Scattering of Electromagnetic Radiation by Complex Microstructures in the Resonant Regime

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By

Erik Shepard Thiele

1998
Dedication

To my family.
Acknowledgments

I begin by thanking and applauding my research advisor, Roger French, who first encouraged me to embark on this journey. Roger has helped me to appreciate the real point of forming a piece of work like this thesis. His support and guidance has been indispensable, and without these I would have missed out on most of the deep satisfaction of this process. I am very grateful to my faculty advisor, Peter Davies, whom I have had the good fortune of knowing since my undergraduate days. I have always respected Peter for his scientific leadership, but even more for his genuine concern for all of us who have worked with him. I am also very thankful for the guidance and encouragement I have received from Professors Dawn Bonnell and Takeshi Egami throughout the development of this dissertation.

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pour toujours.
Abstract

A computational optics approach is used to determine the scattering properties of complex microstructures in the resonant regime. The time-domain finite element method employed in this research to solve Maxwell’s equations can be used to determine the scattering properties of scattering systems exhibiting arbitrary, complex shapes and optical anisotropy. A detailed study of the factors influencing the accuracy of this numerical method demonstrates that the construction of the finite element model strongly influences accuracy; error in these computations is confined to <3% for typical models. The computational optics approach is applied to determine the light scattering efficiencies of several different white pigment systems. It is demonstrated that the light scattering efficiency of core-shell white pigment particles is limited by the content of low-index material and therefore cannot attain the same efficiency as optimized particles of the high-index material. Optically anisotropic spheres of rutile titania exhibit the expected dependence of scattering properties upon the angle of light incidence and polarization. Under conditions of random illumination, the scattering efficiencies of these spheres can be approximated to within 10% using models based upon isotropic materials. The agglomeration of both colloidal titania and latex particles causes substantial deviation from the light scattering properties of the isolated primary particles. In the case of rutile titania particles of optimal size, for example, losses in volume-normalized scattering efficiency of 70% occur for the largest agglomerates studied. The use of single, equivalent mass spheres to approximate the light scattering properties of the agglomerate structures succeeds in predicting trends in these properties
but fails as a rigorous description of these properties. For small clusters of either latex or titania particles with varying interparticle separation distance, optical interactions between neighboring particles diminish rapidly with increasing particle separation. In most cases, changes in scattering efficiency with interparticle separation distance could be well fit using an exponential decay. The decay constant of these spatial variations varies in the range 0.25-0.45 light wavelengths for these systems, with appreciable optical interactions not extending beyond 2-3 light wavelengths.
# Table of Contents

Scattering of Electromagnetic Radiation by ................................................................. i
Complex Microstructures in the Resonant Regime ...................................................... i
Dedication ...................................................................................................................... iii
Acknowledgments .......................................................................................................... iv
Abstract ....................................................................................................................... vi
Table of Contents ......................................................................................................... viii
List of Tables .................................................................................................................. xi
List of Illustrations ........................................................................................................ xii
Chapter 1. Introduction .................................................................................................. 1
  1.1 Single Scattering ..................................................................................................... 1
  1.2 Scattering by Ensembles of Scattering Features ................................................... 4
  1.3 Formulation of the Present Research .................................................................... 6
  1.4 On Vector Notation .............................................................................................. 7
Chapter 2. Literature Review ....................................................................................... 8
  2.1 Electromagnetic Radiation Scattering in Materials Science ................................. 8
  2.2 Light Scattering Properties of Complex Microstructures ................................. 9
    2.2.1 Light Scattering by White Pigment Particles ................................................. 9
      2.2.1.1 Application of Mie Theory to Optically Anisotropic Materials .......... 11
      2.2.1.2 Kubelka-Munk Analysis of Paint Film Scattering Efficiencies .......... 12
      2.2.1.3 Computational Modeling of Scattering by White Pigments: Previous
          Studies ........................................................................................................... 14
    2.2.2 Light Scattering by Concentrated Particle Dispersions .............................. 16
      2.2.2.1 The Crowding Effect in Paint Films .................................................... 16
      2.2.2.2 Light Scattering in Stereolithography ................................................. 21
    2.2.3 Light Scattering by Particle Agglomerates ............................................... 23
      2.2.3.1 Computational Approaches ............................................................... 23
      2.2.3.2 Computational Results for Particle Agglomerates ............................ 25
  2.3 Principles of Light Scattering .............................................................................. 27
    2.3.1 Maxwell’s Equations ................................................................................... 27
    2.3.2 Exact, Analytical Solutions of Light Scattering ........................................... 30
    2.3.3 Approximate and Numerical Solutions of Light Scattering ....................... 33
      2.3.3.1 Rayleigh Theory ............................................................................... 33
      2.3.3.2 Geometrical Optics ......................................................................... 35
      2.3.3.3 Point Matching ................................................................................. 38
      2.3.3.4 Perturbation Methods ....................................................................... 38
      2.3.3.5 Coupled-Dipole Method .................................................................. 39
      2.3.3.6 T-Matrix or Extended Boundary Condition Method ......................... 41
      2.3.3.7 Method of Moments ......................................................................... 42
      2.3.3.8 Finite Difference Time-Domain Method ........................................... 45
      2.3.3.9 Finite Element Method .................................................................... 47
Chapter 3. Computational Methods ............................................................................. 55
6.3 Near-Field Interactions Between Neighboring Latex Particles ..........................157
Chapter 7. Clusters of Titania Particles: A High-Contrast System .........................165
  7.1 Materials Systems of Interest ..............................................................................165
  7.2 Light Scattering by Titania Sphere Clusters of Increasing Size .......................168
  7.3 Near-Field Interactions Between Neighboring Titania Particles .......................173
  7.4 Near-Field Interactions Between Two Morphological Rutile Particles ..............176
Chapter 8. Discussion: Light Scattering by Complex Microstructures in the Resonant
  Regime .....................................................................................................................184
  8.1 Accuracy of the Time-Domain Finite Element Method .................................184
  8.2 Light Scattering by Complex, Resonant Particles ............................................185
  8.3 Light Scattering by Densely Packed Particle Aggregates .................................188
  8.4 Near-Field Optical Interactions Between Particles .........................................195
    8.4.1 Titania and Latex Systems .........................................................................195
    8.4.2 Extension to Other Materials Systems .......................................................201
Chapter 9. Conclusions ............................................................................................203
Appendix. Typical EMFlex Input Deck .................................................................207
Bibliography ............................................................................................................210
List of Tables

Table 1. Error in scattering cross section as a function of separation distance between the bottom of the sphere and the bottom wall of the model. The corresponding models are shown in Figure 20. .............................................................. 97

Table 2. Error in scattering cross section of finite element calculations in which the model edge length was systematically varied. All calculations are for the case of a 40-nm sphere at the center of a cubic model. ........................................ 101

Table 3. Error in scattering cross section of finite element calculations in which the model edge length was systematically varied. All calculations are for the case of a 200-nm sphere at the center of a cubic model. ........................................ 101

Table 4. Error in scattering cross section as a function of sphere diameter for the three cases indicated on the plot in Figure 22. ................................................................. 104

Table 5. Scattering coefficients $S$ and $\sigma$ computed for anisotropic spheres of different diameter using the finite element approach. ........................................ 130

Table 6. Values of $\chi^2$ (Equation 80) associated with $S$ and $\sigma$ values for the average index and weighted sum approximation, compared to anisotropic sphere scattering data generated using the finite element approach. .................. 135

Table 7. Comparison between the far-field scattering coefficients for the single rutile particle and the equivalent volume sphere, using both the average index and weighted sum approximations. ................................................................. 143

Table 8. Diameters of spheres exhibiting the same far-field scattering coefficients as the single rutile particle, using both the average index and weighted sum approximations. ................................................................. 143

Table 9. Diameters of spheres exhibiting the same far-field scattering coefficients as the system of two rutile particles for each interparticle separation distance considered, using both the average index and weighted sum approximations. ................. 183

Table 10. Results of parametric fits of the six curves shown in Figure 69 and Figure 70 using the expression in Equation 81. ................................................................. 200
List of Illustrations

Figure 1. Schematic diagram of scattering object size versus radiation wavelength identifying three scattering domains: geometrical optics, the resonant regime, and the Rayleigh scattering regime. .............................................................................................................................................. 4

Figure 2. The ordinary (lower, dashed curve) and extraordinary (upper, dotted curve) refractive indices of rutile titania versus light wavelength. These data were compiled from multiple sources by Ribarsky.13 ........................................................................................................ 11

Figure 3. The scattering coefficient $S^*$ for rutile titania particles in a typical paint film as a function of pigment volume concentration. (After Braun25) ................................................................. 21

Figure 4. Schematic diagram of a stereolithography apparatus for producing complex ceramic parts using rapid prototyping. (After Liao.) .................................................................................. 23

Figure 5. Schematic diagram showing reflection and refraction of a light ray using the geometrical optics approximation. (After Bohren and Huffman1) .................................................................... 38

Figure 6. Flow chart showing the formulation and evaluation of light scattering problems using the Illuminator software. ........................................................................................................... 73

Figure 7. A representation of the spherical illumination coordinate system used in Illuminator runs. In this case, there is an $18^\circ$ increment in the spherical coordinate angles phi and theta between adjacent surface area elements. The individual illumination directions pass through the centers of the surface area elements. ...... 74

Figure 8. Dependence of the scattering coefficient $S$ upon sphere diameter for the case of a sphere with $n = 2.74$ embedded in a resin with $n = 1.51$. The illumination wavelength is 560 nm. ................................................................................................................................. 78

Figure 9. Dependence of the angle-weighted scattering coefficient $\sigma$ upon sphere diameter for the case of a sphere with $n = 2.74$ embedded in a resin with $n = 1.51$. The illumination wavelength is 560 nm. ................................................................................................................................. 78

Figure 10. Finite element model of a 200-nm sphere with $n = 2.74$ embedded in a polymeric resin with $n = 1.51$. The 560-nm illuminating light propagates in the $+x$ direction and is polarized in the $z$ direction. This model contains 1,340,000 volume elements. ........................................................................................................................................ 79

Figure 11. Time history of $z$-polarized electric field amplitude at the center of the sphere shown in the computation of Figure 10. ........................................................................................................... 80

Figure 12. Finite element model of a 200-nm sphere with $n = 2.74$ embedded in a polymeric resin with $n = 1.51$. The 560-nm illuminating light propagates in the $+x$ direction and is polarized in the $z$ direction. This model contains 168,000 volume elements. ........................................................................................................................................ 81

Figure 13. Dependence of Cray C-94 memory requirement upon the number of volume elements in the finite element model for the present series of EMFlex computations .................................................................................................................. 83

