MODELING SCATTER IN COMPOSITE MEDIA

by

Eric Carl Fest

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SIGNED: Eric Carl Fest
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DEDICATION

This dissertation is dedicated to my wife, Gina,

and to my daughters, Fiona and Marlena.
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ABSTRACT

A theoretical model of optical scattering in materials consisting of densely packed spherical particles is developed that can be used to predict its optical properties given its physical characteristics. The inputs to this model are the waveband of interest, the complex refractive indices and particle size distribution of the materials that comprise the media (including any contaminants), the density and sizes of any pores in the media, and the dimensions of the media slab. The outputs of this model are the specular transmittance and emissivity vs. wavelength of the media, and it’s Bidirectional Scattering Distribution Function (BSDF) versus scatter angle, wavelength, and incident polarization. The results of this model are compared to measured transmittance and BSDF data.
CHAPTER 1- Introduction

Introduction

An optical model of media that consists of densely packed spherical particles is developed in this dissertation in order to predict its transmittance and Bi-Directional Scattering Distribution Function (BSDF) for the media as a function of wavelength and incident polarization. The transmittance and BSDF are determined in this model from the electric field scattered by the particle collection, hence the emphasis of this dissertation on computing scatter. This model is important in that it allows pre-selection of these materials prior to fabrication, which is often expensive, and can be used to identify the presence of contaminants in the material. This model takes as input the waveband of interest, the complex refractive indicies and particle size distribution of the materials that comprise the media (including any contaminants), the density and sizes of any pores in the media, and the dimensions of the media slab. An example of such a material is a nanocomposite optical ceramic (NCOC), which is being investigated for use in mid-wave IR (3-5 μm) optical systems that are subjected to high mechanical and thermal stress, such as cameras used in aerospace applications. A scanning electron micrograph (SEM) of an NCOC sample is shown in Figure 1. The sample shown consists of nanoparticles of yttria (Y₂O₃) and magnesium oxide (MgO) that have been densified using a hot isotatic press (HIP) process. This process is carefully controlled to avoid percolation (melting together) of the nanoparticles and to reduce the number of pores. Maintaining the
integrity of the nanoparticles increases the strength of the material and (as will be shown) reduces scattering.

Figure 1. A scanning electron micrograph of a nanocomposite optical ceramic.

Another advantage of NCOCs that is demonstrated in this dissertation is that their refractive index and dispersive properties (Abbe number) can be chosen by changing the volume fractions of their constituent materials. This is not possible with traditional glasses and IR materials whose refractive index and Abbe number are fixed. Figure 2 illustrates the locations of three typical NCOC constituent materials on the mid-wave IR glass map. The Abbe number $\nu$ of each of these glasses was computed using a modified formula for the Abbe number:
\[ v = \frac{n_4 - 1}{n_3 - n_5} \]  

(1)

where \( n_3, n_4, \) and \( n_5 \) are the refractive indices at 3, 4, and 5 µm, respectively. The refractive index and Abbe number of an NCOC made from the materials shown in Figure 2 can lie anywhere within the triangle defined by the end members. This allows for the image quality of an optical system to be better optimized by using NCOC lenses whose refractive index and Abbe number were chosen to maximize image quality.

Figure 2. The mid-wave IR (3-5 µm) glass map with three typical NCOC constituent materials.
Scope of Dissertation

Assumptions

There are a tremendous number of variables to consider when developing an optical model of a composite material, such as the number and composition (i.e. complex refractive index) of constituent materials, their size relative to the wavelength of incident light, their shape and arrangement inside the composite, to name a few. No single model can be used for all possible permutations of these variables, and since the model developed here primarily models NCOCs, this dissertation considers materials only with the following characteristics:

- The material is composed of particles that are roughly spherical in shape
- The particles are many times larger than their constituent molecules, and therefore they have the same refractive index as bulk samples
- The particles are arranged randomly, and are fixed in place
- The particles are roughly the same size as the wavelength of incident light
- The particles can be either non-absorbing (dielectric) or absorbing
- The particles and host medium are isotropic
- The particles are non-magnetic
- The particles do not exhibit non-linear optical effects

Goals

This dissertation is focused on establishing a particle scatter model that accurately predicts the optical performance (transmittance and BSDF) of NCOC materials with only
a priori knowledge of the particles comprising the material. This dissertation does not discuss their fabrication. A predictive model based on solutions to Maxwell’s equations is developed and implemented in a computer program. Predictions from this program are validated by comparing predicted to measured values. No specialized test equipment was developed to measure the optical performance of these materials; all measurements were performed using widely available test equipment. Comparisons of predicted and measured performance (transmittance and BSDF) are made for various NCOCs in the mid-wave infrared (3-5 µm) and for Polycrystalline Alumina (PCA) in the visible and near-infrared (0.4-2.0 µm). PCA is a transmitting material used in high-temperature, corrosive environments such as high-pressure sodium lamps, and is evaluated in this dissertation because its structure is similar to that of NCOCs and it demonstrates a broader application of the developed model.

**Summary**

Although this dissertation focuses on the development of a model to predict optical scattering in NCOCs, it is likely to be applicable to other composite materials, provided those materials have similar characteristics, such as a composition consisting of a random distribution of approximately spherical particles in a host medium. This model is important in that it allows pre-selection of composite materials prior to fabrication, which decreases the cost and time of material development and allows for more precise performance. By comparing the optical performance predicted by the model with
measurements, the presence of contaminants and/or pores in a fabricated sample can also be detected.
CHAPTER 2- History of Optical Scattering Models

Optical scattering models have a long and rich history. Much of the early work on this subject relates to scattering of particles in dilute concentrations, such as molecules of gas in the atmosphere. These models assume no coupling of the electric fields generated by adjacent particles, which is called the “single-scattering” approximation. Later models were developed to account for multiple scattering by collections of absorbing particles. Though many of these models are similar to the one derived in this dissertation, it will be shown that none have the combination of features required for the problems considered here, such as the ability to compute both transmittance and BSDF for a collection of particles of varying sizes using an approximate representation of the spatial distribution of the particles.

Single-Scattering Models

Though the model developed in this dissertation is a multiple-scattering model and is therefore not limited to the single-scattering approximation, it is important to review single-scattering models since they form the foundation of many multiple-scattering models, including the model derived in this dissertation. One of the earliest (and probably best known) of these models was developed by Lord Rayleigh in 1871 to explain the effects of atmospheric scattering of sunlight (see Figure 3). Rayleigh found that the intensity of scattered light was proportional to $1/\lambda^4$, where $\lambda$ is the wavelength of
light, and thus explained why the sky is blue (see Figure 4). Rayleigh considered only particles that were much smaller than the wavelength of incident light.

![Figure 3. Rayleigh scattering in the atmosphere^3.](image)

![Figure 4. $1/\lambda^4$ dependence of Rayleigh scattering^2.](image)

Another seminal work was published by Gustav Mie^3 in 1908, in which he derived a solution of Maxwell’s equations for scattering from spheres. This solution is
not limited to spheres much smaller than the wavelength of incident light and therefore has a wide range of applicability. Mie’s solution converges to Rayleigh’s for particles much smaller than the wavelength, and also accounts for absorption in the spheres. One of the most significant findings from Mie’s theory is that particles large compared to the wavelength scatter more strongly in the forward direction than in the backwards direction, as opposed to small particles which scatter equally in both directions (as was also shown by Rayleigh), as shown in Figure 5.

Figure 5. Polar plots of normalized intensity vs. scatter angle from incident beam for small particles (left) and large particles (right)
Another extension to Rayleigh’s theory was developed by Richard Gans\textsuperscript{4} which allows Rayleigh’s theory to be applied to non-spherical particles that have a low refractive index contrast with the surrounding (matrix) medium. This theory was successfully used to predict the transmittance of polycrystalline alumina (PCA) by Apetz and van Bruggen\textsuperscript{5}.

**Effective Medium Models**

If the particles are small enough relative to the wavelength of incident light, the amplitude of the forward-scattered component approaches zero, and the material can be treated with effective medium theory. In this theory, an effective dielectric constant (and hence an effective refractive index) is computed for the composite material. Two of the most widely used effective medium theories are the Maxwell-Garnett\textsuperscript{6} and the Brueggeman\textsuperscript{7}, which compute the effective dielectric constant of the material using a weighted average of the dielectric constants of the constituent materials. Stroud and Pan\textsuperscript{8} showed that both of these theories can be derived using the Rayleigh theory for coated and bare spheres (respectively) and setting the forward scattered amplitude equal to zero. Gehr and Boyd\textsuperscript{9} had some success applying these theories to layered nanostructured materials in which the layers were much thinner than the wavelength of light. Effective medium theories assume that the scattering in the media is very small, and since the materials modeled in this dissertation have significant levels of scatter, effective medium theories cannot be applied.
Conditions of Single-Scattering Model Validity

In order to choose the best single-scattering model for a particular modeling task, their conditions of validity need to be compared. The model should be chosen such that unnecessary computations are eliminated (e.g. using the Mie when the Rayleigh would do) and that the model is as flexible as possible (e.g. using the Rayleigh-Gans, which allows for non-spherical particles to be evaluated relatively easily). As will be shown, the conditions of validity of many of the models are not rigidly defined and are therefore open to interpretation. In most cases this problem can be mitigated by using a more computationally-intensive model to check the results of a less-intensive one.

Table 1 defines the regions of validity of the four scattering models and lists the sources of these definitions. Regions of validity are based on two parameters: (1) the size parameter \( x \) and (2) the relative refractive index \( m \). The size parameter is defined as

\[
x = \frac{2\pi \text{Re}(n_h) a}{\lambda}
\]

where \( \text{Re}(n_h) \) is the real part of the refractive index of the host medium, \( a \) is the particle radius, and \( \lambda \) is the vacuum wavelength of the incident light. The relative refractive index \( m \) is defined as

\[
m = \frac{n_p}{n_h}
\]

where \( n_p \) is the complex refractive index of the particle and \( n_h \) is the complex refractive index of the host medium.
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<td>Stroud and Pan$^x$</td>
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<tr>
<td>Rayleigh-Gans</td>
<td>$</td>
<td>m-1</td>
</tr>
<tr>
<td>Rayleigh</td>
<td>$x &lt;&lt; 1$, $</td>
<td>mxl</td>
</tr>
<tr>
<td>Mie</td>
<td>No restrictions on $x$ or $m$</td>
<td>van de Hulst$^{10}$</td>
</tr>
</tbody>
</table>

Table 1. Conditions of validity of single-scattering and effective medium models

It can be seen from the table that many times the conditions are defined in terms of “much greater than” (>>) or “much less than” (<<), which are ambiguous. By interpreting these symbols as “10X greater than” and “10X less then”, respectively, the plot in Figure 6 can be derived which shows the conditions of validity of these models. In general, both models are valid only for small values of $x$, though the Rayleigh-Gans model is accurate for larger values of $x$ if $m$ is near unity. Both of these models require many fewer computations than the Mie model, which is valid for spheres of arbitrary $m$ and $x$. Relative to Figure 6, effective medium models are only valid for values of $x$ even less than 0.1, since this is a necessary condition for zero forward scattered amplitude. It will be shown in Chapter 4 how the values of $x$ and $m$ for the materials of interest compare to these conditions.
A review of existing multiple-scattering models is necessary to determine if any can be applied or extended to the composite materials investigated in this dissertation. An early treatment of scattering by multiple particles was performed by Foldy\textsuperscript{11}. This paper assumed that both the host medium and the particles were non-absorbing, and that the particles were much smaller than the wavelength. Lax\textsuperscript{12} generalized this theory to absorbing scatterers of arbitrary size, and produced a set of equations sometimes referred
to as the Foldy-Lax equations. These equations follow directly from the volume integral equation counterpart of the Maxwell equations, are exact, and are applicable to a broad set of multiple scattering problems. Borghese et al.\textsuperscript{13} developed a method for predicting the scatter from a cluster of spheres of arbitrary size. More rigorous methods include the T-matrix method\textsuperscript{14,15}, which is widely used and can compute cross-sections (which can be thought of as the effective size of the particle that scatters and absorbs light) and the full polarization-dependent scattered intensity vs. scatter angle for single or multiple nonspherical scatterers. This method relies on decomposition of the incident and scattered electric fields into spherical harmonic functions and uses a transition matrix (or “T-matrix”, whose form is highly dependent on the morphology of the scatterers) to transform from one to the other.

Another rigorous method is the Discrete Dipole Approximation\textsuperscript{16} (DDA), which solves the scattering problem by decomposing the geometry into a collection of dipole oscillators.

Though both the T-matrix and the DDA are quite complex, both have been well-researched and are implemented in public-domain computer codes\textsuperscript{17}. One drawback to most of these multiple scattering methods is that they require detailed information about the internal structure of the scattering media, and in many cases (including the cases considered in this dissertation) this information cannot be easily obtained. Another drawback is that they are difficult to implement, consisting of thousands of lines of computer code, and are therefore less desirable than simpler models that give equally accurate results.
An approximate technique to solving the multiple scattering problem was
developed by Kuga et al.\textsuperscript{18}, in which a simple heuristic model of the extinction
coefficient in lossy media is used. This model is based on the idea that the absorption in
the host media is proportional to the host volume (i.e. that the electric field is uniform in
the volume). Yang et al.\textsuperscript{19} developed a similar heuristic model that accounts for the
change in extinction of the particles due to losses in the host media. These methods have
been shown\textsuperscript{20} to work well for dilute media, but begin to break down for denser media
such as the composite materials considered in this dissertation.

**BSDF Models**

Though nearly all of the multiple scattering methods discussed provide a means of
computing the intensity of light scattered from particles as a function of angle, none
explicitly provide a means of computing the BSDF of a slab containing the particles. In
order to do this, a radiative transfer algorithm must be used to transform the scattered
angular intensity into BSDF. A simple method based on Monte-Carlo raytracing is
discussed in Frieden\textsuperscript{21}. Similar methods have been implemented in optical system
modeling programs such as FRED\textsuperscript{22}. The atmospheric modeling program MODTRAN\textsuperscript{23}
uses a radiative transfer algorithm called DISORT\textsuperscript{24} to compute scattered radiance, which
could also be used to compute BSDF. Figure 7 shows a MODTRAN calculation of
atmospheric radiance computed using single and multiple scattering and illustrates the
importance of multiple scattering for some problems.
Summary

This chapter reviewed some of the existing scattering models for predicting optical scatter. Many of the early models focused on predicting single-scattering in dilute media. Though these models form the foundation of many multiple-scattering models, they are not suitable to use for the composite materials considered in this dissertation because they do not account for interaction between the electric fields of densely-packed particles. Later models were developed to predict multiple-scattering in more dense media, however, as will be discussed in the next section, all of these models have drawbacks when using them to predict scattering in the composite materials considered in
this dissertation. For this reason, an alternate model will be developed in the next Chapter.
CHAPTER 3- The Composite Media Scattering Model

Introduction

As shown in the previous chapter, there are many scattering models from which to choose. In order to reduce the number of choices, it is necessary to review some of the characteristics of NCOCs, which are the materials of primary interest:

- NCOCs can consist of densely packed grains, as shown in Figure 8. This suggests that a model that incorporates multiple scattering must be used.
- The constituent materials of the NCOC can be lossy in the MWIR, as shown in Figure 8 for two typical constituents, Y$_2$O$_3$ and MgO. This suggests that a model that can account for absorption be used.
- At this time, little data are available which describe the internal geometric structure of NCOCs. About the only available data consists of micrographs such as the one shown in Figure 8. Because many of the more advanced scattering computation methods (such as the T-matrix and DDA methods) require detailed knowledge of the geometric structure of the scatterer, these methods may not be suitable for this modeling task.

