[
 j_l(z) \approx \frac{z^l}{(2l + 1)!!}, \tag{A.8}
\]
\[
 y_l(z) \approx \frac{- (2l - 1)!!}{z^{l+1}}, \tag{A.9}
\]

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Appendix A. Riccati-Bessel Functions

where the double factorial is defined as

\[
n!! = \begin{cases} 
n \cdot (n-2) \ldots 5 \cdot 3 \cdot 1 & \text{if } n > 0 \text{ is odd}, \\
n \cdot (n-2) \ldots 6 \cdot 4 \cdot 2 & \text{if } n > 0 \text{ is even}, 
\end{cases}
\]  
(A.10)

and \(-1!! = 0!! = 1\). For \(l = 1\) and \(|z| \ll 1\),

\[
\begin{align*}
\psi_1(z) & \approx \frac{z^2}{3}, & \psi_1'(z) & \approx \frac{2z}{3}, \\
\chi_1(z) & \approx \frac{1}{z}, & \chi_1'(z) & \approx -\frac{1}{z^2}, \\
\xi_1(z) & \approx -\frac{i}{z}, & \xi_1'(z) & \approx \frac{i}{z^2}.
\end{align*}
\]  
(A.11) (A.12) (A.13)
Appendix B

Infrared Spectroscopic Methods

B.1 KBr Pellet Method

A common method to measure the infrared transmittance of a sample is the KBr pellet sampling method [Alpert et al., 1970]. A schematic of the measurement is shown in Fig. B.1. A small amount of sample (SiC spheres or powder) is mixed with KBr powder and pressed into a pellet of thickness $L$. When put under intense pressure the KBr forms a solid mass, and acts as a host with index of refraction $n_h = n_{KBr} = 1.525$. The number density $N$ of the sample particles embedded in the pellet is kept low to avoid multiple scattering between the particles. An IR spectrometer supplies an incident irradiance $I_i$, which passes through the pellet. The transmitted irradiance $I_t$ is collected by the spectrometer. The transmittance $T$ is the ratio of $I_t$ measured for a SiC/KBr sample to a reference measurement of $I_t$ for a pure KBr pellet.

There are two possible methods to model the sample/KBr pellet. One way is to model the pellet as a metamaterial. The sample particles are embedded in a host, and as such the effective medium values can be calculated using (4.18). Since $N$ is very small, (2.6) can be used to arrive at

$$n_{eff} \approx n_h \left[ 1 + \frac{3\pi i}{k_h^2} N (a_1 + b_1) \right], \quad (B.1)$$

Figure B.1: Transmission through a KBr pellet. The shaded region is the KBr, and the black dots are the sample particles representing either SiC spheres or powder.
where \(a_1\) and \(b_1\) are calculated for a single SiC sphere in KBr host. The reflectance \(R\) of a normally-incident beam at either interface of the pellet and free space is [Bohren and Huffman, 1983],

\[
R = \left| \frac{n_{\text{eff}} - 1}{n_{\text{eff}} + 1} \right|^2 \approx \left| \frac{n_h - 1}{n_h + 1} \right|^2 = 0.04, \tag{B.2}
\]

since as a crude approximation \(n_{\text{eff}} \approx n_h\). An even more crude yet convenient and satisfactory approximation is \(R \approx 0\). Then the transmittance through the pellet is [Bohren and Huffman, 1983]

\[
T = \frac{(1 - R)^2 \exp(-\gamma L)}{1 - R^2 \exp(-2\gamma L)} \approx \exp(-\gamma L), \tag{B.3}
\]

where \(\gamma\) is the attenuation coefficient

\[
\gamma = \frac{4\pi}{\lambda_0} \text{Im} \{n_{\text{eff}}\}. \tag{B.4}
\]

An equivalent model of the pellet is a dilute collection of non-interacting particles, all of which extinguish a portion of the power in the incident beam, either due to absorption or scattering. The transmittance through the particles is [Bohren and Huffman, 1983, pp. 77–80]

\[
T \approx \exp(-\gamma L) \quad \text{where} \quad \gamma = N C_{\text{ext}}, \tag{B.5}
\]

and \(C_{\text{ext}}\) is calculated for a single sphere in a KBr host using (3.81b). The interpretation of the pellet as a metamaterial slab by (B.3) and (B.4) is equivalent to the collection of inclusions (B.5) since, from (B.4) and using (B.1) and (3.81b),

\[
\gamma = \frac{4\pi}{\lambda_0} \text{Im} \{n_{\text{eff}}\} \approx \frac{4\pi}{\lambda_0} \frac{3\pi}{k_h^2} N \text{Re} \{a_1 + b_1\}
= \frac{6\pi}{k_h^2} N \text{Re} \{a_1 + b_1\}
= N C_{\text{ext}}, \tag{B.6}
\]

and keeping in mind that this is only true since the particle density \(N\) is very small. As \(N\) becomes larger, the interactions between the particles cause the model (B.5) to fail, while the metamaterial slab model (B.4) remains valid as long as \(N\) is kept to moderate values. This is because the effective medium model includes such interactions through the local field (4.4). On the other hand, the effective media approach will fail if the spheres are too large, since it does not include any scattering coefficients (3.32) for \(l > 1\).