Figure 14. Dependence of Cray C-94 CPU time requirement upon the number of volume elements in the finite element model for the present series of EMFlex computations .................................................................................................................. 84
Figure 15. CPU time required for a single far-field extrapolation is shown in as a function of the angular discretization on the surface of the far-field sphere. 86
Figure 16. CPU time required for a single far-field extrapolation is shown in as a function of the number of surface elements on the far-field sphere. 86
Figure 17. Error in scattering cross section compared to the exact result from Mie theory as a function of $\rho$, the number of volume elements in a model per minimum wavelength of the 560-nm light propagating in the finite element models. 89
Figure 18. Error in scattering cross section compared to the exact result from Mie theory as a function of as a function of angular discretization on the surface of the far-field sphere surface. 91
Figure 19. Error in scattering cross section compared to the exact result from Mie theory as a function of as a function of far-field sphere radius. 92
Figure 20. Cross-sectional slices through the centers of four finite element models in which the spacing between the 200-nm sphere and the bottom wall of the model has been systematically varied. Scattered light intensity is shown in each case. 96
Figure 21. Finite element model of a 40-nm sphere with $n = 2.74$ embedded in a polymeric resin with $n = 1.51$. The 560-nm illuminating light propagates in the $+x$ direction and is polarized in the $z$ direction. 100
Figure 22. The scattering coefficient $S(\mu m^{-1})$ as a function of sphere diameter for the case of a sphere with $n = 3.0$ in a medium with $n = 1.0$. This represents a more resonant system than can be achieved in practice, since no known, non-lossy material exhibits such a high refractive index in the visible spectrum. 104
Figure 23. Schematic representation of titania coated on a core particle of lower refractive index. 109
Figure 24. Scattering coefficient $\sigma(\mu m^{-1})$ versus coated particle diameter and refractive index of the core material for titania-coated particles with coating thickness equal to 10% of the particle radius. 112
Figure 25. Scattering coefficient $\sigma(\mu m^{-1})$ versus silica core diameter and titania shell diameter for a coated particle. The global maximum of this plot corresponds to a solid titania sphere of 0.2 $\mu m$ diameter. 112
Figure 26. Scattering coefficient $\sigma$ for five coated particles with different outside diameters. 114
Figure 27. Scattering coefficient $\sigma$ versus particle diameter for a solid titania sphere and a titania-coated silica particle with coating thickness equal to 10% of the particle radius. 115
Figure 28. Scattering coefficient $\sigma$ divided by the density of the coated particle. The global maximum of this plot corresponds to a solid titania sphere with no silica present. 117
Figure 29. Scattering coefficient $\sigma$ divided by the weight fraction of titania present in each coated particle. The global maximum of this plot corresponds to a solid titania sphere with no silica present. 117
Figure 30. Scattering coefficient $\sigma$ for the five particles shown in Figure 26, with the cellulose surrounding medium replaced by air (refractive index 1.0 instead of 1.45). ................................................................. 120

Figure 31. Scattering coefficient $S$ versus sphere diameter for an optically isotropic sphere from Mie theory, using the average index approximation. .................. 123

Figure 32. Angle-weighted scattering coefficient $\sigma$ versus sphere diameter for an optically isotropic sphere from Mie theory, using the average index approximation. ................................................................. 123

Figure 33. Scattering coefficient $S$ versus sphere diameter for an optically isotropic sphere from Mie theory, using the weighted sum approximation. .......... 124

Figure 34. Angle-weighted scattering coefficient $\sigma$ versus sphere diameter for an optically isotropic sphere from Mie theory, using the weighted sum approximation. ................................................................. 124

Figure 35. Finite element model and scattered intensities for a 0.2-$\mu$m anisotropic sphere of rutile titania. The 560-nm radiation propagates in the +x direction, with unit incident intensity. Polarization is parallel to the y direction. ...................... 128

Figure 36. The scattering coefficient $S$ as a function of sphere diameter computed using the finite element method (solid points) for anisotropic spheres of rutile titania with $n = 2.74$ embedded in a medium with $n = 1.51$. The illumination wavelength is 560 nm. The long dashed curve corresponds to the average index approximation, while the dotted curve corresponds to the weighted sum approximation.............. 129

Figure 37. The angle-weighted scattering coefficient $\sigma$ as a function of sphere diameter computed using the finite element method (solid points) for anisotropic spheres of rutile titania embedded in a medium with $n = 1.51$. The illumination wavelength is 560 nm. The long dashed curve corresponds to the average index approximation, while the dotted curve corresponds to the weighted sum approximation.............. 129

Figure 38. Scattering coefficient $S$ as a function of the angle of incidence (relative to the optic axis) for the 0.2-$\mu$m anisotropic sphere of rutile titania. Hollow circles are for polarization perpendicular to the optic axis of the sphere; filled circles are for polarization coplanar with the optic axis. ................................................................. 132

Figure 39. High resolution scanning electron micrograph of rutile titania particles, showing their characteristic, morphological shapes. (Micrograph courtesy E.D. Boyes, DuPont Central Research and Development.) ................................................................. 137

Figure 40. Finite element model and near field scattering results for an anisotropic, morphological rutile particle with a width of 0.175 $\mu$m, and a length of 0.35 $\mu$m in $n = 1.51$ resin; the light wavelength is 560 nm..................................................... 140

Figure 41. The scattering coefficient $S$ as a function of sphere diameter for a latex particle with $n = 1.50$ in a water medium with $n = 1.33$. The illuminating light wavelength is 488 nm. The 200-nm sphere diameter studied in this chapter is marked with an “x.” ................................................................. 148

Figure 42. The angle-weighted scattering coefficient $\sigma$ as a function of sphere diameter for a latex particle with $n = 1.50$ in a water medium with $n = 1.33$. The illuminating light wavelength is 488 nm. The 200-nm sphere diameter studied in this chapter is marked with an “x.” ................................................................. 148
Figure 43. Finite element model for a 200-nm latex sphere with $n = 1.50$ in a water medium with $n = 1.33$. The illuminating wavelength is 488 nm, and light propagates in the $+x$ direction.

Figure 44. Finite element models of latex sphere clusters containing 3, 7, 13, and 27 spheres.

Figure 45. Finite element model of a cluster of seven 200-nm latex spheres $n = 1.50$ in a water matrix with $n = 1.33$. The 488-nm illuminating light propagates in the $+x$ direction and is polarized in the $z$ direction.

Figure 46. The scattering coefficient $S$ as a function of the number of 200-nm latex particles composing a particle cluster under conditions of random illumination.

Figure 47. The quantity $(1 - g)$ as a function of the number of 200-nm latex spheres composing a particle cluster under conditions of random illumination.

Figure 48. The scattering coefficient $\sigma$ as a function of the number of 200-nm latex spheres composing a particle cluster under conditions of random illumination.

Figure 49. Finite element model of a cluster of seven 200-nm latex spheres $n = 1.50$ in a water matrix with $n = 1.33$. The surface-to-surface interparticle spacing is 0.4 $\mu$m. The 488-nm illuminating light propagates in the $+x$ direction and is polarized in the $z$ direction.

Figure 50. Dependence of the scattering coefficient $S$ upon surface-to-surface interparticle separation distance for the clusters of seven latex spheres. The dashed line corresponds to the value associated with a single 200-nm latex primary particle.

Figure 51. Dependence of the quantity $(1 - g)$ upon surface-to-surface interparticle separation distance for the clusters of seven latex spheres. The dashed line corresponds to the value associated with a single 200-nm latex primary particle.

Figure 52. Dependence of the angle-weighted scattering coefficient $\sigma$ upon surface-to-surface interparticle separation distance for the clusters of seven latex spheres. The dashed line corresponds to the value associated with a single 200-nm latex primary particle.

Figure 53. The scattering coefficient $S$ as a function of sphere diameter for a rutile particle with $n = 2.74$ in a polymer medium with $n = 1.51$ under the average index approximation. The illuminating light wavelength is 560 nm. The 200-nm sphere diameter studied in this chapter is marked with an “x.”

Figure 54. The angle-weighted scattering coefficient $\sigma$ as a function of sphere diameter for a rutile particle with $n = 2.74$ in a polymer medium with $n = 1.51$ under the average index approximation. The illuminating light wavelength is 560 nm. The 200-nm sphere diameter studied in this chapter is marked with an “x.”

Figure 55. Finite element model of a cluster of seven 200-nm titania spheres with $n = 2.74$ in a polymer matrix with $n = 1.51$. The 560-nm illuminating light propagates in the $+x$ direction and is polarized in the $z$ direction.

Figure 56. The scattering coefficient $S$ as a function of the number of 200-nm titania spheres composing a particle cluster. These results are for the case of random illumination of each cluster, resulting in orientation-averaged results.
Figure 57. The scattering coefficient $\sigma$ as a function of the number of 200-nm titania spheres composing a particle cluster. These results are for the case of random illumination of each cluster, resulting in orientation-averaged results.............. 172

Figure 58. Dependence of the scattering coefficient $S$ upon surface-to-surface interparticle separation distance for the clusters of seven titania spheres. The dashed line corresponds to the value associated with a single 200-nm titania primary particle..................................................................................................... 175

Figure 59. Dependence of the angle-weighted scattering coefficient $\sigma$ upon surface-to-surface interparticle separation distance for the clusters of seven titania spheres. The dashed line corresponds to the value associated with a single 200-nm titania primary particle..................................................................................................... 175

Figure 60. Finite element model cross section and near field scattering results for two anisotropic morphological rutile particles in $n = 1.51$ resin for light incident normal to the cross section shown and with a wavelength of 560 nm. The interparticle spacing is 0.5 $\mu$m. ................................................................................................. 179

Figure 61. Finite element model cross section and near field scattering results for two anisotropic morphological rutile particles in $n = 1.51$ resin for light incident normal to the cross section shown and with a wavelength of 560 nm. The interparticle spacing is 0.3 $\mu$m. ................................................................................................. 180

Figure 62. Finite element model cross section and near field scattering results for two anisotropic morphological rutile particles in $n = 1.51$ resin for light incident normal to the cross section shown and with a wavelength of 560 nm. The interparticle spacing is 0 $\mu$m. .................................................................................................... 181

Figure 63. Scattering coefficient $S$ for two morphological rutile particles as a function of interparticle separation. The horizontal line shows the results for one of the morphological rutile particles. .............................................................................. 182

Figure 64. Angle-weighted scattering coefficient $\sigma$ for two morphological rutile particles as a function of interparticle separation. The horizontal line shows the results for one of the morphological rutile particles.............................. 182

Figure 65. The scattering coefficient $S$ as a function of the number of 200-nm latex particles composing a particle cluster (solid curve). For comparison, the results of Mie theory computations on single, equivalent-mass spheres are shown (dashed curve). ................................................................................................................... 193

Figure 66. The scattering coefficient $\sigma$ as a function of the number of 200-nm latex particles composing a particle cluster (solid curve). For comparison, the results of Mie theory computations on single, equivalent-volume spheres are shown (dashed curve). ................................................................................................................... 193

Figure 67. The scattering coefficient $S$ as a function of the number of 200-nm titania particles composing a particle cluster (solid curve). For comparison, the results of Mie theory computations on single, equivalent-mass spheres are shown (dashed curve). ................................................................................................................... 194

Figure 68. The scattering coefficient $\sigma$ as a function of the number of 200-nm titania particles composing a particle cluster (solid curve). For comparison, the results of
Mie theory computations on single, equivalent-mass spheres are shown (dashed curve). ................................................................................................................... 194

Figure 69. Scattering coefficient $S$ (%) for the three different multiple-particle systems as a function of the center-to-center interparticle spacing expressed in wavelengths. The value 100% corresponds to the $S$ value for an isolated primary particle in each case........................................................................................................................ 200

Figure 70. Angle-weighted scattering coefficient $\sigma$ (%) for the three multiple-particle systems as a function of the center-to-center interparticle spacing expressed in wavelengths. The value 100% corresponds to the $\sigma$ value for an isolated primary particle in each case. ................................................................................................................... 201
Chapter 1. Introduction

Scattering phenomena underlie the human perception of the natural world through the sense of sight, and the scattering properties of physical systems are widely exploited in both science and technology. Scattering of electromagnetic radiation by microstructures encompasses a broad range of physical phenomena. Wavelengths in the electromagnetic spectrum span an infinite range, and those exploited technologically range from kilometer-long radio signals to sub-angstrom gamma rays. The nature of the scattering interaction between electromagnetic radiation and materials is determined primarily by the relationship between radiation wavelength and the physical dimensions of scattering features in materials systems. With an appreciation of this premise, a unified view of electromagnetic radiation scattering by microstructures is possible, spanning the orders of magnitude in size which exist in both the electromagnetic spectrum and the physical world.