A scatter model that fits these criteria was proposed in Durant et al$^{20,25}$. It can be used for densely packed particles (it will be shown that it works well even at 50% volume fraction), works for lossy media, and does not require exact knowledge of the structure of the material, though some statistical information about to the distribution of particles in
the host media is necessary. In addition, this model reduces to a result called the Foldy-Twersky\textsuperscript{26} approximation if all of the scatterers are considered independent, which helps to confirm its validity. The end result of the model is an extinction coefficient for the material as a function of the complex refractive indicies of its constituents and their size and statistical distribution. The extinction coefficient $K_{\text{ext}}$ is related to the transmittance of the material $T$ by Beer’s law

$$ T = \left(1 - R\right)^2 \exp\left(-K_{\text{ext}} t\right) $$

where $R$ is the Fresnel reflectance of the entrance and exit faces of the slab (as computed from Eq. 70) and $t$ is the thickness of the material. The derivation presented here is very similar to the one presented in the original paper, although its derivation is extended to polydisperse (multiple-sized) spheres and to BSDF calculations.
Figure 8. The real and imaginary parts of the refractive index for Y$_2$O$_3$ and MgO (top), and an SEM of a 50/50 Y$_2$O$_3$/MgO NCOC (bottom). In the SEM, the white areas are Y$_2$O$_3$ and the black are MgO.
**Model Derivation**

When analyzing the propagation of an electromagnetic field in a random media in which the dielectric constant fluctuates, it’s useful to split the field into a mean component $<\mathbf{E}>$ and a fluctuating component $\delta \mathbf{E}$:

$$\mathbf{E} = <\mathbf{E}> + \delta \mathbf{E}$$  \hspace{1cm} (5)

where $<\delta \mathbf{E}> = 0$. If the statistics of the particle distribution does not vary spatially (i.e. if the random medium is statistically homogeneous), it can be shown that the mean field satisfies the propagation equation

$$\nabla \times \nabla \times <\mathbf{E}> - n_{\text{eff}}^2 k_o^2 <\mathbf{E}> = 0$$  \hspace{1cm} (6)

where $n_{\text{eff}}$ is the effective index of the composite medium, which is equal to $k/k_o$, where $k$ is the effective wavenumber of the wave in the composite medium and $k_o$ is the wavenumber in the host medium in the absence of particles. Eq. (6) shows that, like the case of propagation in homogeneous media, the mean field is invariant with position, and therefore it follows that its solutions are plane waves. Therefore, the mean field has all of the usual properties associated with a plane wave: spatial coherence, well-defined propagation direction, and well-defined polarization state. Hence, this component will be referred to as the coherent component.

By taking the modulus squared of the electric field in (4), the flux intensity of the total field can be found as

$$I = <\mathbf{E} \mathbf{E}^*> = |<\mathbf{E}>|^2 + |<\delta \mathbf{E}>|^2 = I_{\text{coh}} + I_{\text{incoh}}$$  \hspace{1cm} (7)
The first term is called the coherent intensity, and corresponds to propagation in an effective homogeneous medium. The second term is called the incoherent intensity, and corresponds to the energy of the fluctuations in the field. When a beam illuminates a random medium, part of its energy passes through as coherent intensity (which is collimated) and part is scattered as incoherent intensity. The real part of the effective refractive index of the media can be used to compute the phase delay of coherent intensity, and the imaginary part can be used to compute the extinction of the coherent intensity. Therefore, the effect of scattering and absorption gives rise to the extinction coefficient, which is related to the effective complex index of refraction as

\[ K_{\text{ext}} = 2 \text{Im}(k) = 2k_o \text{Im}(n_{\text{eff}}) \]  

The extinction coefficient from the optical and statistical properties of the random medium will now be derived, starting with the following homogeneous solution to the partial differential propagation equation (6).

\[ E(r) = E_{\text{inc}}(r) + E_{\text{sca}}(r) = E_{\text{inc}}(r) + k_o^2 \int G_h(r; r') [\varepsilon(r') - \varepsilon_h] E(r') d^3 r' \]  

where \( E, E_{\text{inc}}, E_{\text{sca}}, \) and \( G_h \) are the total field, incident field, scattered field, and Green’s tensor function of the host homogeneous medium, respectively; \( \varepsilon(r) \) and \( \varepsilon_h \) are the local permittivity at \( r \) and the permittivity of the host medium, respectively. It can be seen in Eq. (9) that the sources of scattering are the inhomogeneities in contrast with the host medium that are excited by the total electric field. After taking the statistical average of Eq. (9) and manipulating\(^{28}\) we obtain

\[ \langle E(r) \rangle = E_{\text{inc}} + \int G_h(r; r') \times Q(r, r') \langle E(r') \rangle d^3 r d^3 r' \]
which is the vectoral version of the Dyson equation where $Q(r,r')$ is the mass-operator, which depends on the statistical distribution of the permittivity. For a homogeneous random medium, the mass operator is equal to $Q(r-r')$. By taking the Fourier transform of Eq. (10) and manipulating, it can be shown that the mean field satisfies an equation of propagation in a homogeneous medium with an effective permittivity given by

$$\tilde{\varepsilon}_{\text{eff}}(\omega,k) = \varepsilon_o + \frac{\tilde{\Delta}_T Q(k)}{k_o^2}$$

(11)

Where $Q(k)$ is the Fourier transform of the scalar mass operator and $\tilde{\Delta}_T$ takes the transverse part of the mass operator with elements given by $\Delta_{ij} = \delta_{ij} - k_i k_j / k_h^2$, and $k_h = n_h \omega / c$. If the random medium is isotropic on average, then the effective permittivity reduces to a scalar:

$$\varepsilon_{\text{eff}}(\omega,k) = \varepsilon_o + \frac{Q(k)}{k_o^2}$$

(12)

or, equivalently,

$$k^2 = \varepsilon_{\text{eff}}(\omega,k) k_o^2 = k_h^2 + Q(k)$$

(13)

where $k_h$ is the wavenumber in the host medium. The extinction coefficient can be obtained by solving Eq. (13) for $k$ and substituting into Eq. (8):

$$K_{\text{ext}} = 2 \text{Im} \left( \sqrt{k_h^2 + Q(k)} \right)$$

(14)

It remains now to determine the mass operator $Q(k)$. 
Determination of the Mass Operator via Diagrammatic Expansion

In this section a diagrammatic expansion of the mass operator is derived, which accounts for interactions of the electric field with multiple particles. Interaction diagrams are introduced as a means of symbolically representing these interactions. We also introduce several important operators such as the scattering operator of a single scatterer, the scattering operator of a set of scatterers, and the connection between these operators and the mass operator. A key point in our derivation is to establish a link between the scattering operator formally introduced here and the scattering matrix for spheres as determined by Mie scatter theory\textsuperscript{29}. It is also shown how correlations between the particles’ positions can be accounted for when the particle volume fraction is large.

Scattering Theory

Scattering Operator \( t \) for a Single Scatterer

Consider a medium that is composed of a single particle embedded in a host. The permittivity is \( \varepsilon_h \) outside the particle and \( \varepsilon_p \) inside. The scattering potential function can be defined as

\[
v(r) = \frac{j \omega^2}{c^2} (\varepsilon_p - \varepsilon_h) \Theta(r)
\]

(15)

where \( \Theta(r) = 1 \) if \( r \) is inside the particle and 0 otherwise. In order to simplify the equations used in this derivation, we introduce the linear operators \( v \) and \( G_h \), which are defined as
Using these operators, the solution to Maxwell’s equations shown in Eq. (9) can be rewritten in a more compact notation as

$$E = E_{\text{inc}} + G_h v E$$

This equation is called Lipmann-Schwinger’s equation. Notice that it’s recursive with respect to the total field $E$. Thus, it can be rewritten as

$$E = E_{\text{inc}} + G_h v E_{\text{inc}} + G_h v E_{\text{inc}} + G_h v (E_{\text{inc}} + ...)$$

or in terms of the incident field only as

$$E = E_{\text{inc}} + G_h t E_{\text{inc}}$$

where the operator $t$ is the scattering operator for a single particle defined by

$$t = v \sum_{n=0}^{\infty} (G_n v)^n$$

Note the similarity between Eqs. (19) and (20) and the total field predicted by Mie scatter theory given in Bohren and Huffman\textsuperscript{29}, Eq. 4.45:

$$E = E_{\text{inc}} + \sum_{n=0}^{\infty} i^n E_o (2n+1) \left( i a_n N_{n1n}^{(3)} - b_n M_{n1n}^{(3)} \right)$$

$E_o$ is the magnitude of the incident field, $N_{n1n}^{(3)}$ and $M_{n1n}^{(3)}$ are the nth vector spherical harmonic functions, and $a_n$ and $b_n$ are the scattering coefficients associated with these functions. From this we can see that Eqs. (19) and (20) are a generalized way of expressing the scattered field as series expansion.
Scattering Operator $T$ for Multiple Scatterers

For $N$ particles, the scattering potential can be expressed as a function of the scattering potential of a unique particle:

$$V(r) = \frac{\omega^2}{c^2} (\varepsilon_p - \varepsilon_h) \sum_{i=0}^{N} \Theta(r - R_i) = \sum_{i=0}^{N} v_i(r)$$  \hspace{1cm} (23)

where $v_i(r) = v(r - R_i)$ is the scattering potential of the $i$th particle located at $R_i$. Eq. (23) can be inserted into the definition of the scattering operator $t$ (Eq. 21) to derive the scattering operator for multiple particles $T$:

$$T = \sum_{i=0}^{N} v_i + \sum_{i=0, j=0}^{N,N} v_i G_h v_j + \sum_{i=0, j=0, k=0}^{N,N,N} v_i G_h v_j G_h v_k + ...$$  \hspace{1cm} (24)

Following Frisch\textsuperscript{27}, we can see that this expansion can also be written as a function of the single scattering operator $t_i$:

$$T = \sum_{i=0}^{N} t_i + \sum_{i=0, j=0, j \neq j}^{N,N} t_i G_h t_j + \sum_{i=0, j=0, k=0}^{N,N,N} t_i G_h t_j G_h t_k + ...$$  \hspace{1cm} (25)

where the scattering operator of the $i$th scatterer is given by

$$t_i = v_i \sum_{n=0}^{\infty} (G_h v_i)^n$$  \hspace{1cm} (26)

Eq. (25) can be substituted into Eq. (20) to yield an expression for the total field:

$$E = E_{inc} + G_h T E_{inc}$$  \hspace{1cm} (27)

This scattering operator can now be related to the scattering matrix predicted by Mie theory.
Scattering Operator and Scattering Matrix

The operator for a single scatterer $t$ (Eq. 21) is a multiple-scattering expansion of the electric field inside the particle. We can establish a relationship between this equation and the scattering matrix $S(\theta, \phi)$, as defined in Bohren and Huffman\textsuperscript{29}, which is a function of the refractive index of the particle and the host media. Using their notation, the field scattered by a sphere under plane-wave illumination is given by

$$E_{\text{scat}} = \frac{e^{ik_h r}}{-ik_h r} S_{ik} (\theta, \phi) E_o$$

where $E_o$ is the amplitude of the incident field at the center of the axis system, $E_{\text{scat}}$ is the scattered electric field at the base of the scattering plane, and $S$ is the 2 x 2 scattering matrix. As shown in the previous section, the scattered field can also be written using the scattering operator:

$$E_{\text{scat}}(r) = \int G_h (r - r') t(r', r'') E_{\text{inc}}(r'') d^3r' d^3r''$$

Note that the scattering matrix yields the scattered field only in the far-field, whereas the scattering operator is valid everywhere. Here the asymptotic expansion of the Green’s tensor function in the far field\textsuperscript{30} is introduced as:

$$G_h (r - r') = e^{ik_h r} e^{-ik_h |\mathbf{r} - \mathbf{r}'|}$$

Where $r = |\mathbf{r} - \mathbf{r}'|$ and $\mathbf{u}_r = \mathbf{r}/r$. The incident field is a plane wave propagating along the $z$ direction. Inserting Eq. (30) into Eq. (29) yields
\[
E_{\text{scat}} = \frac{e^{i k_r r}}{4 \pi r} \tilde{\Delta}_t \mathbf{t}(k_h \mathbf{u}_r, k_h \mathbf{u}_z) E_o
\]  
\[\text{(31)}\]

Where \( \mathbf{u}_z \) denotes the unit vector along the z axis and \( \mathbf{t} \) denotes the Fourier transform of the single-scatterer operator defined by

\[
\mathbf{t}(k', k'') = \int \mathbf{t}(r', r'') e^{-i k r'} e^{i k r''} d^3r'd^3r''
\]  
\[\text{(32)}\]

By equating Eqs. (28) and (31), we can express the single-scattering operator as a function of the scattering matrix

\[
\tilde{\Delta}_t \mathbf{t}(k_h \mathbf{u}_r, k_h \mathbf{u}_z) = \frac{i 4 \pi S_{k_h}(\theta, \phi)}{k_h}
\]  
\[\text{(33)}\]

A number of techniques can be used to compute the \( S \) matrix, among them the Rayleigh, Rayleigh-Gans, and Mie theories. Selection of the appropriate theory is determined by the shape of the particle, its refractive index contrast with respect to the host, and its size relative to the wavelength of incident light. These calculations must be performed assuming an incident wavenumber of \( k_h \), which is complex in the case of an absorbing host medium. We will be assuming spherical scatterers, so \( S \) in the forward direction is always independent of the polarization of the incident wave\(^{29} \), and hence it’s a scalar.