### B.2 Diffuse Reflectance Method

An alternate method of characterizing the infrared response of a sample is by diffuse reflectance [Griffiths and de Haseth, 2007]. The diffusion of light is often studied in the fields of radiative transfer and the multiple-scattering of light [Ishimaru, 1997; Bohren, 1987; Kokhanovsky, 2004; Mishchenko et al., 2006]. The diffuse reflectance method is particularly convenient for powdered materials, and it eliminates
Figure B.2: Schematic of diffuse reflectance on a sample of dilute SiC particles in KBr.

the effort and mess of producing KBr pellets. It can also be preferable over the KBr pellet method since results obtained from the pellet method may vary depending on the preparation [Fuller and Griffiths, 1978]. Furthermore, since the KBr is not pressed, the sample particles do not get aggregated at the grain boundaries between the fused KBr crystallites [Pecharroman and Iglesias, 1996]. The price to be paid, however, is that the theoretical model is more complex than the pellet method.

Samples are prepared by mixing a small amount of the SiC powder with powdered KBr. The mixture is placed in a metal sample cup. An FTIR spectrometer [Perkin-Elmer Spectrum BX with a deuterated triglycine sulfate (DTGS) detector] with a diffuse reflectance accessory provides an incident diffuse irradiance $I_i$, and collects the reflected diffuse irradiance $I_r$. The diffuse reflectance $R$ is the ratio of $I_r$ measured for a SiC/KBr sample to a reference measurement of $I_r$ for pure KBr. A schematic of the measurement is shown in Fig. B.2. The diffuse radiation penetrating the sample surface can be multiply reflected, scattered, or absorbed by the SiC particles within the sample mixture.

The diffuse reflectance $R$ can be calculated with the general Kubelka-Munk equation [Kubelka, 1948],

$$ R = \frac{1 - R_b \left[ A - B \coth (BSh) \right]}{A + B \coth (BSh) - R_b}, \quad (B.7) $$

where $R_b = 1$ is the reflectance of the metal sample cup, $A = (S + K)/S$, $B = \sqrt{A^2 - 1}$, $h = 5$ mm is the thickness of the sample mixture, $K$ is an absorption coefficient, and $S$ is a scattering coefficient. Although $K$ and $S$ are phenomenological values, it has been shown that [Ishimaru, 1997]

$$ K \approx 2N(C_{abs}), \quad (B.8a) $$

$$ S \approx N(C_{sca}), \quad (B.8b) $$

where these cross sections are the sums of magnetic dipole (6.9) and electric dipole (6.23) contributions. The constants (B.8) are valid for low concentrations of inclusions; otherwise the correlation of particle positions must be incorporated [Kokhanovsky, 2004; Ishimaru, 1997].

There are two secondary issues to point out about the Kubelka-Munk equation (B.7). First, most software packages included with infrared spectrometers have a feature called a “Kubelka-Munk transform”. This is a special case of (B.7), which is only valid when the sample is effectively infinitely deep ($BSh \to \infty$).
and the backing material is perfectly absorbing \((R_b = 0)\). Under such conditions (B.7) reduces to

\[
R = \frac{1}{A + B} = A - B, \quad (B.9)
\]

which can be re-arranged into a form found in many chemistry publications [FULLER AND GRIFFITHS, 1978] and spectrometer manuals,

\[
\frac{(1 - R)^2}{2R} = \frac{K}{S}. \quad (B.10)
\]

Although when scattering is much stronger than absorption these are reasonable approximations, the SiC powder has a zero in the scattering cross section in the frequency range \(\omega > \omega_L\) where \(\varepsilon_{SiC} \approx \varepsilon_b\). That is, there is a small frequency range where the particles are almost transparent, and \(BS_\theta \to 0\). Therefore, the general reflectance (B.7) must be used.