1.1 Single Scattering

The fundamental case in the analysis of electromagnetic radiation scattering is that of single scattering, in which the interaction between radiation and a single, isolated scattering feature is considered. Results of single scattering can be extended to ensembles which contain a sufficiently small number of particles with interparticle separations large enough that each particle develops its individual scattering pattern without influence from its neighbors. A qualitative criterion for the assumption of single scattering is that each particle in an ensemble experiences the same incident
electric field, with negligible scattered field from other features in the ensemble. The treatment of an ensemble of scatterers in the single scattering regime is straightforward: the scattering properties of the ensemble is simply the sum of contributions from the individual scatterers.\textsuperscript{1,2}

The degree of mathematical complexity in the treatment of the radiation scattering by an isolated scattering feature is strongly affected by the relationship between radiation wavelength and the physical size of a scattering feature, as suggested above. In general, simplifying approximations can be applied to the separate cases in which the wavelength is at least an order of magnitude greater or less than the size of a scattering feature. The former case includes the well-known Rayleigh scattering theory which explains the basis of the blue color of the daytime sky on a clear day, for example, while the latter case includes the application of geometrical optics techniques to the prediction of visible image formation by macroscopic objects. For cases in which the wavelength of electromagnetic radiation is on the order of the size of a scattering feature, the mathematical description of scattering is potentially intractable using even the most sophisticated analytical approaches. This is especially true for material systems exhibiting high optical contrast between the scattering feature and its surrounding medium, since very strong coupling and resonance can occur. Scattering efficiencies in this resonant regime can be very high. An example of one such system is the scattering of visible light by an optimized white pigment particle, where near-field scattered intensities in the vicinity of the particle can be an order of magnitude greater than that of the incident light and the scattering cross section of a particle can be many
times greater than its geometric cross section. These domains of Rayleigh scattering, the resonant regime, and geometrical optics are illustrated in the schematic diagram in Figure 1 showing object size mapped versus radiation wavelength.

The potentially high scattering efficiency of systems in which the radiation wavelength is on the order of the size of scattering features makes them of particular interest in science and technology. In the scientific community, the use of scattering techniques to characterize structures is most effective when there is strong coupling between the features in a structure and the probe radiation. Likewise, technology uses this resonance to advantage in applications as diverse as paint films and cellular telephone technology. Unfortunately, the mathematical analysis of scattering by objects with size on the order of the radiation wavelength is complex. Indeed, rigorous analytical approaches to solving Maxwell’s equations for scattering in three dimensions have been historically limited to coordinate systems in which solutions to the scalar wave equation can be separated in the three spatial variables. In the important case of the spherical coordinate system, the result is the well-known Mie theory (1908). Mie theory describes the scattering of electromagnetic radiation of arbitrary wavelength by an isolated, optically isotropic sphere of arbitrary diameter. An advantage of Mie theory is that it is easily implemented computationally. A disadvantage of Mie theory is that it is limited to a spherical particle and is not applicable to the myriad systems in which the scattering features are irregularly shaped and/or optically anisotropic. In addition, spherical particles can exhibit surface wave resonances which do not occur with more irregularly shaped particles. The radiation scattering properties of irregularly
shaped objects with size on the order of the radiation wavelength are of growing importance in the scientific community as the detailed understanding of physical microstructures increases.

Figure 1. Schematic diagram of scattering object size versus radiation wavelength identifying three scattering domains: geometrical optics, the resonant regime, and the Rayleigh scattering regime.

1.2 Scattering by Ensembles of Scattering Features

In ensembles containing sufficiently large numbers of scattering features, the collective radiation scattering properties of the ensemble can deviate substantially from the superposed scattering properties of the constituent individual features. These deviations can be the result of diffraction or near-field optical interactions between neighboring particles. The term *multiple scattering* refers to the phenomenon of collective scattering by a large ensemble of individual scattering features and is a well-established subject area which encompasses, and expands upon, the study of radiation
scattering by isolated scattering features. Multiple scattering theories describe mathematically the transfer of radiation through a collection of optically isolated scattering features, each having known scattering properties. A criterion for the application of multiple scattering theories is that no near-field optical interactions exist between the scattering features in the ensemble. Multiple scattering theories are widely applied in diverse subject areas, including meteorology, astronomy, colloid science, optical lithography, materials science, and color science. An important aspect of multiple scattering theories is the presumption of optical isolation of the individual scattering features in an ensemble. This condition requires that the scattered wave front produced by an individual feature develops independently of neighboring features; that is, the scattering features are sufficiently spaced physically that there exist no near-field optical interactions between neighbors. This condition is met only in dilute dispersions of scattering not exceeding ~5% by volume.

In concentrated dispersions, the scattering properties of individual features are affected by near-field optical interactions with neighbors; this regime of scattering by ensembles of isolated features has therefore been described as dependent scattering. The detailed mathematical description of near-field interactions between individual scattering features is complex, and the development of understanding of these effects in systems of practical interest is still in its earliest stages. The use of large-scale numerical computation is essential in approaching these problems rigorously, and recent advances in the scale of available computing power promise substantial advances in the understanding of dependent scattering effects in the near future.
1.3 Formulation of the Present Research

In the present research, the electromagnetic radiation scattering properties of several different classes of complex microstructures are studied using a numerical approach. Of particular interest are systems containing scattering features which are on the order of the radiation wavelength in size, in which near-field interactions occur among the scattering features. The numerical approach used is a time-domain finite element formulation of Maxwell’s equations which produces full near-field solutions to cases of electromagnetic radiation scattering by microstructures having arbitrary geometry. The method can be applied to isolated scattering features of arbitrary shape with anisotropic optical properties, overcoming the restrictions of analytical approaches such as Mie theory. In addition, the finite element approach can be readily applied to ensembles of multiple scattering features to determine, quantitatively, the effect of near-field interactions on the radiation scattering properties. The time-domain finite element method allows precise control of microstructures, facilitating systematic study of the effects of microstructure on system scattering properties which is not possible experimentally. The structure-property relations in light scattering by complex microstructures is the primary focus of this dissertation.

Chapter 2 reviews electromagnetic radiation scattering studies in materials science, emphasizing previous work on scattering by systems of multiple particles, and describes analytical and numerical approaches to the computation of radiation scattering. Chapter 3 discusses the computational approaches applied in the present research. In Chapter 4, the factors controlling the accuracy of the time-domain finite
element approach employed in the present research are identified. Chapter 5 considers three diverse cases of light scattering by single, resonant white pigment particles containing titania. Chapter 6 describes the light scattering properties of multiple-particle clusters of low-contrast, weakly scattering latex spheres. Chapter 7 presents an analogous study of the light scattering properties of clusters of high-contrast, strongly resonant titania particles. Chapter 8 contains a unifying discussion of the results presented in Chapters 4-7. Finally, Chapter 9 contains general conclusions drawn from these collective studies.

1.4 On Vector Notation

Many of the physical quantities of interest in the present work, such as electric field, are vectors. Throughout this dissertation, vectors are denoted in equations as italic characters with superscript arrows, $\mathbf{E}$, and in the text as boldface characters, $\mathbf{E}$.


Chapter 2. Literature Review

This chapter reviews previous publications in the scientific literature relevant to the present research and consists of three main sections. In Section 2.1 presents introductory comments on the role of radiation scattering in materials science. Section 2.2 reviews previous studies of electromagnetic radiation scattering by complex microstructures. Section 2.3 reviews the mathematical basis for electromagnetic radiation scattering (Maxwell’s equations), followed by description of diverse analytical and numerical approaches to computing the scattering properties of microstructures.

2.1 Electromagnetic Radiation Scattering in Materials Science

Electromagnetic radiation scattering plays a critical role in materials science. Scattering measurements are widely used to gain information about the microstructures of systems. For example, x-ray diffraction and scattering are widely used as a means to gain statistical information about the arrangement of scattering features within a system.¹ In addition, visible light scattering is an important experimental tool for determining the distribution of particle sizes in a sample.²

The scattering properties of a materials system is often a key design consideration facing its developers. For example, the scattering efficiency of particles in a pigmented film are affected dramatically by the ability of the formulator to control particle size and dispersion quality. Likewise, surface roughness affects the optical appearance, and therefore the aesthetic appeal, of commercial engineering polymers. In these examples, the formulation of a materials system requires microstructural control
to impart the desired light scattering properties. This ability to impart the desired optical properties requires understanding of how systematic changes to a microstructure affect its radiation scattering properties.

The questions of a) how measurement of radiation scattering properties can be used to gain microstructural information and b) how microstructure affects radiation scattering properties are two sides of the same coin. The former is the “hard” or “inverse” problem; the radiation scattering properties of a particular microstructure are uniquely determined for any wavelength. The latter is the “simple” or “forward” problem; it requires the application of models to recover imputed microstructures from convoluted data. In the present research, the latter question is of primary interest: determination of the radiation scattering properties of complex microstructures. By improving the existing understanding of how complex microstructures scatter radiation, the dual challenges of building desired optical properties into microstructures and determination of microstructure from scattering data are simultaneously diminished.

2.2 Light Scattering Properties of Complex Microstructures

2.2.1 Light Scattering by White Pigment Particles

White pigments form one of the most widely used classes of optical materials, the most important of which is titania. Annual worldwide sales of titania total ~10 billion pounds. Titania pigment is used as an opacifying agent in paint films, plastics, and paper. Titania is non-toxic, inexpensive, and its stoichiometric phases are virtually non-absorbing in the visible spectrum. These characteristics, combined with the high
refractive indices of both the rutile and anatase titania phases in the visible, have contributed to its universal acceptance in the marketplace.\textsuperscript{3,4} The prediction and optimization of the optical performance of titania in end-use applications has been an active area of research for decades. In 1993, Fields, et al., presented a set of experimental data and approximate modeling which suggest that the scattering efficiency of commercial rutile titania grades could be improved by as much as 20% by controlling the particle size distribution and minimizing particle agglomeration.\textsuperscript{5}

Titania occurs in three distinct, naturally occurring polymorphs: rutile, anatase, and brookite. Of these, both rutile and anatase are commonly manufactured for use as a white pigment. Both phases exhibit tetragonal crystal structures,\textsuperscript{6} with a single optic axis (parallel to the $c$-axis). Both crystals therefore exhibit two different refractive indices at a given wavelength: the ordinary $n_o$ (for radiation polarized perpendicular to the $c$-axis) and the extraordinary $n_e$ (for radiation polarized parallel to the $c$-axis). The electronic and optical properties of rutile titania in and surrounding the visible spectrum have been studied both experimentally\textsuperscript{7,8} and theoretically.\textsuperscript{9,10,11,12} The optical properties of rutile over a wide range of wavelengths from multiple investigators have been compiled by Ribarsky.\textsuperscript{13} The ordinary and extraordinary refractive indices of rutile are plotted versus wavelength in Figure 2 over the range 400-700 nm. Experimental investigations of anatase\textsuperscript{14,15} have been comparatively limited, apparently due to the relative scarcity of large, defect-free single crystals.\textsuperscript{14} As in the case of rutile, the electronic and optical properties of anatase have been studied theoretically.\textsuperscript{11} Rutile titania exhibits both higher ordinary and extraordinary refractive indices throughout the
visible spectrum and therefore is superior to anatase in its light scattering performance as a white pigment, with particle size optimized. At the light wavelength 560 nm, the center of the visible spectrum, the ordinary and extraordinary refractive indices of rutile titania are 2.64 and 2.94, respectively. At this same wavelength, the ordinary and extraordinary refractive indices of anatase titania are 2.58 and 2.50, respectively.