**Mass Operator and Diagrammatic Technique**

So far the general scattering formalism has been introduced. In this section, the scattering operator is averaged over all the realizations of the system. In order to do this, it is necessary to know the correlations of the positions of particles, which can be dealt with using the diagrammatic technique.
**Average of the Scattering Operator: Diagrammatic Expansion**

Consider a large volume $V$ of an isotropic and homogeneous medium that contains a large number $N$ of spherical particles. The particles are uniformly distributed so that the medium is statistically isotropic and homogeneous. Let $\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N$ be the positions of the $N$ particles. Note that $n = N/V$, which is the number of particles per volume. This set of positions defines the realization of the system. The average of the operator $T$ is then equal to

$$
\langle T \rangle = \int T P(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N) d^3 \mathbf{R}_1 d^3 \mathbf{R}_2 \ldots d^3 \mathbf{R}_N
$$

where $P(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$ is the probability density of the realization. Because the particles are statistically uniform, they have an equal probability of being anywhere within the volume, so the probability density of a given particle $P_1$ at a point $\mathbf{R}_i$ is

$$
P_1(\mathbf{R}_i) = \frac{1}{V}
$$

When determining the joint probability density $P_2(\mathbf{R}_i, \mathbf{R}_j)$, which is equal to the probability of having a particle at $\mathbf{R}_i$ and a second particle at $\mathbf{R}_j$, we need to account for the fact that both particles cannot be at the same location. To do this, we use the pair correlation function $g_2$, which is equal to the probability of encountering two particles with a given separation, normalized by the volume of the shell that contains one particle on its edge and the other in its center. For small separations, this is related to the way that the particles are packed together. For instance, consider the $g_2$ function for a 2-D distribution of hard circles (i.e. circles that cannot penetrate one another) of equal diameter shown in Figure 9. The area under the graph is shaded to match the
corresponding circles in the distribution. We can see that the value of \( g_2 \) is zero for separations less than or equal to the circle diameter, since the circles are hard and they cannot penetrate each other. As the separation increases the probability of encountering a circle spikes, since the circles are packed tightly together and therefore many circles surround the central circle. As the separation continues to increase the probability of encountering two particles with this separation approaches a constant which is related to the density of the circles.

Figure 9. The pair correlation function \( g_2 \) (left) for a 2-D distribution of circles (right)\(^{31} \)
The value of $g_2$ can be computed using an analytic approximation given in Percus and Yevick\textsuperscript{32}, or more simply using a Monte-Carlo computer program. More details of this algorithm can be found in Chapter 4 for the particular materials modeled in this dissertation. The joint probability density is related to $g_2$ as

$$ P_2(R_i, R_j) = P_1(R_i)P_1(R_j)\left[1 + g_2(R_i, R_j)\right] = \frac{1}{V^2}\left[1 + g_2(R_i, R_j)\right] $$

(36)

Higher-order correlation functions $g_M$ can also be computed to describe the correlation between $M$ particles. For instance, the joint probability density between three particles ($M=3$) is

$$ P_3(R_i, R_j, R_k) = \frac{1}{V^3}\left[1 + g_2(R_i, R_j) + g_2(R_j, R_k) + g_2(R_i, R_k) + g_3(R_i, R_j, R_k)\right] $$

(37)

This expansion of the joint probability density is called a cluster expansion. By using the expansion of $T$ given by Eq. (25) and the cluster expansion of the joint probability density, the average of $T$ can be written as a sum of integrals. However, writing the integrals rapidly becomes cumbersome, so instead of writing them explicitly, a diagrammatic notation becomes very useful. The rules for the diagrams are listed in Table 2.
Event or Relationship | Meaning
--- | ---
Propagation described by Green’s operator, \(G_h\), in the host medium | (line)
Scattering event by a single scatterer described by the operator \(t\) | (circle)
Integral contains a correlation function involving \(S\) scatterers | (dashed line above the main line linking the scatterers)
Integral contains several scattering events with the same scatterer | (solid line below the main line linking the scatterers)

Table 2. Diagrams used in diagrammatic expansion and their meanings

The factor \([N(N-1)(N-2)\ldots(N-M+1)]/V^M a\), which appears in front of each integral involving \(M\) different scatterers, is implicit. When \(N \gg M\), this factor can be approximated by \((N/V)^M = n^M = f/v_p\), where \(n\) is the number of particles per unit volume, \(f\) is the volume fraction of the particles, and \(v_p\) is the volume of the particle. This suggests that only the lowest-order terms need be retained for low-volume fractions.
The meaning of the diagrams may be clearer if the explicit form of the scattering operator is compared with the diagrammatic form. Here we do so for a two-particle system by plugging Eq. (25) into Eq. (34):

\[
\langle T \rangle = \frac{1}{V^2} \left[ \sum_{i=0}^{2} t_i \right] + \sum_{i=0, j=0, i \neq j}^{2} t_i G_{ij} t_j + \int \left[ \sum_{i=0}^{2} t_i \right] + \sum_{i=0, j=0, i \neq j}^{2} t_i G_{ij} t_j \right] g_2 \left( R_i, R_j \right) d^3 R_1 d^3 R_2 \right]
\]

(38)

Because a single scatterer has no pair correlation with itself, the integral of the third summation term is zero, leading to

\[
\langle T \rangle = \frac{1}{V^2} \left[ \sum_{i=0}^{2} t_i \right] + \sum_{i=0, j=0, i \neq j}^{2} t_i G_{ij} t_j \left[ 1 + g_2 \left( R_i, R_j \right) \right] d^3 R_1 d^3 R_2 \right]
\]

(39)

It can be seen in this example that the total scattering operator is equal to the sum of the scattering operators for each particle, plus the sum of the two scattering operators acting on each other. The scattering operator is then used in Eq. (27) to compute the total electric field, and therefore the total electric field is equal to the incident field, plus the field generated by each particle scattering individually, plus the field generated by every pair of particles scattering as a single particle, as shown in Figure 10 and Figure 11.
Figure 10. Graphical representation of independent scattering by a pair of particles
Figure 11. Graphical representation of dependent scattering by a pair of particles.

The higher-order diagrams of \( <T> \) appear as

\[
<T> = \quad + \quad + \quad + \quad \quad + \quad \quad + \quad \quad + \quad \quad + \ldots
\]  

(41)

**Diagrammatic Expansion of the Mass Operator**

The Dyson equation given by Eq. (10) can be written in operator notation as

\[
\langle \mathbf{E} \rangle = \mathbf{E}_{mc} + \mathbf{G}_h \mathbf{Q} \langle \mathbf{E} \rangle
\]

(42)
Averaging Eq. (27) yields
\[
\langle E \rangle = E_{inc} + G_h \langle T \rangle E_{inc}
\]  
(43)

Using Eqs. (42) and (43), the relation between the mass operator and the scattering operator can be derived as
\[
\langle T \rangle = \langle Q \rangle \langle E \rangle = Q + QG_h Q + QG_h QG_h Q + QG_h QG_h QG_h Q + \ldots
\]  
(44)

Using Eq. (44) and the diagrammatic expansion of \( \langle T \rangle \), the expansion of the mass operator can be derived as

\[
\langle Q \rangle = \quad + \quad + \quad + \quad + \quad + \quad + \quad + \quad + \ldots
\]  
(45)

**Determination of the Extinction Coefficient**

In practice, it is difficult to evaluate diagrams of high order. For low-volume fractions, one expects the first diagram to dominate the expansion of the mass operator, since the diagrams involving \( M \) different scatterers are proportional to \( n^M \). Higher volume fractions require the evaluation of higher terms, though it will be shown that just the first two diagrams are sufficient to accurately model NCOCs up to 50% volume fraction.
Evaluation of the First Diagram (Independent Scattering Approximation)

In the simplest approximation, only the first term of the mass operator is retained:

\[ <Q> = \bigcirc \]  

(46)

This approximation should not be confused with such single-scattering approximations as the Rayleigh approximation. In the first diagram, the effect of multiple scattering is taken into account, but all correlations between adjacent particles are neglected. This first-order approximation, called the independent scattering approximation, is commonly assumed in radiative transfer theory\(^\text{33}\). Considering hard scatterers that cannot be superimposed, correlations between scatterers can be reasonably ignored when the average distance between them is large compared to the scatterers’ size. The explicit form of the mass operator under this approximation is

\[
Q(r, r') = \left\langle \sum_{i=0}^{N} t_i \right\rangle = \sum_{i=0}^{N} \langle t_i \rangle = \sum_{i=0}^{N} \int (r - R_i, r' - R_i) P_i(R_i) d^3R_i
\]

\[
= \frac{N}{V} \int t(r - R_i, r' - R_i) P_i(R_i) d^3R_i = n \int t(k', k'') e^{ik'r} e^{-ik'r'} e^{-i(k'-k')r} d^3R \frac{d^3k'}{(2\pi)^3} \frac{d^3k''}{(2\pi)^3}
\]

\[
Q(r, r') = n \int t(k', k'') e^{ik(r-r')} \frac{d^3k'}{(2\pi)^3}
\]

(47)

It can be seen from Eq. (47) that, under this approximation, the mass operator is the inverse Fourier transform of the scattering operator, and that therefore the Fourier transform of the mass operator is equal to

\[
Q(k, k) = n t(k, k)
\]

(48)
If identical spherical scatterers are assumed, then the mass operator can be computed using Eq. (33) as

\[ Q = n \frac{i 4 \pi S_{k_i}(0)}{k_h} \]  

(49)

Using Eqs. (8), (14), and (49), the extinction coefficient can now be computed as

\[ K_{ext} = 2 \text{Im}(k) = 2 \text{Im} \left( \sqrt{k_h^2 + i \frac{f}{v_p} \frac{4 \pi S_{k_i}(0)}{k_h}} \right) \]  

(50)

where the substitution \( n = \frac{f}{v_p} \) has been made. In the case of a non-absorbing host medium, this approximation is also called the Foldy-Twersky approximation\(^{26}\). Historically, Foldy\(^{11}\) was the first to provide a similar expression for particles small compared to the wavelength and for scalar waves. Lax\(^{12}\) generalized it for absorbing scatterers of arbitrary size, and Frisch\(^{27}\) derived a similar result using diagrammatic expansion. This expression for the extinction coefficient is referred to in this dissertation as the independent scattering approximation.

**Evaluation of the Second Diagram**

By keeping the first two diagrams of the mass operator, an expression similar to the one obtained by Keller\(^{34}\) is derived:

\[ \langle Q \rangle = \circ \ + \ \bullet \circ \ ]  

(51)
In this approximation, the correlation between the positions of the particles cannot be neglected. It’s important to remember that the second diagram is a perturbation term to the first, and therefore will not (and should not) change it by a large value. The explicit form of this diagram, which will be called the double-scattering correlated operator (DSCO), is given by

\[
\text{DSCO}(\mathbf{r}, \mathbf{r}') = n^2 \int \mathbf{t}(\mathbf{r} - \mathbf{R}_1, \mathbf{r}_1 - \mathbf{R}_1) G_1(\mathbf{r}_1 - \mathbf{r}_2) \mathbf{t}(\mathbf{r}_2 - \mathbf{R}_2, \mathbf{r}' - \mathbf{R}_2) \\
\times g_2(\mathbf{R}_1 - \mathbf{R}_2) d^3 \mathbf{R}_1 d^3 \mathbf{R}_2 d^3 \mathbf{r}_1 d^3 \mathbf{r}_2
\]

(52)

where \( g_2 \) is the correlation function for a pair of scatterers. The scattering operator of a single spherical dipolar heterogeneity of the permittivity \( \varepsilon_p \) is given by

\[
\mathbf{t}(\mathbf{r}, \mathbf{r}') = 4\pi a^3 \delta(\mathbf{r}) \varepsilon_h \frac{\varepsilon_p - \varepsilon_h}{\varepsilon_p + 2\varepsilon_h} \frac{\omega^2}{c^2} \mathbf{I} \delta(\mathbf{r} - \mathbf{r}')
\]

(53)

where \( a \) is the radius of the spherical particle. From this, the expression

\[
\text{DSCO}(\mathbf{r}, \mathbf{r}') = n^2 \left( 4\pi a^3 \varepsilon_h \frac{\varepsilon_p - \varepsilon_h}{\varepsilon_p + 2\varepsilon_h} \frac{\omega^2}{c^2} \right)^2 G(\mathbf{r} - \mathbf{r}') g_2(|\mathbf{r} - \mathbf{r}'|)
\]

(54)

can be obtained. Under the scalar approximation, and with some manipulation, an expression of the Fourier transform of this operator can be evaluated as

\[
\text{DSCO}(\mathbf{k}, \mathbf{k}) = n^2 \left( 4\pi a^3 \varepsilon_h \frac{\varepsilon_p - \varepsilon_h}{\varepsilon_p + 2\varepsilon_h} \frac{\omega^2}{c^2} \right)^2 \frac{1}{k} \int_{\mathbb{R}^3} e^{i \mathbf{k} \cdot \mathbf{r}} g_2(|\mathbf{r}|) \sin(kr) d\mathbf{r}
\]

(55)

The term in parentheses can be simplified as

\[
4\pi a^3 \varepsilon_h \frac{\varepsilon_p - \varepsilon_h}{\varepsilon_p + 2\varepsilon_h} \frac{\omega^2}{c^2} = i \frac{4\pi S_{\mathbf{k}_h}(0)}{k_h}
\]

(56)

So that the final explicit form of the second diagram of the mass operator is given by
\[
\text{DSCO}(k, k) = n^2 \left( \frac{i4\pi S_{k_h}(0)}{k_h} \right)^2 \frac{1}{k} \int_0^{+\infty} e^{ikr} g_2(r) \sin(kr) dr
\]  

(57)

This solution is exact only under the scalar wave approximation and for spherical scatterers small compared to the wavelength.

The total extinction coefficient is then given by

\[
K_{\text{ext}} = 2 \text{Im} \left( \sqrt{k_h^2 + i \frac{f}{v_p} \frac{4\pi S_{k_h}(0)}{k_h} + i \frac{f}{v_p} \frac{4\pi S_{k_h}(0)}{k_h}} \right)^2 \frac{1}{k} \int_0^{+\infty} e^{ikr} g_2(r) \sin(kr) dr
\]

(58)

where the pair-correlation function \( g_2 \) depends on the volume fraction of the scatterers \( f \) and the gap between the scatterers \( r \). This expression for the extinction coefficient is referred to in this dissertation as the dependent-scattering approximation. It can be seen that this relation is recursive, since \( k \) is a function of itself. In practice, \( k_h \) is used as the initial value of \( k \) and then refined through successive iterations. Once the value of \( k \) has converged it can be used to compute the extinction coefficient using Eq. (6). Note that it is possible for the imaginary component of the double-scattering correlated operator term of Eq. (58) to be negative, which would result in a lower predicted extinction coefficient than that predicted by independent scattering alone. Physically, this corresponds to adjacent particles interfering in such a way as to increase the amplitude of the transmitted field.
Extension to Particle Distributions

Eq. (58) is valid for composite material composed of spherical particles of identical size and refractive index. However, the materials considered in this dissertation (e.g., NCOCs) are composed of particles with a range of sizes and possibly with different refractive indicies, as would be the case in three-phase NCOCs (such as Yttria-Zirconia-Magnesium Oxide). Therefore, it is necessary to extend the Durant model to account for a range of particle sizes and differing refractive indicies. One of the simplest ways to do this is to assume that there are \( N \) types of particles, each particle type having a unique combination of size and refractive index, and replace the variables in Eq. (58) that vary with particle type with their average values, which yields

\[
K_{\text{ext}} = 2^* \frac{4\pi}{k_h} \sum_{j=0}^N f_j S_{hj}(0) \left[ i \frac{4\pi}{k_h} \sum_{j=0}^N \frac{f_j S_{hj}(0)}{v_{p,j}} \right]^2 \frac{1}{k} \int_0^{+\infty} e^{ikr} g_2(r) \sin(kr) dr
\]

(59)

where \( f_j, v_{p,j} \) and \( S_{hj}(0) \) are the volume fraction, particle volume and scattering matrix of the jth particle type (respectively), and \( g_2 \) is the pair correlation function for the entire collection of particles. Eq. (59) was not derived in Durant’s paper and is new to this dissertation.
Determination of the Scattering Matrix of the Particle Collection

Diagrammatic expansion of the mass operator leads to a scattering matrix for the collection of particles that differs from that of a single particle $S_{kh}(\theta, \phi)$. The matrix $S_{c}(\theta, \phi)$ can be determined by making the appropriate substitution in Eq. (42):

$$\langle \mathbf{E} \rangle = \mathbf{E}_{\text{inc}} + \mathbf{E}_{\text{sca}} = \mathbf{E}_{\text{inc}} + \mathbf{G}_k \langle \mathbf{T} \rangle \mathbf{E}_{\text{inc}} = \mathbf{E}_{\text{inc}} + S_{c}(\theta, \phi) \mathbf{E}_{\text{inc}}$$  \hspace{1cm} (60)

Therefore

$$S_{c}(\theta, \phi) = \mathbf{G}_k \langle \mathbf{T} \rangle \hspace{1cm} (61)$$

Using the first term of Eq. (44) this can be written as

$$S_{c}(\theta, \phi) = \mathbf{G}_q \mathbf{Q} \hspace{1cm} (62)$$

or

$$S_{c}(\theta, \phi) = \int \mathbf{G}_h (r - r') \mathbf{Q}(r', r'') d^3 r' d^3 r'' \hspace{1cm} (63)$$

This equation is similar to Eq. (29) and can be solved for in a similar manner by using the asymptotic expansion of Green’s tensor function in the far field given in Eq. (30).