A second comment on the Kubelka-Munk equation (B.7) is that it does not account for any reflections from the air-sample surface. Although this can be modeled rigorously by re-solving the model differential equations [ISHIMARU, 1997], a simple formula for the corrected reflectance \(R'\) is often adequate for samples mixed with KBr [VÖLZ, 1985, 2001],

\[
R' = \frac{0.36R + 0.04}{1 - 0.6R}. \quad (B.11)
\]

This correction is negligible, and will not be used here.
Appendix C

Gaussian Beam Design

An experimental setup to create a good approximation to a plane wave at microwave frequencies was summarized in Sec. 7.3. In this section the details on the design are given. This design process is useful because although the focal lengths of the lenses might be known, it is not necessarily true that they indicate where the source and sample should be placed. That would only be the case in the ray optics approximation, where the wavelengths are much smaller than the samples [Saleh and Teich, 1991, pp. 92–95]. For the desired case of samples much smaller than the wavelength, a design using Gaussian beam principles [Saleh and Teich, 1991] provides information not only about where to place the source and sample, but also about the beam width, wavefront radius, and Rayleigh range.

A Gaussian beam, propagating along the $z$ axis, has a field amplitude in a cross section which has a circularly symmetric Gaussian function dependence. The beam width $w(z)$ is the distance from the propagation axis to the points of $1/e$ amplitude. The beam has a minimum width, or waist $w_0$, at $z = 0$. The Rayleigh range $z_0$ is related to the beam waist by

$$z_0 = \frac{\pi w_0^2}{\lambda_h},$$

(C.1)

where $\lambda_h$ is the wavelength in the medium. A beam is completely specified by its $q$-parameter,

$$q(z) = z + iz_0,$$

(C.2)

where $z$ is the coordinate along the axis relative to the location of the waist. The $q$-parameter may also be specified by the beam width $w(z)$ and wavefront radius $R(z)$,

$$\frac{1}{q(z)} = \frac{1}{R(z)} - i\frac{\lambda_h}{\pi w^2(z)}.$$  

(C.3)

Within a longitudinal distance $z_0$ on either side of the waist the wavefronts are roughly planar, and furthermore at transverse points closer to the axis than the beam width the field is roughly uniform, so within this region the beam is a reasonable approximation to a plane wave.
Appendix C. Gaussian Beam Design

An optical element is modeled by a $2 \times 2$ ABCD matrix,

$$
\begin{bmatrix}
A & B \\
C & D
\end{bmatrix},
$$

which transforms an input beam $q_1$ to an output beam $q_2$,

$$
q_2 = \frac{Aq_1 + B}{Cq_1 + D}.
$$

The setup shown in Fig. 7.3 has five distinct optical elements between the horn aperture and sample plane. There are two classes of elements. The first class is a bulk region where the beam propagates unimpeded. There are three in the setup, contained within the dimensions $d_1$, $d_L$, and $d_2$. The matrix for beam propagation through a distance $d$ in a medium of any refractive index is

$$
P(d) = \begin{bmatrix} 1 & d \\ 0 & 1 \end{bmatrix}.
$$

The second class of element in the setup is a curved interface. There are two of these, one at each lens face. For an interface of radius $R$, input side index $n_1$, and output side index $n_2$, the matrix is

$$
L(n_1, n_2, R) = \begin{bmatrix} 1 & 0 \\ n_1 - n_2 & n_1 \\ Rn_2 & n_1/n_2 \end{bmatrix},
$$

where $R > 0$ when the center of curvature is on the output side of the interface. The experimental setup from the horn aperture to the sample-side lens face is modeled by the matrix (operating from right to left),

$$
L(n_L, 1, R_2) P(d_L) L(1, n_L, R_1) P(d). \tag{C.8}
$$

This matrix transforms a beam from the horn aperture to just beyond the lens.

The parameter $q_1$ for the beam emanating from the horn can be specified from the dimensions of the horn [Goldsmith, 1998]. The values for the effective beam width at the aperture $w_a$ and slant radius $R_a$ were given in Sec. 7.3. Substituting these values into (C.3) gives $q_1$. The beam just beyond the lens, described by $q_2$, may be found from (C.5) and (C.8). Interpreting $q_w$ using (C.2) yields the space between the lens and sample to be $d_2 = 30$ cm, the beam waist at the sample plane to be $w_{0,s} = 2.7$ cm, and the Rayleigh range to be $z_{0,s} = 11.7$ cm.

Another benefit of this design process is that it may be confirmed that the beam never exceeds the width of the lens. The lenses used in the experiment have a cross-sectional radius of 9 cm. Using this model it can be shown that the beam width does not exceed 7.5 cm anywhere within the lens, so scattering from the edges is avoided.
Bibliography


Bibliography


Bibliography