![Figure 2. The ordinary (lower, dashed curve) and extraordinary (upper, dotted curve) refractive indices of rutile titania versus light wavelength. These data were compiled from multiple sources by Ribarsky.](image)

2.2.1.1 Application of Mie Theory to Optically Anisotropic Materials

All previous computational investigations of the light scattering properties of rutile titania have been based upon Mie theory (Section 2.3.2), which is limited to the case of an isolated, optically isotropic sphere. This restriction presents the difficulty of how to address the optical anisotropy of rutile titania using a model which presumes isotropic materials. Two different approximations have been used. In the first, which is
termed the average index approximation, the refractive indices encountered by light polarized parallel to each of the three principal axes \((a, b, \text{ and } c)\) of the rutile titania crystal are averaged. This average refractive index \(n_{\text{ave}}\) is then used in Mie theory calculations. Since the ordinary refractive index \(n_o\) is encountered by light polarized parallel to both \(a\) and \(b\) and the extraordinary refractive index \(n_e\) is encountered by light polarized parallel to \(c\) only, the expression for \(n_{\text{ave}}\) is:

\[
\text{Equation 1} \quad n_{\text{ave}} = \frac{2n_o + n_e}{3}
\]

In the second approximation, which is termed the weighted sum approximation, the scattering properties of a rutile titania sphere are computed using the ordinary and extraordinary refractive index separately. The two results are then summed together in a weighted fashion. Since the ordinary refractive index \(n_o\) is encountered by light polarized parallel to both \(a\) and \(b\) and the extraordinary refractive index \(n_e\) is encountered by light polarized parallel to \(c\) only, this weighted sum consists of two-thirds the result for the ordinary refractive index plus one-third the result for the extraordinary refractive index. The weighted sum approximation was used in the work of Ross.\(^{17}\) The average index approach has been used by Palmer, et al.,\(^ {18}\) who suggest that this method is as equally justifiable as the weighted sum approximation for titania sphere diameters near that (~0.2 \(\mu m\)) which produces optimal scattering of green light.

2.2.1.2 Kubelka-Munk Analysis of Paint Film Scattering Efficiencies

Experimental characterization of the performance of white pigments in a paint film is typically based upon reflectance measurements. The resulting data are then
analyzed using the Kubelka-Munk theory,\textsuperscript{19,20,21} an approximate multiple scattering theory which presumes only two fluxes of light. These fluxes propagate in directions normal to the film surface: one upward toward the film surface and one downward toward the substrate. Kubelka-Munk analysis of scattering by a film yields two parameters: the scattering coefficient $S^*$ and the absorption coefficient $K^*$,\textsuperscript{a} both are expressed in units of inverse length. The reciprocals of these quantities have units of length and can be interpreted as mean free path lengths between scattering or absorption events. In white paint films with no colorants present, $K^*$ is very close to zero, and only $S^*$ is considered. The Kubelka-Munk scattering coefficient can be expressed either on a particle basis, $S^*_{\text{particle}}$, or on a film basis, $S^*_{\text{film}}$. The latter is obtained by multiplying the former by the volume fraction $\phi$ of white pigment in the film:

\begin{equation}
S^*_{\text{film}} = S^*_{\text{particle}} \phi
\end{equation}

The quantity $S^*_{\text{film}}$ depends upon the concentration of pigment in a film and is therefore an extensive quantity; in the limit of low pigment concentrations in the film, it is directly proportional to pigment concentration. The quantity $S^*_{\text{particle}}$, on the other hand, is the scattering efficiency of the white pigment itself; in the limit of low pigment

\textsuperscript{a} It is not standard practice in the literature to denote the Kubelka-Munk coefficients with an asterisk. This notation has been adopted here to differentiate these experimentally determined scattering coefficients from the computed coefficients $S$ and $\sigma$ used in the present research. This conflict arises from different usage of the symbol $S$ by different researchers. In the present work, the experimentally determined $S^*$ is directly proportional to $\sigma$.\textsuperscript{a}
concentrations in the film, it is independent of pigment concentration. The normalization of results on a particle volume basis therefore facilitates comparison of pigments in different paint formulations by placing the scattering coefficient $S^*$ on an intensive rather than extensive basis. For this reason, experimentally determined scattering efficiencies are presented on a particle basis throughout the present chapter.

2.2.1.3 Computational Modeling of Scattering by White Pigments: Previous Studies

Mie theory computations were used by Ross\textsuperscript{17} in 1971 to investigate the theoretically maximum scattering efficiency of rutile titania in paint films, work which included comparison to the scattering efficiency of air voids in paint films. The computations for rutile titania were based upon the weighted sum approximation for a sphere embedded in a resin having the refractive index of a typical acrylic resin. Ross then applied corrections for surface reflections by a paint film on a substrate of arbitrary reflectance to the Mie theory results so that they could be compared directly with scattering coefficients derived from experiment. These experimentally determined scattering coefficients were derived from the Kubelka-Munk theory. Mie theory is a single scattering approach and does not include the effects of near-field optical interactions between neighboring particles in a paint film. It has therefore been widely suggested that Mie theory results can be realistically related only to paint films containing less than 5-10% titania by volume. The computations performed by Ross showed that the maximum scattering coefficient for rutile titania occurs at a diameter 0.20 µm for 560-nm illuminating light. Ross concludes that actual pigmented films
exhibit scattering efficiencies about 40% less than that associated with the optimal rutile sphere. In addition, his results show that the light scattering by the optimal spherical air void is only 12% that of the optimal rutile titania sphere.

In 1989, Palmer, et al., used Mie theory to compute the optical performance of rutile titania spheres compared to different coated particle architectures. The average index approximation was used to address the optical anisotropy of rutile. Palmer, et al., performed spectral computations which allowed them to calculate light scattering properties of a sphere for both tungsten light and sunlight and to correct for the response of the human eye. In some of the computations, they applied the Kubelka-Munk multiple scattering theory to estimate the films thickness required for complete opacity of a film over a black substrate. Their computations yield the result that 0.22 µm is the optimal sphere diameter for rutile titania, in close agreement with the value cited by Ross. In addition, Palmer, et al., investigated the light scattering properties of coated spheres consisting of hollow titania, air-encapsulated titania, titania-coated quartz, and quartz-coated titania. They conclude that optimized rutile titania is superior to the optimized form of each of these coated architectures.

In 1993, Hsu, et al., proposed the use of titania-coated silica to achieve opacity in paper systems, claiming scattering efficiency comparable to rutile titania. These claims, which contradict the conclusions of Palmer, et al., were substantiated by Hsu, et al., in part using Mie theory calculations on coated particles. In that same year, a United States Patent was issued to these authors covering a range of coated compositions. Additionally, an international patent application was filed in 1994 by a
separate group of inventors covering compositions of coated titania. The application of Mie theory to compute the light scattering efficiency of these coated particles is performed in detail in Chapter 5.

2.2.2 Light Scattering by Concentrated Particle Dispersions

2.2.2.1 The Crowding Effect in Paint Films

The near-field optical interactions which occur between neighboring particles in a concentrated dispersion can result in very different scattering properties compared to the superimposed properties of the isolated, individual particles. In paint films, the crowding effect manifests itself as a dramatic decrease in scattering efficiency on a volume-normalized basis as the pigment volume concentration (PVC) increases above 5-10%. At low PVC, interparticle spacings are sufficiently large that near-field interactions are very weak. A plot of the volume-normalized scattering coefficient $S^*$ for rutile titania pigment in a typical paint formulation is shown in Figure 3; the scattering coefficient at 35% PVC is only 40% compared to that of the formulation of lowest PVC. An intuitive explanation for the crowding effect is that closely neighboring particles in a film shadow each other from the incident light, resulting in reduced scattering efficiency. An additional consideration is that the scattering cross sections of optimized pigment particles are several times greater than their geometric cross sections, meaning that the effective scattering diameters of the particles can overlap without the particles actually touching.
In 1961, Bruehlman, et al., measured the magnitude of the crowding effect in a series of designed experiments in which both the particle size distribution of the pigments and the refractive index of the alkyd dispersing media were systematically varied.\textsuperscript{26} They conclude that the optimal size of titanium dioxide particles is a function of PVC, with smaller particle sizes favored at low (0−10\%) PVC and larger particle sizes favored at high (>10\%) PVC. This conclusion is one which cannot be justified using, say, Mie theory, since the conditions of single scattering are not satisfied in concentrated paint films.

In 1974, Tunstall and Hird measured the crowding effect in an alkyd paint system and concluded that the loss in particle scattering efficiency associated with the crowding effect is determined both by particle size and pigment volume concentration. They developed a simple physical model based upon single scattering theory in which the loss of scattering efficiency is determined by the surface-to-surface separation of particles in a film measured in units of light wavelength. The resulting equation fits their data successfully except at low PVC. This equation is of the form

\begin{equation}
S^* = 1 - \frac{K}{\phi} \exp \left[ -\frac{Zd}{\lambda} \left( \sqrt[3]{\frac{X}{\phi}} - 1 \right) \right]
\end{equation}

where $S^*$ is the volume-normalized particle scattering coefficient, $K$ and $Z$ are constants, $\phi$ is the pigment volume fraction, $d$ is the particle diameter, $\lambda$ is the light wavelength, and $X$ is the maximum packing fraction of the pigment in the medium. The second term in the exponential is proportional to the surface-to-surface spacing of particles and is equal to zero when $\phi = X$. According to Equation 3, $S^*$ is unity when $\phi$
18

= 0 and less than unity when \( \phi = X \). Stieg had earlier observed that the scattering coefficient of a pigment is proportional to the surface-to-surface particle spacing divided by the center-to-center spacing,\(^{27}\) which is to say:

**Equation 4** \[ S^* \propto 1 - \frac{1}{D} \]

where \( D \) is the normalized distance between centers of neighboring particles in particle diameters. The expression for \( D \) in terms of the maximum packing fraction and PVC is:

**Equation 5** \[ D = \frac{X}{\sqrt{\phi}} \]

Stieg’s expression for the scattering efficiency of the particles in a film is therefore of the form:

**Equation 6** \[ S^* = K \left( 1 - \frac{1}{\sqrt{\frac{\phi}{X}}} \right) \]

where \( K \) is a constant. Strictly speaking, this equation incorrectly implies that the scattering coefficient equals zero if \( X = \phi \), when in fact any interstitial resin between the pigment particles under this condition would produce some light scattering. Air voids form as \( \phi \) approaches \( X \) in a paint film, and the introduction of this new source of light scattering is not explicitly accounted for in these models of crowding behavior. It must be recognized, therefore, that Equation 6 is applicable only in the range where \( \phi \) does not approach \( X \). A second problem with Stieg’s model, observed by Fitzwater and Hook, is that values of \( \phi \) exceeding unity are sometimes required to fit data, which is physically unreasonable.\(^{28}\)
In 1985, Fitzwater and Hook applied an analytical approach to the crowding effect between spherical particles using Mie theory. Their approach is based upon partial wave analysis of light scattering by a spherical particle. The scattered field from a particle at steady state can be described as a series summation of partial waves, each with a definite location in space (unlike the total scattered wave). Partial waves with low index are located near the particle center, and waves with high index are located far from the center. Only the first few partial waves are required for an accurate solution; higher index waves can be discarded, resulting in a finite series summation. Through analysis of the amplitudes and locations of the scattered partial waves, it can be determined what fraction of the scattered field lies outside the physical diameter of the particle. This allows an estimate of the amount of scattered light “shared” between neighboring particles having a known separation distance and, by extension, an estimate of the reduced scattering efficiency of the particles. Fitzwater and Hook compute the crowding effect for both rutile titania in paint and latex in water. The agreement between their predictions and experiment is qualitatively good, reproducing the major features in the experimental data. Their model is approximate not only because of the assumptions about the effective scattering diameter, but also due to its limitation to spherical particles and a monodisperse particle size distribution. The Fitzwater-Hook model predicts that the scattering efficiency losses due to the crowding effect are less severe for larger particles than smaller particles. This is because the scattered partial waves are more completely contained within the physical diameters of larger particles than of smaller particles. This prediction is in agreement with the experimental
observations of Bruehlman, et al., cited above. Based upon their model, Fitzwater and Hook propose a modified version of Stieg’s model of crowding (Equation 6), incorporating an additional constant $m$:

$$\text{Equation 7} \quad S^* = K \left(1 - \frac{m^3 \phi}{X}\right)$$

The addition of this constant eliminates the problem in Stieg’s model of packing fractions exceeding unity.

Proposed approaches to reducing the crowding effect in paints have centered upon optimizing pigment particle dispersion (that is, maximizing the average distance between particles in a film). Stieg has emphasized the importance of using large (several micron) particles of inexpensive material to reduce the demand for binder at a given PVC, thus providing more free binder for the pigment particles to occupy.\textsuperscript{29} Inexpensive filler materials are referred to in the paint industry as extenders; the volume they contribute to a film is considered in computing PVC. Braun, on the other hand, has suggested that the use of very small (sub-micron) extender particles could provide effective spacing of titania pigment particles by occupying interstitial volume between neighboring pigment particles.\textsuperscript{25} Acknowledging that such an approach creates the problem of higher specific surface areas of the particles within a film, Braun suggests that the use of thick coatings on titania pigment particles is a viable approach to enforce separation between neighboring particles in a film.
2.2.2.2 Light Scattering in Stereolithography

This discussion of light scattering by concentrated particle dispersions has focused entirely upon pigmented paint films; it is in this field where the most extensive characterization of the optics of concentrated dispersions has occurred historically. Recently, there has been a rapid growth in interest in the behavior of concentrated ceramics dispersions in photopolymer solutions. In stereolithography, complex geometries are formed by ultraviolet laser exposure of a ceramic particle slurry in a photosensitive solution. Exposure by the laser causes the solution to polymerize, and the laser position is controlled very accurately by computer. Generation of three-dimensional shapes is possible since the laser scans with two degrees of freedom in the x-y plane and the slurry bath can be translated in the z direction. The geometry of a
stereolithography apparatus is shown in Figure 4. Once a three-dimensional geometry is formed, the part is fired to burn out the polymer and form a dense ceramic.

A critical issue in stereolithography is control of the exposure depth of the laser into the ceramic particle slurry; prediction of this depth requires an understanding of its dependence upon such factors as laser power, laser dose, laser wavelength, the refractive index of the ceramic particles, the volume concentration of ceramic particles, and ceramic particle size. The relationship between cure depth $D_c$ and the scattering coefficient $S^*$ of the particles (neglecting absorption) is:

$$D_c = \frac{1}{S^* \phi} \ln \left( \frac{E_0}{E_c} \right)$$

where $\phi$ is the volume fraction of particles, $E_0$ is the exposure energy of the laser at the surface of the suspension, and $E_c$ is the critical exposure energy required to polymerize the monomer solution. In 1997, Griffith and Halloran performed a series of model experiments using alumina and silica particles in UV curable solutions and proposed the following empirical form of the cure depth in concentrated dispersions:30

$$D_c = \frac{2d\lambda}{3s} \frac{n_0^2}{\Delta n^2} \ln \left( \frac{E_0}{E_c} \right)$$

where $d$ is the average particle diameter, $\lambda$ is the laser wavelength in the photopolymer medium, $s$ is the average surface-to-surface interparticle spacing in the medium, $n_0$ is the refractive index of the medium, and $\Delta n$ is the difference in refractive index between the particles and the medium. Equation 9, when written in the form used above in the case of paint films, is:
Equation 10 \[ S^* = \frac{K}{\phi} \sqrt[3]{\frac{X}{\phi}} \]

where \( K \) is a constant (containing \( \lambda, n_0 \) and \( \Delta n \)). Equation 10 exhibits the obvious problem of diverging to infinity as \( \phi \) approaches zero. While Equation 9 apparently provides a reasonable fit to the limited data of Griffith and Halloran, this relation cannot apply to systems exhibiting wide variations in the parameters contained in the expression.

Figure 4. Schematic diagram of a stereolithography apparatus for producing complex ceramic parts using rapid prototyping. (After Liao.31)

2.2.3 Light Scattering by Particle Agglomerates

2.2.3.1 Computational Approaches

During the past three decades, there has been considerable progress in the experimental and rigorous theoretical understanding of the light scattering behavior of
multiple-particle agglomerates or clusters. Spherical particles have been by far the most extensively investigated particle shape, owing to the availability of analytical expressions for radiation scattering by a single sphere from Mie theory. In this case, the light scattered by one sphere in the cluster is decomposed into a series expansion of outgoing spherical waves which, in turn, impinge upon the other spheres in the cluster. The field incident upon any sphere in the cluster is therefore a superposition of the total incident field and scattered fields from all of the other particles in the cluster. Coefficients coupling the multipole modes in one sphere to those in every other sphere in the system appear explicitly in the solution. Solution of the problem requires overcoming the challenge of representing the spherical waves about any sphere in the cluster as an expansion about any other arbitrary origin. The addition theorems for spherical vector wave functions in integral form which produce the required translation coefficients were established by Stein\textsuperscript{32} and Cruzen\textsuperscript{33} in the early 1960s. In 1971, Bruning and Lo published the first comprehensive solution for a two-sphere cluster.\textsuperscript{34,35} In 1988, the order-of-scattering approach was developed by Fuller and Kattawar, who extended Bruning and Lo’s solution to the case of larger clusters by considering pairwise interactions between the constituent spheres. In 1991, Mackowski\textsuperscript{36} developed a set of recurrence relations for the translation coefficients which provide a significantly more efficient computational approach than the integral forms. Borghese, et al., in 1984 were the first to produce expressions for the cross sections of multiple sphere clusters.\textsuperscript{37} In 1995, Xu derived expressions for both the scattering cross sections and the elements of the Mueller scattering matrix of multiple-sphere clusters.\textsuperscript{38} (The Mueller scattering
matrix describes changes in polarization of the incident light due to the scattering interaction.) In 1996, Mackowski and Mishchenko described a T-matrix approach to the problem of light scattering by sphere aggregates, facilitating computation of the scattering properties under conditions of random illumination. Fuller points out that the convergence rate of the solution for a multiple-sphere cluster depends upon the maximum spacing between a pair of spheres in the cluster, resulting from additional terms required to compute accurately the translation terms required to transform multipole coefficients from one sphere location in the cluster to another.

2.2.3.2 Computational Results for Particle Agglomerates

Computational results for multiple-sphere clusters have been limited, with most of the activity in the literature focusing upon the development of more computationally efficient methods as opposed to the application of those methods. Borghese, et al., present computed results on the scattering cross sections of two-sphere systems as a function of illumination direction and sphere separation distance. For even the largest sphere separation distances studied (200 sphere diameters), the scattering cross section of the two-sphere system failed to converge to the sum of the cross sections of the two independent spheres. The explanation for this observation is that the spheres studied in this work were very small compared to the radiation wavelength, corresponding to the Rayleigh scattering limit. While the maximum sphere separation distance studied was very large compared to the sphere diameter, this distance was smaller than the light wavelength, causing the two particles to behave like a single Rayleigh scatterer with twice the volume of the individual spheres. It can be stated, in general, that deviations
in the optical behavior of an ensemble of spheres from the behavior of the isolated
spheres as a function of interparticle separation (expressed in diameters of the spheres)
will be greatest for small particles. This is consistent with the experimental
observations of Bruehlman, et al.,\textsuperscript{26} and the predictions of Stieg\textsuperscript{27} and Fitzwater and
Hook\textsuperscript{28} for crowded paint systems. In their computations on touching, slightly
absorbing two-sphere clusters, Mishchenko, et al.,\textsuperscript{40} reported that two randomly
oriented spheres with diameters greater than one wavelength can become effectively
independent scatterers at surface-to-surface separations as small as one sphere diameter;
this is not the case for spheres with size smaller than the incident wavelength. Fuller\textsuperscript{39}
has observed that the scattering cross sections of two touching spheres which are each
large compared to the wavelength rapidly approach those of the independent spheres
with increasing separation, provided that one particle is not in the shadow of the other.
If shadowing effects are significant, Fuller reports that the cross sections may deviate
from those of the independent sphere by $5\text{--}10\%$ for separations as large as $25$
diameters.

Approximate methods which have been applied to the study of light scattering
by particle agglomerates include geometrical optics models (Section 2.3.3.2), which are
limited to the case where the primary particle size is substantially greater than the light
wavelength, and coupled-dipole models (Section 2.3.3.4), which are limited to the case
where the primary particles are substantially smaller than the light wavelength.
Geometrical optics models have been applied to the study of light scattering by ice
crystal agglomerates\textsuperscript{41} and fractal agglomerates of spheres.\textsuperscript{42} The coupled-dipole
method (Section 2.3.3.5) has been applied to the study of light scattering by fractal agglomerates.\(^\text{43}\)

### 2.3 Principles of Light Scattering

The phenomenon of electromagnetic radiation scattering is governed by Maxwell’s equations, a set of physical laws which provides a rigorous basis for the mathematical description of classical wave propagation. Their validity appears to be universal, applying to all interactions between electromagnetic energy and matter. The historic development of the physics underlying Maxwell’s equations can be found in virtually any elementary physics text. Maxwell’s equations are described in Section 2.3.1. Exact, analytical solutions to Maxwell’s equations for different scattering geometries are described in Section 2.3.2. Finally, a variety of approximate and numerical solutions of light scattering are described in Section 2.3.3.