Inserting into (63) yields

$$S_{c}(\theta, \phi) = \frac{e^{ikr}}{4\pi} \tilde{\Lambda}_r \mathbf{Q}(k, k) \hspace{1cm} (64)$$

Using the two-term diagrammatic expansion of the mass operator derived earlier, this equation can be rewritten as

$$S_{c}(\theta, \phi) =$$

$$\frac{e^{ikr}}{4\pi} \left\{ \frac{4\pi}{k_h} \sum_{j=0}^{N} \frac{f_j S_{k_h,j}(\theta, \phi)}{v_{p,j}} + \left[ \frac{4\pi}{k_h} \sum_{j=0}^{N} \frac{f_j S_{k_h,j}(\theta, \phi)}{v_{p,j}} \right]^2 \frac{1}{k} \int_0^\infty e^{ikr} g_2(r) \sin(kr) dr \right\} $$  \hspace{1cm} (65)
and therefore the scattered intensity is equal to

$$\left| S_c(\theta, \phi) \right|^2 = \left( \frac{e^{ikr}}{4\pi} \left\{ i \frac{4\pi}{k_h} \sum_{j=0}^{N} \frac{f_j S_{k_h,j} (\theta, \phi)}{v_{p,j}} \right\}^2 + \left[ i \frac{4\pi}{k_h} \sum_{j=0}^{N} \frac{f_j S_{k_h,j} (\theta, \phi)}{v_{p,j}} \right]^2 \right)^2$$

It can be seen from Eq. (66) that the scattering matrix for the collection of particles is roughly equal to the weighted average of the scattering matrices of the constituent particles. Note that, under the independent scattering approximation, Eq. (66) becomes

$$\left| S_c(\theta, \phi) \right|^2 = \left( \frac{e^{ikr}}{4\pi} \left\{ i \frac{4\pi}{k_h} \sum_{j=0}^{N} \frac{f_j S_{k_h,j} (\theta, \phi)}{v_{p,j}} \right\} \right)^2$$

This approximation is used in the BSDF algorithm described next.

**Determination of the BSDF**

The definition of the Bi-Directional Scattering Distribution Function, or BSDF, is given in Stover\(^3^5\). Briefly, the BSDF is equal to the radiance of the scatterer (in units such as Watts/cm\(^2\)-str) divided by the irradiance incident on the scatterer (in units such as W/cm\(^2\)). The BSDF often varies as a function of scatter and incident angle as measured from the surface normal. The angle-dependent BSDF is computed using a Monte-Carlo raytracing simulation whose parameters are derived from the model developed here. A schematic of this simulation is shown in Figure 12. An incoming ray is traced from the left, refracts into the media, and either passes through it, or is scattered or absorbed. If it
is scattered, its direction is changed and the raytrace begins again, stopping only when it is refracted out of the media, is absorbed, or undergoes TIR. If it passes through the media, its scatter angle $\theta_s$ and its flux are binned. After all rays have been traced, the binned information is used to compute the cosine-corrected BSDF($\theta_s$). The cosine-corrected BSDF does not account for the change in the apparent size of the illuminated area with scatter angle, and is the most common method of reporting BSDF$^{35}$. Note that BSDF is a general term encompassing both BTDF (Bi-directional Transmittance Distribution Function) and BRDF (Bi-directional Reflectance Distribution Function), which are different from each other only in the direction of propagation of the scattered light relative to the incident light (transmitted or reflected). Therefore, this algorithm can be used to compute either BTDF or BRDF. Whenever possible, this algorithm has been optimized for quick evaluation, since it is Monte-Carlo based and therefore necessary to trace many rays in order to reduce statistical noise.

Figure 12. Schematic of the Monte-Carlo raytrace used to compute BSDF
Assumptions

There are a number of assumptions made in performing this calculation:

- The BSDF is computed for a plane-parallel slab of the composite medium.
- Light is incident on the slab at normal incidence.
- The spectrum of the incident light is uniformly weighted between $\lambda_{min}$ and $\lambda_{max}$.
- The incident light can be s-polarized, p-polarized, or unpolarized.
- The BSDF is computed along different points of a collection strip located far away from the slab and centered about the x-z plane, as shown in Figure 13. This is done to mimic the geometry of the scatterometer, which is the device used to make BSDF measurements for comparison to the aforementioned model. The y-extent of the strip is determined by the y-extent of the scatterometer collection aperture (see Chapter 5), and the center of curvature of the strip is centered about the exit face of the slab. The strip extends from -90° to +90° scatter angles.
- Because this strip is located in the far-field, it is not necessary for the incident rays to have any extent along the x or y axis.
- Because the strip has a very narrow extent along the y-axis, it is not necessary to trace rays outside of the x-z plane. It will be assumed that the collection strip has such a narrow extent along the y-axis that there is no variation in BSDF along this axis. Thus, it is not necessary to trace scattered rays from particles at angles that are outside of this extent. This requires that the ratio of the total amount of light
scattered from a particle that’s within the angular extent of the strip to the total amount of light scattered by the particle be computed.

Figure 13. Orientation of the scatter plane (x-z) with respect to the incident polarization

- Two extinction mechanisms are modeled within the slab: extinction by the particles, and absorption by the host medium. The total extinction coefficient is therefore the sum of two values:

\[
K_{\text{ext}} = K_{p-\text{ext}} + K_{h-\text{abs}}
\]

(68)

where \(K_{p-\text{ext}}\) is the portion of the extinction coefficient proportional to the extinction of the particles, \(K_{h-\text{abs}}\) is proportional to the absorption of the host medium.

- Losses at the entrance and exit faces to the slab are accounted for using the Fresnel equations. These equations use the effective refractive index of the medium \(n_{\text{eff}}\), which is equal to
\[ n_{eff} = \frac{k}{k_0} = \frac{k}{2\pi/\lambda} \]  

(69)

and therefore the reflectance \( R \) is equal to

\[ R = \left( \frac{n_{eff} - 1}{n_{eff} + 1} \right)^2 \]  

(70)

- Light that undergoes TIR at the exit face of the slab is lost. This is a valid assumption, as most of this light either leaves the slab through its edges or is trapped inside of it.

**Raytracing Algorithm**

The raytracing algorithm requires that a number of computations be performed prior to raytracing.

**Algorithm Pre-computations**

- The ratio \( \eta \) of the scattered intensity from a sphere that lies in the scatter plane divided by the total scattered intensity must be pre-computed for the particle collection as

\[ \eta = \frac{\int_0^{\pi/2} \int_0^{\pi/2} |S_c(\theta, \phi)|^2 \sin(\theta) d\theta d\phi}{\int_0^{\pi/2} \int_0^{\pi/2} |S_c(\theta, \phi)|^2 \sin(\theta) d\theta d\phi} \]  

(71)
where $\theta$ is the polar angle of the scattered ray with respect to the incident ray direction and $\phi$ is the azimuthal angle with respect to the same direction (as shown in Figure 14 for a single particle), and $S_c(\theta, \phi)$ is the scattering matrix of the particle collection given in Eq. (63).

Figure 14. Coordinate system for describing scattering from a particle.

In practice, it is difficult to evaluate Eq. (71) exactly. Specifically, it is difficult to evaluate $S_c(\theta, \phi)$ exactly, since it is proportional to the scattering matrix $S_{kh}(\theta, \phi)$, and the routines by Bohren and Huffman$^{29}$ that we’re using to compute $S_{kh}$ compute it only at $\phi=0^\circ$ and $\phi=90^\circ$. So, in order to evaluate Eq. (71), a number of approximations are made, starting with

$$
\eta \approx \frac{\Delta \phi \int_{-\pi/2}^{\pi/2} |S_c(\theta)|^2 \sin(\theta) d\theta}{\int_{0}^{2\pi} \int_{-\pi/2}^{\pi/2} |S_c(\theta, \phi)|^2 \sin(\theta) d\theta d\phi} (72)
$$

which assumes that $\Delta \phi = \phi_1 - \phi_2$ is small. Since the predicted BSDF will be compared to the BSDF measured using a scatterometer whose receiver angular extent is small (see Chapter 5), this approximation is appropriate. Next, $S_c(\theta, \phi)$ is
approximated using the independent scattering approximation shown in Eq. (67), which yields

\[
\eta \approx \frac{\Delta \phi \int_{-\pi/2}^{\pi/2} \left| e^{-i k r} \frac{4 \pi}{k} \left( \sum_{j=0}^{N} \frac{f_j S_{k_{j},j}(\theta)}{v_{j,p}} \right) \right|^2 \sin(\theta) d\theta}{2 \pi \int_{0}^{\pi/2} \int_{-\pi/2}^{\pi/2} e^{-i k r} \left| \frac{4 \pi}{k} \left( \sum_{j=0}^{N} \frac{f_j S_{k_{j},j}(\theta,\phi)}{v_{j,p}} \right) \right|^2 \sin(\theta) d\theta d\phi}
\]

(73)

This assumes that the change in \( S_c(\theta, \phi) \) due to the dependent scattering term is small, which is valid, given that the dependent scattering term is a perturbation to the independent scattering term. Finally, if it is assumed that the scattering occurs in or near the Rayleigh scattering regime, the values of \( S_{k_{j},j} \) will be mostly imaginary, and thus further approximation can be made as

\[
\eta \approx \frac{\Delta \phi \sum_{j=0}^{N} f_j \int_{-\pi/2}^{\pi/2} \left| S_{k_{j},j}(\theta) \right|^2 \sin(\theta) d\theta}{2 \pi \int_{0}^{\pi/2} \int_{-\pi/2}^{\pi/2} \sum_{j=0}^{N} f_j \int_{-\pi/2}^{\pi/2} \left| S_{k_{j},j}(\theta,\phi) \right|^2 \sin(\theta) d\theta d\phi}
\]

(74)

It is shown in Chapter 4 that scattering in NCOCs and PCA occurs in the Rayleigh or the Rayleigh-Gans scattering regimes, and thus this approximation is valid. The denominator can be rewritten as

\[
\eta \approx \frac{\Delta \phi \sum_{j=0}^{N} f_j \int_{-\pi/2}^{\pi/2} \left| S_{k_{j},j}(\theta) \right|^2 \sin(\theta) d\theta}{\sum_{j=0}^{N} f_j k^2 C_{\text{sca},j}}
\]

(75)
where $C_{\text{sc},j}$ is the scattering cross-section of the jth particle group.

- The angular distribution of rays scattered from a particle is determined using the Cumulative Density Function (CDF) $F_{Sc}$ of the scattering matrix $S_c(\theta)$, which is computed as

$$
F_{Sc}(\theta) = \frac{\int_{0}^{\theta} S_c(\theta')d\theta'}{\int_{0}^{\pi/2} S_c(\theta')d\theta'}
$$

(76)

$S_c$ and $F_{Sc}$ for 0.2 μm diameter particles of MgO in Y$_2$O$_3$ for 1 μm and 10 μm incident wavelength are shown in Figure 15.
Figure 15. $S_c$ and $F_{Sc}$ for 0.2 µm diameter particles of MgO in Y$_2$O$_3$ for 1 µm and 10 µm incident wavelength.

- The values of $K_{h-abs}$ and $K_{p-ext}$ are approximated from the model by using the first term of the binomial series expansion of Eq. (59), which yields

$$K_{h-abs} = 2 \text{Im}(k_h)$$  \hspace{1cm} (77)

$$K_{p-ext} = \text{Im}\left(\frac{b}{k_h}\right)$$  \hspace{1cm} (78)

where

$$b = i \frac{4\pi}{k_h} \sum_{j=0}^{\infty} f_j S_{k,j}(0) \frac{1}{v_{p,j}} + \left[ i \frac{4\pi}{k_h} \sum_{j=0}^{\infty} f_j S_{k,j}(0) \frac{1}{v_{p,j}} \right]^2 \frac{1}{k} \int_0^{+\infty} e^{i r} g_2(r) \sin(kr) dr$$  \hspace{1cm} (79)
It can be seen that $K_{h-abs}$ is the portion of the extinction coefficient that is related to absorption by the host medium and $K_{p-ext}$ is the portion related to particle scattering. It will be shown in Chapter 4 that the binomial series expansion is valid for NCOCs and for PCA.

- The reflectance $R$ at the entrance and exit faces of the slab is given by

$$R = \left( \frac{n_{\text{eff}} - 1}{n_{\text{eff}} + 1} \right)^2$$

where the effective index of the medium $n_{\text{eff}}$ is given by

$$n_{\text{eff}} = \frac{k}{k_\circ} = \frac{k}{2\pi/\lambda}$$

- The cosine-corrected $BSDF_i$ of the $i$th bin (hereafter referred to as simply $BSDF_i$) in the collection strip shown in Figure 13 is computed from the flux accumulated in the bin $\Phi_i$ (in Watts) using the equation

$$BSDF_i = \frac{\Phi_i / A_i}{\Omega_i (\Phi_{inc} / A_{inc})}$$

where $A_i$ is the area of the $i$th angular bin, $\Omega_i$ is the solid angle of the incident beam footprint area $A_{inc}$ as seen from the $i$th bin, $\Phi_{inc}$ is the flux incident on the slab and $A_{inc}$ is the area of the incident beam. We can solve for $BSDF_i$ as a function of the outer angle of the bin $\theta_i$:

$$BSDF_i = \frac{\Phi_i}{\Phi_{inc}} \frac{1}{\cos \theta_{i-1} - \cos \theta_i}$$

Note that this equation neglects the azimuthal extent of the collection strip $\Delta \varphi$ because it has been accounted for in Eq. (75).
Algorithm Computations

Using the above assumptions and pre-computed values, the algorithm to trace a ray through the medium can be performed as follows, where \( u \) is a uniformly-distributed random number between 0 and 1. The flowchart for this algorithm is shown in Figure 16.