#### 2.3.1 Maxwell’s Equations

Maxwell’s equations are two partial differential equations relating the five vector quantities \(\mathbf{B}, \mathbf{E}, \mathbf{D}, \mathbf{J},\) and \(\mathbf{H}\). These are magnetic induction, electric field intensity, electric displacement, current density, and magnetic field intensity, respectively. These two equations are:

**Equation 11** \[ \frac{\partial \mathbf{B}}{\partial t} = \nabla \times \mathbf{E} \]

**Equation 12** \[ \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} = \nabla \times \mathbf{H} \]
The set of three constitutive equations which interrelate these five vector quantities make this pair of differential equations determinate. The constitutive relations for isotropic materials are:

**Equation 13** \[ \vec{B} = \mu \vec{H} \]

**Equation 14** \[ \vec{D} = \varepsilon \vec{E} \]

**Equation 15** \[ \vec{J} = \sigma \vec{E} \]

where \( \mu \) is the magnetic permeability, \( \varepsilon \) is the dielectric permeability, and \( \sigma \) is conductivity. In the case of anisotropic materials, these three scalars are replaced by tensors. Substituting the constitutive relations into the partial differential equations in Equation 11 and Equation 12 and eliminating \( \vec{B} \), \( \vec{D} \), and \( \vec{J} \) yields the following determinate pair of Maxwell’s equations in \( \vec{E} \) and \( \vec{H} \):

**Equation 16** \[ -\mu \frac{\partial \vec{H}}{\partial t} = \nabla \times \vec{E} \]

**Equation 17** \[ \varepsilon \frac{\partial \vec{E}}{\partial t} + \sigma \vec{E} = \nabla \times \vec{H} \]

Eliminating \( \vec{H} \) between these two equations with the assumption that \( \mu \) is not a function of position (which is the case in non-magnetic materials) yields the second order partial differential equation in \( \vec{E} \):

**Equation 18** \[ \varepsilon \frac{\partial^2 \vec{E}}{\partial t^2} + \sigma \frac{\partial \vec{E}}{\partial t} + \frac{1}{\mu} \nabla \times \nabla \times \vec{E} \]

This equation is a point form of Maxwell’s equations, meaning that it is valid at a mathematical point in space, within an arbitrary material. It is the basis for time-
domain solutions to scattering problems using Maxwell’s equations. Below, in the
description of the finite element approach, this point form is elaborated into an integral
form which facilitates numerical solution of this equation throughout an extensive
three-dimensional volume.

In Equation 16 and Equation 17, the time dependence of electric field is
expressed explicitly. In general, the steady-state radiation scattering properties of a
body are of interest; only in cases with time-varying materials properties or fields are
variations in scattering properties of direct interest. It is therefore useful to express the
time dependence of Maxwell’s equations implicitly rather than explicitly. To
accomplish this, electric and magnetic field are represented as phasors. In the case of
electric field, for example, this representation has the form:

\[
\mathbf{E}(x, y, z, t) = \text{Re}\{\mathbf{E}(x, y, z) e^{i\omega t}\}
\]

where \(\omega\) is the angular frequency of the propagating electromagnetic wave. Equation
18 can therefore be rewritten as:

\[
-\varepsilon \omega^2 \mathbf{E} + i \omega \sigma \mathbf{E} = -\frac{1}{\mu} \nabla \times \nabla \times \mathbf{E}.
\]

The vector identity:

\[
\nabla \times \nabla \times \mathbf{E} = \nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E}
\]

in conjunction with the fact that, with no free charges present,

\[
\nabla \cdot \mathbf{E} = 0
\]

can be used to rewrite Equation 20 as:
Equation 23 \[ -\varepsilon \omega^2 \vec{E} + i \omega \sigma \vec{E} = \frac{1}{\mu} \nabla^2 \vec{E}. \]

This is the Helmholtz equation for electric field expressed implicitly with respect to time. This equation is the starting point for frequency-domain solutions to scattering problems using Maxwell’s equations.

2.3.2 Exact, Analytical Solutions of Light Scattering

Of interest in this dissertation is the study of light scattering by complex materials microstructures, with most of this work focusing upon the light scattering behavior of systems containing complex single scattering features or multiple features which exhibit near-field optical interactions. Even in ensembles of multiple scattering features where the assumption of single scattering is violated, the scattering properties of single particles remain the starting point for analysis. The subject of single scattering has therefore received a great deal of attention, with comprehensive surveys presented by Bohren and Huffman,\textsuperscript{1} van de Hulst,\textsuperscript{2} and Kerker.\textsuperscript{44}

The development of exact, analytical solutions to Maxwell’s equations for electromagnetic radiation scattering by isolated, three-dimensional bodies is possible in cases where the surfaces of these bodies correspond to coordinate surfaces of coordinate systems in which the solution to the scalar wave equation:

Equation 24 \[ \nabla^2 \psi + k^2 \psi = 0 \]

is separable. This has been accomplished in the cases of an infinite circular right cylinder,\textsuperscript{45,46} an infinite elliptical right cylinder,\textsuperscript{47} a sphere,\textsuperscript{48} and an ellipsoid.\textsuperscript{49,50,51}
The solutions for infinite cylinders are of interest in the case of fibers which are very long compared to their radii. The solution for the case of a sphere is the well-known Mie theory, named for the German scientist Gustav Mie who presented this solution to Maxwell’s equations in 1908. Mie theory figures centrally in the problem of radiation scattering by any isolated particle which can be reasonably approximated as a sphere and has therefore been widely applied in diverse fields where scattering by particles is of interest. Owing to its importance, a survey of this theory is presented below. Solutions for the case of an ellipsoid involve computational effort which is far more intensive than that required for a sphere, compounded by the necessity of averaging over all orientations of the particle relative to the incident radiation, and application of these solutions has therefore not become commonplace. It should be noted that separation of variables can also be applied to systems in which the optical properties vary with diameter. This has been accomplished for the case of a sphere and an infinite right cylinder. In this way, systems with coatings or radial segregation of materials can be rigorously treated.

Clear and detailed developments of the mathematical treatments underlying Mie theory are presented by Bohren and Huffman, van de Hulst, and Kerker. Given an isotropic, spherical particle of arbitrary radius and optical properties illuminated by electromagnetic radiation of arbitrary wavelength, of interest are the scattered fields from this particle at far field (i.e., at a position located many wavelengths away from the particle). The relationship between the electric field vectors associated with the incident \((E_i)\) and scattered \((E_s)\) electromagnetic waves is required. The first step in this
development is to identify a pair of vector harmonics, both of which satisfy the vector wave equation, generated from the scalar function $\psi$ in Equation 24. These vector harmonics $\textbf{M}$ and $\textbf{N}$ are of the form:

\begin{align*}
\textbf{M} &= \nabla \times (r\psi) \\
\textbf{N} &= \frac{\nabla \times (M)}{k}
\end{align*}

where $\textbf{r}$ is an arbitrary constant vector. As required for an electromagnetic field, both $\textbf{M}$ and $\textbf{N}$ are divergence-free and satisfy the vector wave equation:

\begin{equation}
\nabla^2 \textbf{A} + k^2 \textbf{A} = 0,
\end{equation}

provided $\psi$ is a solution to the scalar wave equation. The scalar wave equation can be rewritten in spherical coordinates and $\psi$ represented as the product of three functions, each a function of just one of the spherical coordinate system variables $r$, $\phi$, and $\theta$. This accomplished, the vector spherical harmonics $\textbf{M}$ and $\textbf{N}$ are generated from $\psi$. The next step is to represent the incident plane wave as an infinite series with the vector spherical harmonics as basis functions. Finally, by imposing boundary conditions dictated by Maxwell’s equations for the tangential components of electric and magnetic field at the surface of the sphere, the incident and scattered fields outside the sphere can be related in a series expansion employing a pair of determinate scattering coefficients $a_n$ and $b_n$. The forms of these scattering coefficients and the implementation of Mie theory in computer code are described in Chapter 3.
2.3.3 Approximate and Numerical Solutions of Light Scattering

It is often true that the geometries of scattering features whose electromagnetic radiation scattering properties are of interest do not conform to the geometric limitations imposed by the exact analytical solutions produced by the separation of variables. For such cases, which may involve irregular particle shapes or dependent scattering effects, a host of approximate analytical and numerical approaches have been developed to determine the radiation scattering properties of the system. Rayleigh scattering theory and geometrical optics are approximate analytical approaches introduced in Chapter 1 which produce simple expressions for the distribution of scattered light and the scattering efficiency terms. The remainder of the techniques discussed below are numerical approaches which in general require substantial computational resources.

2.3.3.1 Rayleigh Theory

In the case where the wavelength of electromagnetic radiation interacting with a particle is much greater than the particle diameter, the incident electric field can be reasonably approximated as constant throughout the volume of the particle. The solution of scattering problems under this approximation is termed Rayleigh theory.\textsuperscript{58} In Rayleigh theory, the particle is presumed to respond to the applied, time-varying electric field of the radiation as an oscillating dipole which radiates scattered fields in all directions. The induced dipole moment of the particle is a vector quantity proportional to the applied electric field through the polarizability $\alpha$, a tensor. With the induced dipole moment known, it is straightforward to compute the resulting electric
field at an arbitrary point outside the particle. The induced dipole moment has been
determined analytically for a sphere, a coated sphere,\textsuperscript{2} an ellipsoid,\textsuperscript{59} and a coated
ellipsoid.\textsuperscript{1} In addition, anisotropic polarizability can be incorporated into each of these
particle geometries.\textsuperscript{60} The polarizability of a material is often isotropic, in which case it
can be treated as a scalar. The angular intensity distribution of scattered light for
unpolarized incident radiation is then given by:

\textbf{Equation 28} \quad I = \frac{(1 + \cos^2 \theta) k^4 \alpha^2}{2r^2} I_0

where \( \theta \) is the scattering angle, \( r \) is the distance of the observation point from the
particle, \( I_0 \) is the incident intensity, and

\textbf{Equation 29} \quad k = \frac{2\pi n_{med}}{\lambda_0}

where \( n_{med} \) is the refractive index of the surrounding medium and \( \lambda_0 \) is the wavelength
of the incident wavelength in vacuum.

The most fundamental far-field scattering property is the scattering cross
section, defined as the ratio of scattered power to the incident radiation intensity and
expressed in units of area. The scattering cross section of a sphere in the Rayleigh
approximation is given by:

\textbf{Equation 30} \quad C_{sca} = \frac{8\pi \alpha^2}{3} x^4 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2
where $a$ is the particle radius, $m$ is the relative refractive index of the particle (particle refractive index divided by that of the surrounding medium) and $x$ is the unitless size parameter:

$$\text{Equation 31} \quad x = ka.$$

For fixed particle radius in the Rayleigh regime and with the assumption that $m$ is independent of wavelength, Equation 30 can be used to explain at least partially the bluish color of the daytime sky, since scattering cross sections associated with shorter wavelengths (e.g., blue light) exhibit are greater by a factor $(\lambda_{\text{long}}/\lambda_{\text{short}})^4$ than scattering cross sections longer wavelengths (e.g., red light).

The qualitative criterion for validity of the Rayleigh approximation is:

$$\text{Equation 32} \quad |m|x \ll 1.$$

The appearance of both $m$ and $x$ in the validity criterion above arises because even in the case of a particle which is small compared to the radiation wavelength in the medium surrounding outside the particle, the compressed wavelength of the radiation inside the particle could be sufficiently short compared to the particle diameter to excite, say, quadrapole radiation in addition to the dipole radiation solely assumed in the Rayleigh approximation.