1. Begin by checking to see if all the rays have been traced. If so, raytracing is done, and go to Step 10. If not, go to Step 2.
2. Trace a ray into the medium by first setting its flux \( \Phi \) equal to 1 and randomly picking a wavelength in the defined waveband using the equation
   \[
   \lambda = \lambda_{\min} + u(\lambda_{\max} - \lambda_{\min})
   \]  
   (84)
3. Determine if the ray is reflected by the entrance face of the slab of medium by testing the inequality
   \[
   u \leq R
   \]  
   (85)
   where \( R \) is the reflectivity of the surface as defined by Eq. (80). If this condition is met, this ray has been reflected, and a new ray must be traced beginning at Step 1. Otherwise, set the initial position at \( z = 0 \) and the initial angle with respect to the \( z \)-axis at \( \theta = 0 \) and go to Step 4.
4. Determine the new position of the ray by first computing the distance it travels before it’s absorbed or scattered by a particle using the equation
   \[
   l = \frac{-1}{K_{ext}} \ln(u)
   \]  
   (86)
   Then compute its new \( z \) location using the equation
\[ z = z_{old} + l \tan(\theta) \]  
(87)

Now test the following inequality to see if the ray is still inside the slab:

\[ 0 \leq z \leq t \]  
(88)

were \( t \) is the slab thickness. If this inequality is true, then the ray was absorbed or scattered, so go to Step 5. Otherwise, it left the slab, so go to Step 7.

5. Determine if the ray was absorbed by the host medium by testing the inequality

\[ u \leq \frac{K_{h-abs}}{K_{ext}} \]  
(89)

If this condition is met, the ray was absorbed and this single ray trace is done, so go to Step 1 to trace another ray. If the condition is not met, the ray was scattered by a particle, so go to Step 6.

6. Compute the new angle of the ray with respect to the z-axis using the equation

\[ \theta = \theta_{old} + F_{skh}^{-1}(u) \]  
(90)

where \( F_{skh}^{-1} \) is the inverse of the CDF computed in Eq. (76). Compute its new flux as

\[ \Phi = \Phi_{old} \eta \]  
(91)

where \( \eta \) is the scattered flux ratio of the jth particle group. Set \( z_{old} = z, \ \theta_{old} = \theta, \ and \ \Phi_{old} = \Phi \) and continue raytracing inside the slab by going back to Step 4.

7. Determine if the ray underwent TIR by testing for the TIR condition:

\[ \theta \geq \sin^{-1}\left(\frac{1}{n_{eff}}\right) \]  
(92)
If this inequality is true, the ray underwent TIR, so it is lost. Go to Step 1. If it is false, the ray refracted out of the entrance or exit face of the slab. Go to Step 8.

8. Determine if the ray is reflected on exiting the slab by testing the inequality in Eq. (85). If this inequality is true, the ray reflected from the exit face, and its power is lost, so go to Step 1. Otherwise, it refracted into air, so compute its angle in air $\theta$ using Snell’s law:

$$\theta = \sin^{-1} \left[ n_{\text{eff}} \sin(\theta_i) \right]$$ (93)

where $\theta_i$ is the angle computed from Step 6. Now go to Step 9.

9. Determine if the ray left the slab via the entrance face by testing the inequality

$$z < 0$$ (94)

If this inequality is true, then the ray left the slab through the entrance face. If BRDF is being computed, then flux of this ray should be binned by its angle $\theta$. If not, the ray is lost, and a new ray should be traced (go to Step 1). Conversely, if the inequality is false and BTDF is being computed, the ray flux should be binned, otherwise, this ray is lost, and a new ray should be traced beginning at Step 1.

10. Compute the BSDF for each collection bin by normalized the collected flux by Eq. (65).

In order to increase efficiency, the algorithm uses flux weighting only for scaling the scattered flux. All other losses to the ray flux, such as Fresnel reflections and extinction, are handled using Monte-Carlo techniques which reject the appropriate percentage of
rays. This is more efficient than weighting the flux of the rays since it prevents rays with low flux from being traced.
Figure 16. Flowchart for BSDF raytracing algorithm. Step numbers are given in parentheses.
For a medium with no scatter, the BSDF will be a delta function in angle space, as shown in Figure 17. The BSDF of a medium with high scatter will approach that of a Lambertian scatterer, also shown in Figure 17. Most media have BSDF distributions somewhere between these two extremes

![Figure 17. Specular and Lambertian (diffuse) BSDF](image)

**Algorithm Implementation**

The algorithm described in this chapter was implemented in C++ computer code. The object hierarchy of this code is given in Appendix A. Due to space constraints, the source code is not reproduced in this document, but is available by request from the author at ecfest@yahoo.com. The routines to compute the scattering matrix for individual
particles \( S(\theta,\phi) \) are based on the FORTRAN Mie scattering routines given in Bohren and Huffman\textsuperscript{29}.

**Summary**

This chapter focused on the derivation of the Durant model, the extensions necessary to model a composite medium comprised of particles of different sizes and refractive indices (Eq. 59), and the calculation of the medium’s BSDF. Multiple scattering is accounted for in this model, and may increase or decrease the predicted value of the extinction coefficient from the independent-scattering prediction. Unlike many other multiple-scattering models, the Durant model does not require that the size and shape of the particles be known exactly. All that is necessary is to know the statistics of the particle distribution, namely, the pair-correlation function of the particles, which can be determined from the Percus-Yevick equations\textsuperscript{32}, or though Monte-Carlo simulations\textsuperscript{20}. 
CHAPTER 4- Performance Predictions

Introduction

The scatter model derived in this dissertation is applied to the materials of interest, leading to transmittance and BSDF predictions. To do this, the following information about the composite material must be available:

- The complex refractive index of the constituent materials in the waveband of interest
- The volume fraction of each constituent material in the composite
- The size distribution of the particles in the composite, expressed as either tabulated data or a statistical model.
- The pair-correlation function between all particle sizes.
- The thickness of the material.

The materials modeled include NCOCs and PCA.

Nancomposite Optical Ceramics (NCOCs)

The particular NCOCs modeled are composed of varying fractions yttira (Y$_2$O$_3$) and magnesium oxide (MgO). It is possible to fabricate NCOCs using other materials, such as zirconia and gallia, but only Y$_2$O$_3$/MgO samples were available for testing. The model requires that one material be identified as the host material and the other as the particle material (also referred to by material scientists as the “particle phase”), Y$_2$O$_3$ is
chosen as the host and MgO as the particle phase, since the NCOCs we are modeling have volume fractions of MgO at 50% or lower. Throughout this dissertation, NCOCs are referred to using the convention “50/50 Y$_2$O$_3$/MgO”, where the first number corresponds to the volume fraction of the first material listed, the second number corresponds to the second material, etc. A picture of a 50/50 Y$_2$O$_3$/MgO sample is shown in Figure 18.

Figure 18. A 50/50 Y$_2$O$_3$/MgO NCOC sample. This sample is 0.5” in diameter, 0.75 mm thick and was fractured in strength testing.
Refractive Index Data

The complex refractive indices of Y$_2$O$_3$ and MgO are given in Figure 8. These data are from OPTIMATR$^{36}$, which is a commercial computer program which computes the complex refractive index based on solid-state physics model$^{37}$ of the material. Its results were validated by comparing to published data$^{38}$, which agrees to within 10%.

Particle Size Distribution

The only sources of data on the size distribution of the particles are scanning electron micrographs (SEMs) of a small portion of a fabricated sample, as shown in Figure 1. These micrographs were produced by first taking unpolished samples and etching them, using either a chemical etch (nitric acid) or a thermal etch (30 minutes at 1300 degrees C). Etching is necessary in order to bring out the grain boundaries; if it is not performed, the edges of the particles are very blurry. The samples are then imaged in a field emission scanning electron micrometer (FE-SEM) operating in backscattered electron (BSE) mode. The BSE mode results in an image in which the regions of the composite material corresponding to a high atomic number are lighter than those corresponding to a low atomic number. Thus, in Figure 1, the regions corresponding to Y$_2$O$_3$ (atomic numbers of Y=39 and O=8) are lighter than then the regions corresponding to MgO (atomic number of Mg=12). The micrographs were made by Raytheon Company in Sudbury, Massachusetts. As can be seen in Figure 1, the particles of MgO are roughly spherical, which is not an accident: the fabrication process is carefully controlled so that
the Y\textsubscript{2}O\textsubscript{3} and MgO powders used to make this sample do not percolate, that is, they do not melt together to form larger particles. This is done to keep the particles small, which increases the mechanical strength and hardness of the material by making it difficult for cracks to propagate (the cracks must take a more circuitous route if the particles are kept small, as described in Harris\textsuperscript{39}). As will be shown later in the dissertation, keeping the particles small also lowers the scattering, which is important for optical applications.

Of course, these micrographs provide only a two-dimensional slice of the material, and therefore do not directly provide the size distribution, since the location of center of the particles relative to the 2-D slice is not known, as illustrated in Figure 19. It can be seen from this figure that it’s likely that a spherical particle of diameter $d_2$ located randomly with respect to a slice plane will appear as a circle of diameter $d \leq d_2$, since any location of the slice plane other than through the center will be through a smaller diameter of the particle.

![Slice plane diagram](image)

Figure 19. Slice planes through a spherical particle produce different apparent diameters

In order to use the SEMs to determine size distribution, they are rendered as a collection of circles in a Microsoft Word drawing, as shown in Figure 20 for a 50/50 Y\textsubscript{2}O\textsubscript{3}/MgO NCOC. Each circle is sized to subtend, as nearly as possible, the dark spot of
MgO underneath it. In some cases, this is easy, but in others it is difficult because some MgO particles were stuck together. Because it’s known that grains of MgO powder used to make this sample were roughly 0.1-0.15 µm in diameter and because the fabrication process was controlled to minimize grain growth, multiple smaller circles are preferred to single larger circles when the choice between which to use is not clear. Once the rendering is complete, the diameters and locations of the circles are determined and plotted as a histogram, as shown in Figure 21. It can be seen from the histogram that the smaller particle diameters do indeed appear to dominate the distribution. Figure 21 shows that the histogram data are very noisy, which is due to the fact that the SEM contains only 130 circles. Techniques for obtaining better data for the particle size distribution are discussed in Chapter 7.
Figure 20. An SEM of a 50/50 Y$_2$O$_3$/MgO NCOC with the particles of MgO rendered as circles.
Figure 21. Histogram of the circles shown in the SEM for the 50/50 Y$_2$O$_3$/MgO NCOC shown in Figure 20 and the best-fit 3-D sphere distribution.

The histogram is used to generate an equivalent 3-D distribution of spheres by using a Monte-Carlo program to randomly generate spheres with a specified volume fraction within a volume, slicing the volume using a randomly located 2-D plane, and then computing the histogram of diameters of the sliced spheres and comparing to the histogram from the SEM. The C++ source code of this program is given in Appendix B. The histogram of the 3-D distribution is fit to the SEM distribution by assuming that the diameters of the 3-D spheres were described by a Gaussian distribution and changing the mean and standard deviation of the Gaussian until the histograms match as closely as possible. The resulting histogram for the 3-D spheres is also shown in Figure 21. Due to the noise in the SEM data, this fit is difficult to perform, and a number of 3-D
distributions yield histograms that fit about as well as the one chosen. However, this
distribution (mean = 0.27 microns, standard deviation = 0.03 microns) has a low chi-
squared value relative to the others, and also matches the overall shape of the histogram
well. Figure 21 shows that changing the mean of the distribution shifts the peak of the
curve, as would be expected. Also, changing the standard deviation makes the
distribution broader or thinner. The distributions plotted in Figure 21 demonstrate that the
selected distribution is roughly the best fit.

This process is repeated on SEMs of two other NCOC samples, a 70/30
Y₂O₃/MgO and a 90/10 Y₂O₃/MgO, as shown in Figures 22-25.
Figure 22. An SEM of a 70/30 Y$_2$O$_3$/MgO NCOC with the particles of MgO rendered as circles.
Figure 23. Histogram of the circles shown in the SEM for the 70/30 Y$_2$O$_3$/MgO NCOC shown in Figure 22 and the best-fit 3-D sphere distribution.
Figure 24. An SEM of a 90/10 Y$_2$O$_3$/MgO NCOC with the particles of MgO rendered as circles.
Figure 25. Histogram of the circles shown in the SEM for the 90/10 Y$_2$O$_3$/MgO NCOC shown in Figure 24 and the best-fit 3-D sphere distribution.

A summary of the mean and standard deviation of the best-fit 3-D sphere distributions is given in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean Diameter (microns)</th>
<th>Standard Deviation (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50 Y$_2$O$_3$/MgO</td>
<td>0.27</td>
<td>0.03</td>
</tr>
<tr>
<td>70/30 Y$_2$O$_3$/MgO</td>
<td>0.17</td>
<td>0.02</td>
</tr>
<tr>
<td>90/10 Y$_2$O$_3$/MgO</td>
<td>0.17</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Table 3. The mean diameter and standard deviation of the 3-D sphere distributions that best fit the SEMs shown in Figures 20, 22, and 24.

Table 3 indicates a number of interesting trends. The first is that the mean particle size and standard deviation appear to decrease as the volume fraction decreases, with the mean approaching the original MgO powder grain diameter of 0.1-0.15 µm. This is most
likely due to percolation (melting together) of the powder grains at higher volume fractions due to their close proximity to one another. This indicates that a single particle distribution cannot be used to represent the particles at all volume fractions, especially at higher fractions. The second is that the particles are more widely spaced and there are fewer of them at the lower volume fractions, as would be expected. This explains why the sampling in the histograms becomes coarser as the volume fraction decreases – fewer circles appear in the 90/10 histogram (102) than in the 50/50 (130), and therefore the bin sizes need to increase to reduce statistical noise.
Scattering Regime

Using the refractive index data shown in Figure 8 and the mean particle sizes in Table 3, the best scattering model to use for NCOCs can be determined. Figure 26 shows the conditions of validity of the Rayleigh and Rayleigh-Gans models and the values of $m$ and $x$ that correspond to NCOCs. Figure 26 shows that the values of $m$ and $x$ for NCOCs lie near but outside of the boundaries of validity of the Rayleigh-Gans model. Therefore, the scattering matrix for NCOCs will be computed using Mie scatter theory, based on the algorithms given in Bohren and Huffman\textsuperscript{29}.
Figure 26. Conditions of validity of scattering models and the range of $m$ and $x$ for NCOCs.

However, because the $m$ and $x$ values border the region of validity for Rayleigh-Gans, the results from the Mie code should not be radically different, and therefore the Rayleigh-Gans model can be used to gain insight into the scattering behavior. For instance, from the Rayleigh-Gans theory we can compute the angular scattered intensity distribution for p-polarized light $S_p(\theta)$ in the x-z scatter plane depicted in Figure 14 for a single particle:
This function is plotted in 3-D in Figure 27. In this figure, the polarization state of the incident beam is parallel to the y axis and the scattering plane is the x-z plane, and thus the incident beam is s-polarized. A p-polarized incident beam would correspond to the incident polarization parallel with the y-axis and the scattering plane in the x-y plane, as shown in Figure 28. It can be seen from these figures that there is more intensity in the scatter plane for the s-polarized case than the p-polarized, and thus it is expected that the BSDF measurement for s-polarized light to be greater than the measurement of p-polarized light.
Figure 27. Rayleigh-Gans model of scattered intensity for an s-polarized incident beam.

Figure 28. Rayleigh-Gans model of scattered intensity for a p-polarized incident beam.
Particle Pair Correlation Function

Now that 3-D models of the particles in the NCOCs have been derived, they are used to compute the pair correlation functions for different volume fractions. This is done using the Monte-Carlo simulation code given in Appendix B. This program randomly picks a sphere sizes from a Gaussian-weighted distribution and places them at random positions within a volume. The position of each new sphere is tested to make sure that it does not overlap an existing sphere. If overlap exists, the program tries to place it in a new position, and keeps trying this until the particle fits. The results are shown in Figure 29. The data in this figure have been smoothed to remove statistical noise. The correlation functions for single-sized spheres with the same volume fractions are also plotted in Figure 30. These correlation functions are computed assuming that the spheres are hard and therefore cannot penetrate or deform one another. It can be seen that distributions that do not have a fixed size have lower pair-correlation values than single-size distributions. This is because the smaller particles can fit more easily between the gaps in the larger ones, and thus their positions have lower correlation. Also, while single-size spheres have a negative correlation for values of \( R/a < 2 \) (because one sphere cannot penetrate another), size distributions have slightly greater correlation for values of \( R/<a> < 2 \), since the center of smaller particles may be located close to the center of large ones. Thus, the pair correlation function for particles with varying sizes appears as a smoothed version of the correlation function for single-sized particles.
Figure 29. Pair correlation function for NCOC particle distributions. R is the distance from the center of the particle, and <a> is the average radius of the particles.
Figure 30. Pair correlation function for single-size particles. R is the distance from the center of the particle, and a is the particle radius.

Because it’s time consuming to compute $g_2$, it is pre-computed for volume fractions from 10% to 50% and stored in a 2-D table (radius vs. volume fraction) which is linearly interpolated during the performance calculations.

**Performance Predictions**

The predicted transmittance for NCOCs of three different volume fractions are shown in Figures 31-33 using both the 2-term (dependent) and 1-term (independent) scattering models. Though the waveband of primary interest is 3-5 µm, the performance
is predicted in a wider band (1-10 µm) to more thoroughly test the model. At all wavelengths there is a Fresnel reflectance loss of about 8%, even with no scattering or absorption losses, so the maximum possible transmittance is about 92%. The curves all have low transmittance at lower wavelengths due to the particle scattering energy out of the beam. This is due to the classic $1/\lambda^4$ Rayleigh blue-sky effect. The curves also all have low transmittance at high wavelengths due to absorption by both $Y_2O_3$ and by MgO, as shown in the refractive index curves in Figure 8. The predicted transmittance curves show that the dependent scattering term has a larger effect on the extinction coefficient for high volume fractions (like the 50/50) than it does for lower volume fractions. This is because the pair correlation function $g_2$ has lower values for lower volume fractions, and the dependent scattering term is directly proportional to $g_2$. The curves also show that extinction coefficient predicted with the dependent scattering term is less than the extinction predicted with the independent scattering term only, especially for the 50/50 case (Figure 31).
Figure 31. Predicted transmittance for a 0.75 mm thick 50/50 $\text{Y}_2\text{O}_3/\text{MgO}$ NCOC.

Figure 32. Predicted transmittance for a 0.75 mm thick 70/30 $\text{Y}_2\text{O}_3/\text{MgO}$ NCOC.
Figure 33. Predicted transmittance for a 0.75 mm thick 90/10 Y$_2$O$_3$/MgO NCOC.

Figure 34 shows that the predicted transmittance using the dependent-scattering approximation is quite insensitive to volume fraction. This insensitivity results from the fact that as the amount of scattering predicted by the independent scattering approximation increases with volume fraction, the dependent scattering term in Eq. (59) becomes more negative and thus cancels out the increase in extinction. Thus, the coupling of the electric fields between adjacent particles in NCOCs with high volume fractions decreases the extinction coefficient that would result from treating the particles as independent scatterers.
Figure 34. Comparison of predicted transmittance using the dependent scattering approximation for a 50/50, 70/30, and 90/10 \( \text{Y}_2\text{O}_3/\text{MgO} \) NCOC. Simulated thickness = 0.75 mm

The predicted BSDF vs. scatter angle at 3.39 \( \mu \text{m} \) for the 50/50 \( \text{Y}_2\text{O}_3/\text{MgO} \) NCOC with thickness = 0.75 mm is shown in Figure 35 for s-polarized and p-polarized incident light. As predicted previously, the BSDF of the s-polarized beam is greater than that of the p-polarized because there is more power in the scatter plane for the s-polarized case. The small ripples in the curves are due to statistical noise in the Monte-Carlo simulation.
Figure 35. Predicted BSDF for a 0.75 mm thick 50/50 Y$_2$O$_3$/MgO NCOC at 3.39 µm.

The prediction shown in Figure 35 was made with the assumption that no contaminants were present in the sample. As will be discussed in Chapter 5, strength tests and SEM analysis of fabricated NCOC samples indicate the presence a small volume fraction of large (~10 µm in diameter) metal particles. Spectroscopic tests of these particles indicate that they are made of stainless steel. The exact volume fraction is unknown, though density measurements indicate that it is less than 0.1%. It is therefore necessary to include these particles in the model since they affect the BSDF. The BSDF for such a contaminated sample is shown in Figure 36. This prediction assumes an s-polarized input beam, a 0.03% volume fraction of 10 µm diameter stainless steel particles, 50% volume fraction of MgO, and 49.97% volume fraction of Y$_2$O$_3$. Figure 36 shows that the contaminants increase the BSDF at small angles, as would be expected.
since Mie theory predicts that particles large compared to the wavelength scatter more in the forward direction, as shown in Figure 5.

![Image of BSDF graph]

Figure 36. Predicted BSDF for a 0.75 mm thick 49.97/50/0.03 Y$_2$O$_3$/MgO/stainless steel NCOC at 3.39 µm.

**Sensitivity Analysis**

The sensitivity of the predicted transmittance and BSDF to changes in the input parameters is determined by making small changes (usually ±1%) to the inputs and computing the percent difference in the resulting transmittance and BSDF. The total uncertainty in the transmittance and BSDF predictions is computed by multiplying these sensitivities by the percent measurement uncertainties of the input parameters. The input parameter uncertainties used in this analysis are the minimum achievable for the given parameters and are not necessarily applicable to the transmittance and BSDF results.
shown above. For instance, the refractive index data currently used for the constituent materials was generated using the OPTIMATR software program, and it is not possible to know how accurate this data is since no refractive index measurements have been made of the constituent materials that are actually being used. Therefore, it is not possible at this time to assign a measurement uncertainty to this input parameter. However, it is known that refractive index can be measured to 0.1% using the “prism deviation” method, and therefore 0.1% is used as the measurement uncertainty in this dissertation. A summary of the measurement uncertainty for each input parameter is shown in Table 4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Best Measurement Accuracy (Method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average particle diameter</td>
<td>3% (SEM analysis)</td>
</tr>
<tr>
<td>Real part of particle index</td>
<td>0.1% (Prism deviation)</td>
</tr>
<tr>
<td>Absorption coefficient of particle index</td>
<td>5% (FTIR spectrometer)</td>
</tr>
<tr>
<td>Peak value of pair correlation function</td>
<td>5% (SEM analysis)</td>
</tr>
<tr>
<td>Volume fraction of particles</td>
<td>2% (Density measurement)</td>
</tr>
</tbody>
</table>

Table 4. Minimum input parameter uncertainties for a 0.75 mm thick 50/50 Y$_2$O$_3$/MgO NCOC.

The uncertainties in transmittance as a function of wavelength are shown in Figure 37 for a 0.75 mm thick 50/50 Y$_2$O$_3$/MgO NCOC. For NCOCs it is useful to divide the transmission spectrum into the two regions shown in Figure 37: the first region is called the transition region, and occurs from 1-3 μm and from 5-10 μm. In this region, the transmission changes rapidly as a function of wavelength due to either scattering by
the particles or absorption by the particles and the host media. This represents the transmittance cut-on and cut-off regions of the material and therefore the uncertainty in transmittance is highest in this region. The second region is called the plateau region, and occurs from 3-5 μm. This region is characterized by a slowly changing transmittance versus wavelength, and therefore the uncertainty in transmittance is lower in this region. NCOCs are being developed for sensors that operate in the plateau region, and therefore transmittance predictions made for this region are of greater importance than those made for the transition region. Figure 37 shows that the dominant uncertainties in both the plateau and transition regions result from uncertainty in the absorption coefficient and in the peak value of the pair correlation function. The total uncertainty (RSS) in the plateau region varies from 1.13% to 8.42%. In the transition region, the total uncertainty varies from 0% (which occurs when the transmittance is 0%) to 10.44%. NCOCs of different compositions and thickness will have different transmittance uncertainties. For instance, the transmittance of a thicker sample will be more sensitive to uncertainty in particle absorption coefficient.
The uncertainties in BSDF for a 3.39 μm incident beam are shown in Table 5 for the same NCOC sample. Since there is little variation in uncertainty as a function of scatter angle (<10%), the peak uncertainty values from 0 to 90 degrees scatter angle are shown in Table 5. The uncertainties in the input parameters result in much larger uncertainty in BSDF than in transmittance because many more calculations must be made to compute BSDF. For instance, the full angular distribution of the scattered intensity for the collection of particles does not have to be computed in the transmittance calculation but does in the BSDF. The dominant uncertainties are in the average particle diameter
and in the peak value of the pair correlation function. The total (RSS) uncertainty is 127.53%, which indicates that predicted BSDF values can be off by a factor of 2X. Due to the high value of this uncertainty, care must be taken when drawing conclusions based on comparisons between predicted and measured BSDF.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BSDF Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average particle diameter</td>
<td>85.39%</td>
</tr>
<tr>
<td>Real part of particle index</td>
<td>2.65%</td>
</tr>
<tr>
<td>Absorption coefficient of particle index</td>
<td>13.64%</td>
</tr>
<tr>
<td>Peak value of pair correlation function</td>
<td>90.33%</td>
</tr>
<tr>
<td>Volume fraction of particles</td>
<td>24.87%</td>
</tr>
<tr>
<td>Total (RSS)</td>
<td>127.53%</td>
</tr>
</tbody>
</table>

Table 5. BSDF uncertainty for a 3.39 µm incident beam and a 0.75 mm thick 50/50 Y₂O₃/MgO NCOC.

**Polycrystalline Alumina (PCA)**

As discussed in Apetz and van Bruggen⁵, conventional translucent PCA (Al₂O₃) is characterized by very low porosity (<0.1%) and grain sizes approximately 0.5 µm in diameter for the fine-grained case. Each grain can be treated as a uniaxial crystal with the orientation of its crystal axis different than that of the adjacent grains. Due to the low porosity, adjacent grains are flush with each other, as shown in Figure 38.
All data related to PCA, including the measured performance, are taken from the paper by Apetz and van Bruggen\textsuperscript{5}. As with their model, the model developed here neglects the presence of pores, though some will always exist in any real material. The same waveband of interest, 0.4-2.0 μm, is used here, as well as sample thickness (0.8 mm) and grain volume fraction (50%).

**Refractive Index Data**

Modeling each grain as a uniaxial crystal with its own crystal axis orientation is a complicated problem. In order to simplify the task, Apetz and van Bruggen\textsuperscript{5} have proposed modeling the material as a host medium of index 1.76 containing spheres (grains) of index 1.765 to 1.768 and diameter 0.5 μm. This model neglects dispersion in the material, and assumes that the birefringence, when averaged over all crystal axis
orientations, is equivalent to a constant refractive index difference of +0.005-+0.008 for each grain relative to the surrounding host.

**Particle Size Distribution**

Though the effect of particle size distributions on the scattered intensity is discussed in Apetz and van Bruggen\(^5\), no data are given for the specific samples tested; only the mean grain size is given. Therefore, a single grain diameter of 0.5 µm is used, since samples corresponding to this grain size were fabricated and their transmittance measured.

**Scattering Regime**

Using a constant grain size of 0.5 µm, host medium index of 1.76, and wavelengths from 0.4 to 2.0 mm leads to a range of size parameters from \(1.382 \leq x \leq 6.912\), and the particle indicies of 1.765 to 1.768 lead to a range of the relative refractive index from \(1.003 \leq m \leq 1.005\). These ranges put the scattering in the Rayleigh-Gans regime, as shown in Figure 39. Apetz and van Bruggen\(^5\) also identify this as the proper scattering regime for this material.
Particle Pair Correlation Function

Apetz and van Brueggen\textsuperscript{5} give no information about the distribution of grains, however, it is known\textsuperscript{40} that edges of the PCA grains deform during fabrication to match the contours of the adjacent grain. This reduces the pair correlation function to zero, and thus the second term of the diagrammatic expansion in Eq. (59) can be neglected.
Performance Predictions

The predicted transmittance versus wavelength for PCA is shown in Figure 40. As with NCOCs, the drop in transmittance at the shorter wavelengths is due to the Rayleigh blue-sky effect. This curve is indistinguishable from the transmittance predicted in Apetz and van Brueggen\textsuperscript{5} using their simplified model based on Rayleigh-Gans theory.

![Figure 40. Predicted transmittance for a 0.8 mm thick PCA slab.](image)

Since the Apetz and van Bruggen paper\textsuperscript{5} does not contain measured BSDF, there is no way of validating the predictions of the BSDF model, and therefore no prediction for the BSDF of the PCA slab is made.
Sensitivity Analysis

A sensitivity analysis identical to the one described for NCOCs is performed for PCA. The uncertainties in transmittance for the 0.4-2.0 μm band for a 0.8 mm thick PCA sample with 0.5 μm diameter particles are shown in Figure 41. Since the constituent materials of PCA do not absorb in this waveband and since the value of the pair correlation function for PCA is zero, sensitivities to these input parameters are not computed. The same measurement uncertainties assumed for NCOCs in Table 4 are assumed here. It is clear from this figure that uncertainty in the real refractive index of the particles dominates the transmittance uncertainty. The total uncertainty (RSS) varies from 2.83% to 6.99%.
Figure 41. Transmittance uncertainty vs. wavelength for 0.8 mm thick PCA with 0.5 μm diameter particles.