2.3.3.2 Geometrical Optics

In the case where the size of a particle is very large compared to the radiation wavelength, the incident wavefront encountering the particle can be approximated as a group of independent rays. In the \underline{geometrical optics} approximation, the incident
wavefront is divided into rays which encounter the particle directly and rays which pass along its surface. The scattering problem is treated as a separable combination of reflection, refraction, and diffraction. The reflected and refracted rays conform to the laws of Fresnel and Snell, which determine the fraction of light reflected, refracted, and transmitted at each boundary of the particle, as depicted in Figure 5. These events depend intimately upon both the geometry and optical properties of the scattering particle. In the case of irregularly shaped particles, the computational requirements for geometrical optics can be intensive. The method is best suited to convex and highly reflective scattering features; the multiple scattering of rays which can occur in the cases of concave and transparent particles presents computational difficulties. Those incident rays which pass along the surface of the particle undergo Fraunhofer diffraction. The Fraunhofer diffraction pattern is intense and strongly forward-directed. This pattern depends only upon the size and shape of the particle and is independent of the optical properties of the particle. This non-intuitive fact is based in Babinet’s principle (1837), which states that the diffraction created by a large particle with arbitrary optical properties is identical to that created by a hole of the same size cut from a perfectly opaque screen. The diffracted energy is therefore equal to the sum of the reflected and refracted energies, and it is for this reason that the scattering cross-section of any particle in the geometrical optics limit is equal to exactly twice its geometric cross-section.

The light intensity at any observation point is determined in the geometrical optics approximation by summing the ray contributions from different regions of the
particle (or ensemble of multiple particles). If the incident wavefront is coherent, the scattered rays have a regular phase relationship and amplitudes are summed at the observation point rather than intensities. In the case of ensembles of multiple particles having a range of particle sizes, phase relationships can be neglected and intensities of scattered rays are added at the observation point rather than amplitudes.

The qualitative validity criterion for geometrical optics is that the particle size be much greater than the radiation wavelength:

$$x >> 1.$$ 

On a more precise footing, van de Hulst estimates that geometrical optics is valid for particles which are at least 20 wavelengths in extent.\(^2\) For particles smaller than this, it is difficult to distinguish between rays which are incident upon the particle and those which pass along its surface. This estimate is in agreement with results comparing the light scattering properties of hexagonal ice crystals using geometrical optics and a finite difference time-domain method, for which close agreement is claimed for \(x > 20\).\(^6^5\)
2.3.3.3 Point Matching

The point matching method\textsuperscript{66,67} can be used to determine the radiation scattering properties of non-spherical particles of arbitrary size whose shapes are approximately spherical. In this method, fields inside and outside the particle are expanded in a truncated series of vector spherical harmonics and the boundary condition requiring that tangential field components be continuous at the sphere surface is imposed at a number of points on the surface. This number of points corresponding to the number of unknowns in the series expansions, resulting in a set of simultaneous linear equations. This method is conceptually simple but suffers from uncertain convergence and its limitation to nearly spherical particles.\textsuperscript{63}

2.3.3.4 Perturbation Methods

Perturbation methods,\textsuperscript{68,69,70,71} like the point matching method, attempt to determine the radiation scattering properties of particles which deviate from a shape whose scattering properties are known analytically. The shape of any particle can, in principle, be viewed as a sphere with a perturbed shape. Perturbation methods represent the scattering properties of the geometrically perturbed particle as an infinite series in some perturbation parameter of which the results of Mie theory form the first term. These methods suffer from the same problem of uncertain convergence as the point matching method, and the computation of a prohibitive number of terms may be required before the infinite series may be truncated without appreciable error. It
appears that perturbation methods, like the point matching method, are limited to nearly spherical particles.

### 2.3.3.5 Coupled-Dipole Method

A scattering object can be approximated as a collection of radiating electric dipoles which are excited by both the incident electromagnetic radiation and each other. This is the principle of the coupled-dipole, or discrete-dipole, method. This method was first developed by DeVoe in 1964 and applied to scattering by molecular aggregates very small compared to the radiation wavelength.\textsuperscript{72,73} The method was generalized to arbitrary size parameters by Purcell and Pennypacker in 1973, who included retardation effects and applied the method to determine the scattering properties of interstellar dust;\textsuperscript{74} the coupled-dipole method is sometimes still referred to as the Purcell-Pennypacker method. This method has the advantage of ready applicability to arbitrary geometries without restriction to nearly spherical shapes. In addition, since the polarizability of a material is a tensor, the coupled dipole method can be used to compute the scattering properties of anisotropic materials.\textsuperscript{75} Its accuracy is limited in principle only by the density of the electric dipole array, which is in turn limited only by the availability of computational resources.

A critical feature of the coupled-dipole method is the function chosen to relate the polarizability $\alpha_j$ of the discrete dipoles to the dielectric properties of the bulk material being represented. The Clausius-Mossotti relation provides an exact function
for the particular case of an infinite cubic lattice of dipoles in the dc limit, where the size of the dipoles divided by the radiation wavelength approaches zero:  

\[ \alpha^{CM} = \frac{3(\varepsilon - \varepsilon_{med})}{n(\varepsilon + 2\varepsilon_{med})} \]

where \( \varepsilon \) is the dielectric function of the scattering material, \( \varepsilon_{med} \) is the dielectric function of the surrounding medium, and \( n \) is the number of discrete dipoles per unit volume.

Numerous schemes for modifying the Clausius-Mossotti relation have been proposed to improve the accuracy the coupled-dipole method for realistic, finite-sized scattering geometries by adding a term on the order of \((kd^2)^{77,78}\) or \((kd^3)^{77,79}\) where \( k = \frac{2\pi n_{med}}{\lambda_0} \) and \( d \) is the interdipole spacing. Recently, Draine and Goodman\(^8^0\) developed an expression for polarizability of an infinite array of polarizable points so that the array exhibits the same dispersion relation as a continuum with dielectric constant \( \varepsilon \). Draine and Flatau\(^8^1\) claimed in 1994 that this representation yields the best accuracy to date of these expressions for dipole polarizability.

The coupled-dipole method features a square matrix with edge length equal to the number \( N \) of discrete dipoles in the scattering geometry being represented. This \( NxN \) matrix expresses the influence of each of the separate dipoles upon each other. The computational memory required for this method increases as \((N^3)^{8^1}\) placing a limit on the number of dipoles which can be used to represent a scattering geometry and, therefore, upon the accuracy of the method.
2.3.3.6 T-Matrix or Extended Boundary Condition Method

Starting with an integral equation formulation of the scattering problem, the T-matrix or Extended Boundary Condition Method is a promising technique which can be used to determine the scattering properties of arbitrarily shaped particles. First proposed by Waterman in 1965 for the special case of perfectly conducting particles, it has continued to be refined and has since been extended to general dielectric particles, including finite cylinders, homogeneous ellipsoids, coated ellipsoids, and clusters of dielectric spheres.

Following here a conceptual development of the T-matrix formulation set forth by Barber and Yeh, the method embodies a series of intuitive steps relying upon the equivalence theorem, which states that the field scattered by a particle can be considered the product of initially unknown electric and magnetic surface currents acting on the surface of the body. The T-matrix approach ultimately defines the fields internal to the scattering object in terms of the incident field, then the surface currents in terms of the internal fields, and finally the scattered field in terms of the surface currents. The incident, internal, and scattered fields are expanded in a series of vector spherical harmonics with $f$ and $g$ the unknown coefficients of the scattered field. The result after applying boundary conditions is the linear transition or T-matrix, which relates the coefficients of the scattered field to the known coefficients $a$ and $b$ of the incident field:

\[
\begin{bmatrix}
  f \\
  g
\end{bmatrix} = T \begin{bmatrix}
  a \\
  b
\end{bmatrix}
\]

\[\text{Equation 34}\]
The elements of the T-matrix are integrals over the surface of the particle which depend only upon the size, shape and optical properties of the particle. These surface integral reduce to line integrals for axisymmetric particles, which is why the T-matrix has been applied almost exclusively to such particles.\textsuperscript{92} Computationally, application of the T-matrix method involves linear algebra operations, either matrix inversion or iterative schemes.\textsuperscript{88} One advantage of the T-matrix approach is that, once the T matrix is computed for a particle, it is simple to compute results for arbitrary orientations of that particle relative to the incident fields. While the T-matrix method can be used to compute the scattering properties of large volumes, computational requirements increase dramatically with size parameter and deviation from rotational symmetry.\textsuperscript{86,93} In addition, numerical instability can arise in T-matrix computations on these lower-symmetry particles.\textsuperscript{91}

\textbf{2.3.3.7 Method of Moments}

Method of moments techniques embody a number of specific methods, each based upon the solution of an integral form of Maxwell’s equations. The method of moments was first implemented for Maxwell’s equations by Harrington in 1968.\textsuperscript{94} Both surface and volume integration approaches have been described. Like the coupled-dipole method, the method of moments is applicable to highly irregularly shaped objects. Method of moments techniques are well-suited to conductive materials and homogeneous dielectrics, but the implementation becomes cumbersome for inhomogeneous bodies and dielectric bodies of large volume.\textsuperscript{63} The method of
moments leads to fully populated matrices and therefore the computer memory required increases rapidly with increasing object size.

In the surface integral formulation of the moment of methods, as in the T-matrix method, the problem of radiation scattering by an arbitrary body is recast using the equivalence principle into unknown electric and magnetic surface currents \( \mathbf{J} \) and \( \mathbf{M} \) acting on the body to create the total \( \mathbf{E} \) and \( \mathbf{H} \) fields both inside and outside the body. Electromagnetic boundary conditions are imposed at the surface of the body to relate the fields inside and outside the body. Following the notation of Medgyesi-Mitschang, et al., these equivalent surface currents appear in the form of a coupled pair of integral equations which have the form:

**Equation 35**

\[
\begin{align*}
\left. \bar{E}^{\text{inc}}(\mathbf{r}) \right|_{\text{tan}} &= (L_1 + L_2) \left. \bar{J}(\mathbf{r}) \right|_{\text{tan}} - (K_1 + K_2) \left. \bar{M}(\mathbf{r}) \right|_{\text{tan}} \\
\end{align*}
\]

**Equation 36**

\[
\begin{align*}
\left. \bar{H}^{\text{inc}}(\mathbf{r}) \right|_{\text{tan}} &= (K_1 + K_2) \left. \bar{J}(\mathbf{r}) \right|_{\text{tan}} + \left( \frac{1}{\eta_1} L_1 + \frac{1}{\eta_2} L_2 \right) \left. \bar{M}(\mathbf{r}) \right|_{\text{tan}} \\
\end{align*}
\]

where \( \mathbf{r} \) is the field point on the surface, \( L \) and \( K \) are known integral operators, the superscript \( \text{inc} \) indicates the incident field, and the subscripts 1 and 2 denote regions outside and inside the body, respectively. The equivalent currents on the surface of the body are expanded in a set of basis functions \( f_n \) spanning the surface and substituted into the pair of equations above. Next, the complex inner product is formed with these equations, transforming the integral operators \( L \) and \( K \) into matrix operators. In the Galerkin form of the method of moments solution, the complex conjugates of \( f_n \) are chosen as the testing functions on the surface, and the inner products are formed.
between the testing functions and the integral equations. The result is a set of linear equations which are solved to determine \( J \) and \( M \). In the determination of the scattering properties of an arbitrarily shaped body, the surface is represented as a mesh of, say, triangular elements, and \( J \) and \( M \) are expanded in terms of a testing function along each element edge.\(^96\)

A volume integral formulation of the method of moments described by Hage, et al., has been applied to inhomogeneous dielectric materials of irregular shape.\(^97\) In their approach, a solid of arbitrary shape is represented as a volumetric mesh of \( N \) cubic elements, with constant electric field assumed in each cell. The mathematical basis of this approach is to represent Maxwell’s equations in \( E \) as the (exact) volume integral taken over the volume \( V \) of the body:

\[
\text{Equation 37} \quad \vec{E}(\vec{r}_1) = \vec{E}^{\text{inc}}(\vec{r}_1) + \frac{k^2}{4\pi} \iiint_V \left[ m^2(\vec{r}_2) - 1 \right] \vec{E}(\vec{r}_2) G(\vec{r}_1, \vec{r}_2) d^3\vec{r}_2
\]

where \( \vec{r}_1 \) is the point of observation, \( \vec{r}_2 \) is a point inside the body, \( m \) is the complex index of refraction of the body, and \( G \) is the divergence-free Green’s dyadic for the vector time-independent form of Maxwell’s equations in \( E \). Discretization of the volume \( V \) into a set of \( N \) cubic elements makes this integral equation approximate and creates a system of \( 3N \) linear equations with \( 3N \) unknowns, the electric field components in each element. The time required for a computation increases as \( (N^2) \), which is the chief disadvantage of this technique. To their credit, Hage, et al., supplement their derivation of the volume integral form of Maxwell’s equations with microwave scattering
experiments on the same arbitrary shaped modeled computationally; good agreement between calculation and experiment was established.