**Summary**

The model developed in Chapter 4 is applied to NCOCs of various volume fractions and to PCA, and performance predictions are made for both. A method for extracting the size and spatial distribution of particles in a NCOC from an SEM is introduced and used to determine input parameters for the model. The difference in predicted NCOC transmittance using independent scattering and dependent scattering
approximations is shown to increase with increasing particle volume fraction. The predicted BSDF of an NCOC sample is shown to be dependent on the input polarization and on the presence of any contaminants in the sample. The transmittance curves of both NCOCs and PCA exhibit higher extinction at shorter wavelengths due to the $1/\lambda^4$ Rayleigh blue-sky effect. NCOCs exhibit higher extinction at longer wavelengths due to absorption by the constituent materials, $Y_2O_3$ and MgO. The uncertainty in the predicted performance (transmittance and BSDF) of NCOCs and PCA is determined using the developed model to compute sensitivity to changes in the input parameters and multiplying by the minimum uncertainty in the input parameters. The transmittance uncertainty in the plateau region (3-5 $\mu$m, which is the region of primary interest in the transmittance spectrum) for a 50/50 NCOC varies from 1.13% to 8.42%. The uncertainty in the transition region (1-3 $\mu$m and 5-10 $\mu$m) varies from 0% (which occurs when the transmittance is 0%) to 10.44%. The maximum uncertainty in the predicted BSDF was 127.53% at 3.39 $\mu$m. Uncertainty in the BSDF calculations is much higher than in the transmittance calculations because the BSDF calculations require many more operations and therefore small uncertainties are amplified. For PCA, the uncertainty in predicted transmittance varies from 2.83% to 6.99% in the 0.4-2.0 $\mu$m band.
CHAPTER 5- Comparison of Predictions with Measurements

Introduction

In this chapter the performance predictions made in the previous chapter are compared with measured data. For each material considered, the preparation of the samples and the measurement techniques used to obtain the transmittance and BSDF data are discussed.

Nanocomposite Optical Ceramics

Sample Preparation

The NCOC samples were fabricated as flat disks 0.75 mm thick. The entrance and exit faces of the disks were polished using conventional optical polishing techniques (rotary grind and ceramic lap). The RMS roughness of the entrance and exit faces is about 90 Angstroms, and therefore we do not expect surface scatter to contribute significantly to the measured BSDF, given that the Total Integrated Scatter (TIS) of such a surface is given by

$$TIS = \left( \frac{\Delta n \pi \sigma}{\lambda} \right)^2$$

where $\Delta n$ is the refractive index difference between the substrate and the surrounding media (~0.7 for NCOCs), $\sigma$ is the RMS surface roughness, and $\lambda$ is the wavelength. For a surface with 90 Angstrom RMS roughness at 3.39 $\mu$m, the TIS is 0.018%, which is much
less than the predicted loss due Fresnel reflections alone (~20%), and therefore can be neglected.

Transmittance Measurements

The transmittance measurements were performed using two instruments: a Cary 5000 UV-VIS-NIR spectrometer and a Bruker Equinox 55 FTIR spectrometer, both located at Raytheon in Sudbury, Massachusetts. The Cary can measure from 1 µm to 3.3 µm, and the Bruker from 3 to 10 µm, and therefore both must be used to cover the waveband of interest. The transmittance measurements from both instruments agree to within 3% for wavelengths in the overlap region (3 to 3.3 µm). Both devices use unpolarized light.

BSDF Measurements

The BSDF measurements were performed at 3.39 µm using a Schmitt Measurement Systems (SMS) CASI scatterometer. This instrument measures the angle-resolved BSDF using a detector mounted on the end of a goniometer that sweeps around the sample, as illustrated in Figure 42. The goniometer arm is 50 cm long, and the aperture of the detector varies from 1060 µm to 13860 µm, and therefore the small-angle approximation made in Eq. (72) is valid. The aperture of the detector can be varied to provide higher angular resolution of the beam near the specular transmitted or reflected beam. The polarization of the beam used to illuminated the sample can be oriented to be
in the scatter measurement plane (p-polarized) or perpendicular to it (s-polarized). These measurements were performed in SMS’s measurement services laboratory in Portland, Oregon.

![Optical layout of the CASI scatterometer](image)

**Figure 42. Optical layout of the CASI scatterometer**

**Comparison of Predictions and Measurements**

Figures 43-46 show the measured transmittance of the 0.75 mm thick NCOC samples for various volume fractions as well as the predicted transmittance using the depdendent scattering model. Good correlation is obtained between predicted and measured for all three volume fractions. Error! Reference source not found. shows that the volume fraction insensitivity seen in the predicted transmittance is observed in the measured transmittance.
Figure 43. Measured and predicted transmittance for a 0.75 mm thick 50/50 Y$_2$O$_3$/MgO NCOC. Error bars are shown for the predicted transmittance.
Figure 44. Measured and predicted transmittance for a 0.75 mm thick 70/30 Y$_2$O$_3$/MgO NCOC. Error bars are shown for the predicted transmittance.
Figure 45. Measured and predicted transmittance for a 0.75 mm thick 90/10 Y$_2$O$_3$/MgO NCOC. Error bars are shown for the predicted transmittance.
Figure 46. Measured transmittance for a 0.75 mm thick 50/50, 70/30, and 90/10 \( \text{Y}_2\text{O}_3/\text{MgO} \) NCOC

The predicted transmittance for all three NCOCs analyzed matches the measurements to within the predicted uncertainty for all wavelengths in the plateau region (3-5 \( \mu \text{m} \)) except for a small wavelength range near 5 \( \mu \text{m} \). As discussed in Chapter 4, the accuracy of predicted transmittance is more important in the plateau region than in the transition region because this is the intended region of use. Therefore, Figures 43-46 demonstrate that the model developed here can be used to predict transmittance in the plateau region to within the uncertainty determined by the input parameter uncertainty. In the transition region, the predicted transmittance for all three NCOCs analyzed deviates from the measurements by more than the predicted uncertainty for a significant fraction.
of the transition region. This discrepancy is explained by the fact that the uncertainty values shown in Figure 37 are achievable only if the input parameters are known to within the uncertainties given in Table 4. For this analysis, the input parameters may have higher uncertainties, and therefore uncertainty in transmittance may be higher. For instance, if the uncertainty in the peak value of the pair correlation function was 13% instead of 5% (which is the best achievable uncertainty), the resulting uncertainty in transmittance would be large enough match the measurements. Because the pair correlation function was determined using a somewhat sparse and noisy data set (Figures 20-25), it’s reasonable to assume that the uncertainty in the peak value of the pair correlation function is 13% for this data set, and therefore it’s reasonable that the measurement deviate from the prediction.

Comparison of the predicted and measured BSDF is shown in Figure 47 and Figure 48. Figure 47 shows that the predicted and the measured BSDF vary in the same way with input polarization. Figure 48 shows that the predicted BSDF agrees with the measured BSDF better for scatter angles less than 10° if the contaminants in the sample are included in the predictions. This suggests that angle-resolved BSDF measurements can be used as a diagnostic tool to study the composition of composite materials. Adding the metal spheres had very little effect (<5%) on the predicted transmittance, so transmittance measurements alone would not have been sufficient to identify the presence of contaminants. As with the transmittance predictions, the BSDF predictions agree with the measurements to within the uncertainty provided reasonable values are assumed for
the uncertainty of the input parameters (such as 15% uncertainty in the peak of the pair correlation function).

Figure 47. Measured and predicted BSDF of a 0.75 mm thick Y$_2$O$_3$/MgO NCOC at 3.39 µm.
Figure 48. Measured and predicted BSDF of a 0.75 mm thick $\text{Y}_2\text{O}_3/\text{MgO}$ NCOC with 0.03% volume fraction of 10 µm diameter metal spheres at 3.39 µm.

**Polycrystalline Alumina**

**Sample Preparation**

The PCA sample was fabricated with a thickness of 0.8 mm. Apetz and van Bruggen\(^5\) specify only that the sample faces were “smooth”, and do not indicate if (or how) they were polished and what the resulting RMS surface roughness was. It will be assumed that the entrance and exit faces of the slab were smooth enough that surface scattering can be neglected, as with NCOCs.
Transmittance Measurements

Apetz and van Bruggen\textsuperscript{5} indicate that the transmittance was measured using a spectrophotometer with a collection angle of 0.5°, which is a typical value. The make and model of the spectrophotometer is not given.

BSDF Measurements

Apetz and van Bruggen\textsuperscript{5} did not make BSDF measurements in their paper.

Comparison of Predictions and Measurements

The measured and predicted transmittance curves are shown in Figure 49. Data for the measured curve was obtained from the paper using a digitizing program. The curves match quite closely, though the model underpredicts the extinction at shorter wavelengths and overpredicts it at longer wavelengths. At most wavelengths, the predicted transmittance matches the measured to within the model uncertainty for PCA determined earlier. However, the two disagree at the shorter wavelengths. As with NCOCs, this can be explained by the fact that the uncertainties determined earlier are best-case uncertainties, and the uncertainties in the input parameters used in this prediction may have been higher. The uncertainty analysis for PCA suggests that uncertainty in the real refractive index of the particle is the major contributor to uncertainty in the transmittance prediction, and that an uncertainty of 0.2% in refractive
index (a reasonable value) is sufficient to explain the discrepancy between the prediction and the measurement.

![Graph showing measured and predicted transmittance for a 0.8 mm thick PCA sample.](image)

**Summary**

Measured and predicted transmittance and BSDF curves are compared for NCOCs and for PCA. The major features in the predicted curves, such as transmittance cut-on and cut-off wavelengths and the volume fraction insensitivity seen in NCOCs, closely match those in measured curves. For NCOCs in the plateau region (3-5 µm), the predicted transmittance matches the measured to within the predicted uncertainty for all NCOCs measured. This demonstrates that the model developed here can be used to...
predict transmittance in the plateau region to within the transmittance uncertainty determined by the uncertainty in the input parameters. In the transition region (1-3 µm, 5-10 µm), the predicted transmittance for two of the samples (70/30 and 90/10) match the measurements to within the transmittance uncertainty. The predicted transmittance for the third NCOC sample (50/50) and for the PCA sample deviate from the measured by more than the predicted uncertainty, which can be explained by the fact that the uncertainties determined in the previous chapter are best-case and may not apply to the input parameters used in the predictions shown here. Reasonable assumptions about the true uncertainty of the input parameters used in these predictions can explain the discrepancies between predicted and measured transmittance. Comparison of the measured and predicted BSDF for an NCOC sample indicates that the model correctly predicts the variation in BSDF with input polarization and confirms the presence of a small volume fraction of large metal contaminants. This suggests that BSDF measurements can be used to test the composition of composite materials.
CHAPTER 6- Discussion

It has been shown that the model developed in this dissertation can be used to accurately predict the optical properties of dense composite media. It has also been shown that BSDF calculations based on this model can be used to analyze the composition of a composite material. Analysis indicates that the transmittance uncertainty for NCOCs in the plateau region (3-5 \( \mu \text{m} \)) varies from 1.13\% to 8.42\% and from 0\% (which corresponds to 0\% transmittance) to 10.44\% in the transition region (1-3 \( \mu \text{m} \), 5-10 \( \mu \text{m} \)). The lowest achievable uncertainty in BSDF for NCOCs is 127.53\%. For both transmittance and BSDF, the uncertainty is most affected by uncertainty in the particle absorption coefficient and particle pair correlation function. For PCA, the uncertainty in transmittance varies from 2.83\% to 6.99\%, and is dominated by uncertainty in the particle refractive index. For NCOCs in the plateau region, the predicted transmittance matches the measured to within the predicted uncertainty for all NCOCs measured. This is important because these NCOCs are being developed for sensors that operate in the plateau region and therefore it is important that the transmittance predictions in this region be as accurate as possible. In addition, it’s reasonable to assume that other composite materials will be designed such that their plateau regions coincide with the sensor waveband, and therefore this model can be used to accurately predict transmittance in the plateau regions of these materials as well. In the transition region, the predicted transmittance for two of the samples (70/30 and 90/10) match the measurements to within the transmittance uncertainty. The predicted transmittance for the
third NCOC sample (50/50) and for the PCA sample deviate from the measured by more than the predicted uncertainty, which can be explained by the fact that the uncertainties determined in the previous chapter are best-case and may not apply to the input parameters used in the predictions shown here. Reasonable assumptions about the true uncertainty of the input parameters used in these predictions can explain the discrepancies between predicted and measured transmittance.

In order for this model to be used to predict the performance of an arbitrary sample, a larger database of particle size distributions and pair-correlation functions needs to be developed, since at present only a few samples have been analyzed and samples made in the future may differ from the analyzed samples.

**Accomplishments**

There are many accomplishments in this dissertation. First, a review of single and multiple scattering theories is conducted. This review shows that a variety of multiple scattering models exist that can be applied to the composite materials of interest. Second, a particular multiple-scattering model, the Durant model, is identified as one that is easily applicable to the materials of interest. The derivation of this model is discussed in detail. Third, this model is extended so that it can be applied to materials with particle size distributions, is extended so that it could be used to predict angle-resolved BSDF, and is implemented in C++ code. Fourth, input parameters for the materials to be modeled are derived and the transmittance and BSDF of these materials are predicted. Fifth, the uncertainty in the predicted transmittance and BSDF as a function of
uncertainty in the input parameters is determined. Sixth, the optical performance of the materials to be modeled is measured and shown (in most cases) to match the predictions to within the predicted uncertainty. Trends observed in the predicted data, such as the insensitivity of the transmittance of NCOCs to volume fraction, are confirmed in the measured data. Seventh, angle-resolved BSDF measurements are identified as a tool with which analyze the composition of composite materials. Eighth, it is shown that the model developed here can be used during the design phase of an optical system to determine the volume fraction of constituent materials such that a composite material of the desired effective index and Abbe number is obtained.

**Additional Model Benefits**

Now that a model exists to predict the optical performance of NCOCs, the effect of contaminants or pores in the material can be quantified. Design trade-offs between NCOCs of different constituent materials can also be studied without the need to fabricate samples. The performance of an NCOC can be optimized for a particular application without the need for expensive trial-and-error tests of fabricated samples. The image quality of an optical design may be enhanced by using composite materials to obtain a specific index and Abbe number for one or more lenses, and the model developed in this dissertation can be used to determine the volume fraction of the constituent materials necessary to obtain a specific index and Abbe number.
There are a number of other materials with which this model can be used to predict optical performance, such as diffuser materials like Spectralon and other composite materials optimized for the long-wave infrared (LWIR) waveband (8-12 µm).

**Summary**

The model developed in this dissertation is a valuable tool in the development of composite materials such as NCOCs and PCA, and can be applied to a variety of other types of materials.
CHAPTER 7- Conclusions

Summary

The purpose of this dissertation is to develop a model that can predict the optical performance of dense composite media. The biggest achievement is extending the Durant scatter model to accurately predict optical transmittance and BSDF of composite media. The model is extended by adding to it the ability to model particle size distributions and BSDF. This tool is used to design NCOCs and to analyze the effect of contaminants or pores in them. This tool is also used to determine the optical performance of a wide variety of materials, provided the refractive indices and internal structure have been sufficiently well-characterized.

Chapter 1 provides an introduction to the nature of the materials to be modeled and the desired outputs of the model. The assumptions used to limit the scope of the model are identified.

Chapter 2 provides a survey of existing optical scattering theories. It is shown that most of the early work in this field related to predicting scatter in dilute media, such as the atmosphere. The development of several theories suitable for predicting scattering in dense media is discussed. It is shown that, while many of these theories are applicable to the materials of interest, most require more information about the size and structure of the particles in the material than was available or are unnecessarily complicated.

Chapter 3 introduces the Durant model and discusses its some of its advantages, namely that the exact internal structure of the material to be modeled need not be known.
Rather, only statistical information about the structure is required, namely the distribution of particle sizes and their pair-correlation function. In this chapter, the model is extended to particle size distributions and an algorithm was developed with which the angle-resolved BSDF of a slab of material could be determined.

Chapter 4 shows how the model developed in this dissertation is applied to the two materials which we wish to model, NCOCs and PCA. It is shown how SEMs are used to determine particle size distribution and pair-correlation function, and C++ code is developed to help determine this data. Transmittance and BSDF predictions are made for a NCOCs of various volume fractions and for PCA, and the uncertainty of these predictions as a function of uncertainty in the input parameters is determined.

Chapter 5 discusses how the transmittance and BSDF were measured for NCOC and PCA samples, and the predicted performance is compared to the measured. It is shown that in most cases the predicted and measured transmittance and BSDF match to within the predicted uncertainty. For NCOCs, the predicted uncertainty in transmittance in the plateau region (3-5 µm) varies from 1.13% to 8.42%, and in the transition region (1-3 µm, 5-10 µm) it varies from 0% (which corresponds to 0% transmittance) to 10.44%. The maximum predicted uncertainty in BSDF for NCOCs is 127.53%. The uncertainty in BSDF is much higher than the uncertainty in transmittance because more calculations are required which amplifies the uncertainties in the input parameters. The uncertainty in transmittance for PCA in the 0.4-0.2 µm band varies from 2.83% to 6.99%. Agreement between the predictions and the measurements demonstrates that the model developed in this dissertation can be used to predict the transmittance of a composite
material to within the uncertainty determined by the input parameters. In the cases where
the predicted transmittance and BSDF does not match the measurement to within the
predicted uncertainty (50/50 $Y_2O_3$ NCOC, PCA) the discrepancy is explained by
assuming reasonable measurement uncertainties in the input parameters. This chapter
also demonstrates that BSDF measurements can be used as a tool to analyze the
composition of a composite material.

**Suggestions for Future Work**

The implementation of the model derived in this dissertation is sufficient for
modeling NCOCs and PCA. However, there are many ways it can be made more
accurate.

In this dissertation, only the first and second terms of the diagrammatic expansion
of the mass operator was performed. Adding more terms to the expansion will increase its
accuracy, especially when modeling materials with high volume fractions of a particular
constituent. This could increase the fidelity of the model for 50/50 NCOCs.

In the derivation of the equations used to model BSDF, only the first two terms of
the binomial series expansion were used in determining $K_{p\text{-ext}}$. Obviously, adding more
terms to this expansion would increase its accuracy.

The scattering matrices for the particle were computed in this dissertation using
Mie theory, which assume that the particles are spheres. Of course, the particles are not
perfectly spherical, and therefore it’s possible to derive more accurate scattering matrices
using techniques for non-spherical particles such as the Rayleigh-Gans and T-matrix
theories.

The complex refractive index data for $\text{Y}_2\text{O}_3$ and MgO were obtained from the
OPTIMATR program. However, a more accurate means of obtaining this data would be
to measure the refractive indices of actual sample materials used in NCOC fabrication,
using prism-deviation or other refractive index measurement techniques.

The particle size distribution and pair-correlation function for NCOCs were
derived from SEMs which contained, at most, 145 particles. Making SEMs that contain
more particles would obviously increase the fidelity of the model. The particles in the
SEMs analyzed for this dissertation were sized and counted by hand, however, if larger
SEMs were available, it may be necessary to use or develop an image-processing
program in order to obtain the particle-size distribution data in a reasonable amount of
time. Even better than taking SEMs of the materials would be to analyze them using x-
ray tomography, which would give the 3-D distribution of the particles and allow the
pair-correlation function to be determine directly, rather than by fitting the SEM to a 3-D
distribution and then computing the pair-correlation from the fit. Doing so would almost
certainly require the use or development of computer software to perform these
calculations on large sets of data.

Further testing of the model by comparing its predictions to measurements from
composite materials whose constituents are different than those considered here is
necessary to prove the model’s broader application.
Conclusion

The design and analysis of dense composite media such as NCOCs are made much easier by the application and development of the model described in this dissertation, which can be used to predict their transmittance and angle-resolved BSDF. This model can be used to predict the optical performance of a wide variety of composite materials, and can be used in conjunction with BSDF measurements to analyze the composition of these materials.
APPENDIX A- Scattering Model Source Code Hierarchy

The object hierarchy for the most heavily used C++ objects written to implement the scattering model developed in this dissertation is shown below in Figure 50. Each object name contains the prefix “SLTK”, which stands for the Stray-Light Toolkit, which is an existing program to which this code was added. The object “SLTKNanocompositeObj” contains all of the data necessary to model any composite material, namely, the refractive indicies and particle size distributions of the constituent materials, as well as the thickness of the sample slab. Each instance of the SLTKNanocompositeObj object maintains a number of object arrays:

- An array of SLTKRefractiveIndexObjs, one for each type (phase) of particle in the composite
- An array of SLTKParticleDistributionDataObjs, one for each type of particle. This object is the base class of SLTKNormalParticleDistributionObj, which contains such information as the mean and standard deviation of the particle size distribution.
- An array of doubles, one for the volume fraction of each particle type.
- An array (“trans”) of SLTKNanocompositeTransmittanceDataObjs, each of which contains the scattering cross section and scattering matrix for each type and size of particle at each computed wavelength. If we are computing the transmittance at $i$ wavelength values, and there are $j$ types of particles, each of which consisting of a particle size distribution of $k$ sizes, then the number of elements in this array
will be \(ijk\). Each SLTKNanocompositeTransmittanceDataObj computes the CDF of the scattering matrix for that wavelength/particle type/size.

- An array ("transAtIndepVar") of SLTKNanocompositeTransmittanceDataObjs, each of which contains the scattering cross section and scattering matrix for each type of particle at each computed wavelength, averaged over the particle sizes as described in the Durant model derivation (Chapter 3). If we are computing the transmittance at \(i\) wavelength values, and there are \(j\) types of particles, then the number of elements in this array will be \(ij\).
Figure 50. C++ code object hierarchy
APPENDIX B- Particle Distribution and Pair Correlation Function Calculation Code

This C++ code computes the histograms shown in Figures 21, 23, and 25 for a given 3-D particle distribution, as well as the pair-correlation function $g_2$ for the distribution. The random-number generation subroutine “ran0” is from *Numerical Recipes in C*.

```c
#include "math.h"
#include "stdio.h"

float ran0(long *idum);

// This routine computes the value of $g_2$ using the Monte-Carlo method described in Durant's second paper
void main()
{
    // Define the dimensions of the volume to fill
    double dimX = 1.9;
    double dimY = 1.9;
    double dimZ = 1.9;

    // For constant-size spheres, define the radius of the spheres a
    // double a = 1.;

    // For Gaussian-distributed spheres, define the min, max, mean and stddev diameter
    double meand = 0.2;
    double sigmad = 0.025;

    // Define the volume fraction f
    double f = 0.4;

    // ************ Computations start here *******************

    // Compute the volume
    double V = dimX * dimY * dimZ;

    // Compute the number of spheres of radius a in the defined volume at the defined volume fraction
    //int n = 3*V*f / (4.*3.1415926*pow(a,3));
    int maxn = 100000;

double* x = new double[maxn];
double* y = new double[maxn];
```
double* z = new double[maxn];
double* a = new double[maxn];
//bool* sphereIsSize1 = new bool[maxn];
//bool* sphereIsSize2 = new bool[maxn];
//for(int i=0; i<maxn; i++)
//{
//  sphereIsSize1[i] = false;
//  sphereIsSize2[i] = false;
//}

int numHisto = 6;
double* histogram = new double[numHisto];
for(int i=0; i<numHisto; i++)
{
  histogram[i] = 0.;
}
//double histomin = .128788; // for f=0.5
//double histomax = .371212;
double histoPeak = 11.;
//double histomin = .10687; // for f=0.3
//double histomax = .29771;
double histomin = .076336; // for f=0.1
double histomax = .236641;
double dHisto = (histomax - histomin) / (numHisto - 1);
int numSpheresAtZZero = 0;

// Pair correlation function calc

// Define the number of bins with which to tabulate g2
int numRa = 30;

// Allocate space for the g2 tabulation and the sphere locations
double* g2 = new double[numRa];
double* g2temp = new double[numRa];
for(int j=0; j<numRa; j++)
{
  g2[j] = 0.;
}
// Define the maximum value of R/a (min is 0)
double maxRa = 3;
double maxR = maxRa * (meand/2);

// Compute how many particles lie within a spherical shell of a
given radius
double dRa = maxRa / numRa;
double dR = dRa * (meand/2);

long idum = 5;
int maxRetries = 10000000;
int numAveraged = 0;
int numSpheres = 0;
int numDistsAveragedForg2 = 0;
for(int ii=0; ii<1; ii++)
{
    // Generate the sphere locations, making sure none overlap
    bool volFractionTooLow = true;

    //for(int i=0; i<n; i++)
    int i = 0;
    double sphereVolume = 0.;
    int n = 0;
    int retryCount = 0;
    while(volFractionTooLow)
    {
        bool tooClose = true;
        // Generate a size
        double temp = sqrt(-2*sigmad*sigmad*log(ran0(&idum)));
        if(ran0(&idum) > 0.5)
        {
            a[i] = 0.5*(meand + temp);
        }
        else
        {
            a[i] = 0.5*(meand - temp);
        }

        // Single size
        //a[i] = meand/2.;
        retryCount = 0;
        while(tooClose && retryCount < maxRetries)
        {
            x[i] = dimX * ran0(&idum);
            y[i] = dimY * ran0(&idum);
            z[i] = -dimZ/2 + (dimZ * ran0(&idum));

            //double dist2=4*a*a+1;
            double dist2 = 0.;
            double dist=0.;
            tooClose = false;
            for(int j=0; j<i; j++)
            {
                double dx = x[i]-x[j];
                double dy = y[i]-y[j];
                double dz = z[i]-z[j];
                dist2 = dx*dx + dy*dy + dz*dz;
                double dist = sqrt(dist2);
                if(dist <= 4*a*a)
                {
                    tooClose = true;
                    break;
                }
            }
            retryCount++;
        }
    }
}
if(retryCount != maxRetries)
{
    sphereVolume +=
(4./3.)*3.1415926*a[i]*a[i]*a[i];
    if(sphereVolume/V > f)
    {
        volFractionTooLow = false;
    }
    i++;
    n++;
    numSpheres++;
    if(i == maxn)
    {
        printf("Too many spheres!\n");
        i = i;
    }

    printf("Creating spheres : %f percent done\n", 100*sphereVolume/V/f);
}
else
{
    volFractionTooLow = false;
}
}

if(retryCount != maxRetries)
{
    printf("Distribution added\n");
    // Sphere cross-section diameter calc
    // Determine which spheres intersect the z=0 plane, and build the histogram
    for(int i=0; i<n; i++)
    {
        if(abs(z[i]) <= a[i])
        {
            // Compute the diameter of the cross-section on the z=0 plane
            double diam = 2*sqrt(a[i]*a[i] - z[i]*z[i]);

            // Bin this diameter in the histogram
            if(diam >= histomin && diam <= histomax)
            {
                double dIndex = (diam - histomin)/dHisto;
                int index = dIndex;
                histogram[index] += 1.;
                numSpheresAtZZero++;
            }
        }
    }
    numAveraged++;
// Pair correlation function calc
// initialize g2temp array
for(int j=0; j<numRa; j++)
{
    g2temp[j] = 0.;
}

int numConsidered = 0;
for(int i=0; i<n; i++)
{
    if(x[i] > maxR && x[i] < dimX-maxR &&
        y[i] > maxR && y[i] < dimY-maxR &&
        z[i] > maxR && z[i] < dimZ-maxR)
    {
        numConsidered++;
        for(int j=0; j<n; j++)
        {
            if(i != j)
            {
                double dx = x[i]-x[j];
                double dy = y[i]-y[j];
                double dz = z[i]-z[j];
                double R = sqrt(dx*dx + dy*dy + dz*dz);
                int bin = R/dR;
                if(bin < numRa)
                {
                    g2temp[bin] += 1.;
                }
            }
        }
    }
}
printf("Computing g2 : %f percent done\n",
(double) 100.*i/n);
if(numConsidered)
{
    // Normalize the temp g2 values and add them to g2
    for(int i=0; i<numRa; i++)
    {
        g2[i] += (g2temp[i] / (numConsidered * (n/V)));
    }
    numDistsAveragedForg2++;
}
printf("Num spheres = %d\n", numSpheres);
int n = numSpheres;
printf("Num averaged = %d\n", numAveraged);
/*
// Normalize the histogram to whatever we want
double peak = -1;
for(int i=0; i<numHisto; i++)
{
    if(histogram[i] > peak)
    {
        peak = histogram[i];
    }
}
FILE* fout = fopen("histogram.txt", "w");
for(int i=0; i<numHisto; i++)
{
    histogram[i] *= histoPeak/peak;
    fprintf(fout, "%f\t%f\n", histomin + dHisto*i, histogram[i]);
}
delete[] histogram;
fclose(fout);
*/

// Now normalize the g2 data
for(int i=0; i<numRa; i++)
{
    // Divide by the number of distributions considered
    //g2[i] /= numConsidered;
g2[i] /= numDistsAveragedForG2;

    // Divide by the volume of the spherical shell
    if(i != 0)
    {
        //double R = dRa *i;
        //g2[i] /= (4*3.1415926*R*R*dRa);
        double R = dR * i;
        g2[i] /= (4*3.1415926*R*R*dR);
    }

    // Divide by the number density
    //g2[i] /= (n/V);

    // Subtract -1 for the Durant implementation
    g2[i] += -1.;
}

// Output the results
FILE* fout = fopen("g2vsRa.txt", "w");
for(int i=0; i<numRa; i++)
{
    double Ra = dRa*i;
    fprintf(fout, "%f\t%f\n", Ra, g2[i]);
}
fclose(fout);
delete[] g2;
delete[] x;
delete[] y;
delete[] z;
delete[] a;
//delete[] sphereIsSize1;
//delete[] sphereIsSize2;

#define IA 16807
#define IM 2147483647
#define AM (1.0/IM)
#define IQ 127773
#define IR 2836
#define MASK 123459876

// This random-number generation routine is from "Numerical Recipies in C"

float ran0(long *idum)
{
    long k;
    float ans;

    *idum ^= MASK;
    k=(*idum)/IQ;
    *idum=IA(*idum-k*IQ)-IR*k;
    if (*idum < 0) *idum += IM;
    ans=AM(*idum);
    *idum ^= MASK;
    return ans;
}
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