2.3.3.8 Finite Difference Time-Domain Method

In the finite difference time-domain approach, Maxwell’s equations are solved numerically in their differential form. This approach is suitable for determining the radiation scattering properties of arbitrary structures. In the usual finite difference time-domain method, a three-dimensional Cartesian model is constructed which consists of the scattering structure of interest and the surrounding medium. It is possible to implement other coordinate systems with the finite difference approach, but the Cartesian system affords by far the greatest flexibility in accommodating irregular geometries. The model is discretized into a large number of rectangular solid mesh cells, and appropriate optical properties are assigned to each cell. Absorbing or radiating (in which only the scattered component of radiation is absorbed) boundary conditions are assigned to the six outer faces of the model. Incident radiation propagates through the model in the time domain, and the computation is allowed to proceed until convergence to steady state is achieved.

The differential equations for \( \mathbf{E} \) and \( \mathbf{H} \) solved in the finite difference time domain approach are the same as those given in Equation 16 and Equation 17:

\[
\text{Equation 38} \quad -\mu \frac{\partial \mathbf{H}}{\partial t} = \nabla \times \mathbf{E}
\]

\[
\text{Equation 39} \quad \varepsilon \frac{\partial \mathbf{E}}{\partial t} + \sigma \mathbf{E} = \nabla \times \mathbf{H}
\]
The spatial and temporal derivatives appearing in these coupled equations are represented approximately at any point in the mesh between time steps \( n \) and \((n+1)\) using an approximate difference expression. In the scheme proposed by Kunz and Luebbers,\(^9\) for example, this differencing scheme is explicit and first-order accurate:

\[
\frac{\partial \vec{E}^{n+1}}{\partial t} \approx \frac{\vec{E}^{n+1} - \vec{E}^n}{\Delta t}
\]

Equation 40

Of course, more accurate schemes can be employed, as can more reliably stable, implicit schemes. Values of \( \mathbf{E} \) and \( \mathbf{H} \) are computed at the nodes or centers of the mesh cells. Accuracy considerations in the finite difference time domain approach are analogous to those encountered in the coupled-dipole method and the volume integral formulation of the method of moments, for example: accuracy is controlled in large part by the density of the finite difference mesh, which is in turn limited by computational resources. In the scheme proposed by Kunz and Luebbers, there is no storage of a large matrix, and the memory requirement increases as \((N^{4/3})\), where \( N \) is the number of mesh cells in the model. This is a considerable advantage over the coupled dipole-method and the volume integral formulation of the method of moments, which exhibit a \((N^3)\) dependency. Another advantage of the finite difference time-domain approach is that it produces full near-field solutions through the volume of the model, which can be of considerable interest; this is not the case in the surface integral formulation of the method of moments, for example. Disadvantages of the finite difference time domain approach include the inability to represent exactly any skewed surfaces in a model using the Cartesian mesh cells, the fact that user intervention is required to identify the steady
state solution, the errors introduced by the approximate boundary conditions, and the necessity of transforming the near-field results to far-field results in an additional computational step. These same considerations arise in the finite element time-domain approach used in the present research; many of these issues are addressed in more detail in Chapter 3.

2.2.3.9 Finite Element Method

Finite element methods in electromagnetics are based upon the solution of an integral form of Maxwell’s equations. In any finite element approach, the governing differential equation is multiplied by an arbitrary weighting or testing function, and this product is integrated over the entire volume of the computational space of interest. This computational space is discretized into a large number of volume elements, the size and shape of which are dictated by the level of accuracy required and the geometry of the features contained in the volume. The total field is then approximated within each element by an arbitrary shape function which interpolates between field values at element nodes or edges. The only restriction on the weighting and shape functions is that they be of sufficiently high order to be differentiable according to the integral form of the governing differential equation. The computational volume is truncated using boundary conditions which attempt to minimize spurious reflection of radiation back into the volume. The system of volume elements is assembled into a global, \( N \times N \) matrix \( K \) which multiplies the vector of unknown field values \( a \) at each element node or edge to form the known vector \( f \) derived from boundary conditions:

\[
\text{Equation 41} \quad [K][a] = \{f\}
\]
The finite element approach thus yields a system of linear equations which can be solved for the field throughout each volume element. In the commonly employed Galerkin formulation, the shape and weighting functions are chosen to be the same yielding a symmetric $K$ matrix. The matrix $K$ is sparse, yielding a computational memory requirement which increases as $N^{100}$.

In frequency-domain finite element approaches to Maxwell’s equations, the time independent form of Maxwell’s equations is employed. Equation 23, for example, therefore takes the form:

$$\int \int \int_V \left[ -\frac{1}{\mu} \nabla^2 \vec{E}' \cdot \vec{E}' - \varepsilon \omega^2 \vec{E} \cdot \vec{E}' + i \omega \sigma \vec{E} \cdot \vec{E}' \right] dV = 0$$

where $\vec{E}'$ is the weighting or testing function, and this scalar integral equation would be solved throughout the discretized computational volume $V$ to yield the system of linear equations in the unknown vector $\vec{E}$.

In the present research, the EMFlex software, a versatile finite element time-domain implementation of Maxwell’s equations, is employed. The EMFlex software has previously been applied to a number of systems of practical interest, including the determination of light scattering properties of features on silicon wafers $^{102}$ and evaluation of the performance of integrated optical devices $^{103}$ and waveguides $^{104,105,106}$. The implementation of this code is described in Chapter 3. Advantages of the time-domain approach used in EMFlex over frequency domain approaches include the use of an efficient, explicit forward integration scheme which requires minimal computer memory, a robust and stable path to the steady-state solution, and easy extension to
include time-dependent optical properties of materials in the system or transient phenomena such as pulsed beams.\textsuperscript{107}


58 Lord Rayleigh, Phil. Mag., 41, 107, 274, and 447 (1871).
59 Lord Rayleigh, Phil. Mag., 44, 28 (1897).


86 P.E. Geller, T.G. Tsuei, and P.W. Barber, “Information Content of the Scattering Matrix for Spheroidal Particles


Chapter 3. Computational Methods

This chapter describes the two methods used in this research to compute the electromagnetic radiation scattering properties of microstructures. The first is Mie theory (Section 3.1), the second is the time-domain finite element approach (Section 3.2).

3.1 Mie Theory

3.1.1 Computation of the Scattering Coefficients $a_n$ and $b_n$

The separation of variables approach which underlies the derivation of Mie theory is described in Section 2.3.2. Here, an elaboration of the mathematical forms of Mie theory is presented, with emphasis on its implementation into computer code which can be used to calculate the far-field scattering parameters of interest. In the present research, Bohren and Huffman’s computer codes BHMIE and BHCOAT are employed to calculate scattering parameters for homogeneous and coated spheres, respectively. Both of these codes have been modified to include computation of the asymmetry parameter (Section 3.1.2).

Given an isotropic, spherical particle of arbitrary radius and optical properties illuminated by electromagnetic radiation of arbitrary wavelength, of interest are the scattered fields from this particle at far field. To this end, the relationship between the electric field vectors associated with the incident ($E_i$) and scattered ($E_s$) electromagnetic waves must be established. Equation 43 evokes the 2x2 scattering
matrix, a mathematical operator which defines the relationship between scattered and incident radiation at the arbitrary point \((x,y,z)\) located a distance \(r\) from the particle. The incident radiation is assumed to propagate in the \(+z\) direction. In general, the scattering matrix is fully populated, but for the case of a spherical particle, it is diagonal\(^1,2\).

\[
\begin{pmatrix}
E_{s,\text{par.}} \\
E_{s,\text{perp.}}
\end{pmatrix} = \frac{e^{ikr}}{-ikr} \begin{pmatrix} S_2 & 0 \\ 0 & S_1 \end{pmatrix} \begin{pmatrix} E_{i,\text{par.}} \\ E_{i,\text{perp.}} \end{pmatrix}.
\]

The subscripts of the electric field vectors refer to polarizations parallel (also called \(p\) polarization) and perpendicular (also called \(s\) polarization) to the scattering plane, and

\[
k = \frac{2\pi \eta_{\text{med}}}{\lambda_0}.
\]

In Mie theory computations, the surrounding medium is infinite in extent and therefore must have zero absorption coefficient; that is, its index of refraction must be a real number. The values of \(S_n\) are given by:

\[
S_1 = \sum_n \frac{2n+1}{n(n+1)} (a_n \pi_n + b_n \tau_n)
\]

\[
S_2 = \sum_n \frac{2n+1}{n(n+1)} (a_n \tau_n + b_n \pi_n).
\]

The functions \(\tau_n\) and \(\pi_n\) are polar functions which depend solely upon the scattering angle \(\theta\). They can be written as simple functions of the Legendre function \(P_n^1\):

\[
\pi_n = \frac{P_n^1}{\sin \theta}, \quad \tau_n = \frac{dP_n^1}{d\theta}.
\]
The functions $\tau_n$ and $\pi_n$ can be conveniently computed by upward recurrence from the relations:

$$\pi_n = \frac{2n-1}{n-1} (\cos \theta) \pi_{n-1} - \frac{n}{n-1} \pi_{n-2},$$

Equations 48

$$\tau_n = n(\cos \theta) \pi_n - (n+1)\pi_{n-1}$$

beginning with $\pi_0 = 0$ and $\pi_1 = 1$.

The terms $a_n$ and $b_n$ are the coefficients of the series expansion for the scattered fields outside the particle. They, like $S_1$ and $S_2$, are generally complex numbers. The mathematical expressions for these angle-independent scattering coefficients are complicated but are computed from only upon materials properties and the spherical Bessel functions $j_n(x)$ and $h^{(1)}_n(x)$. These expressions are:

Equation 49

$$a_n = \frac{\mu m^2 j_n(mx) [xj_n(x)] - \mu_j j_n(mx) [mxj_n(mx)]'}{\mu m^2 j_n(mx) [xh^{(1)}_n(x)] - \mu_j h^{(1)}_n(mx) [mxj_n(mx)]'},$$

Equation 50

$$b_n = \frac{\mu_j j_n(mx) [xj_n(x)] - \mu_j j_n(mx) [mxj_n(mx)]'}{\mu_j j_n(mx) [xh^{(1)}_n(x)] - \mu_j h^{(1)}_n(mx) [mxj_n(mx)]'},$$

where $\mu$ and $\mu_j$ are the permeabilities of the medium and the particle respectively, and

Equation 51

$$[f'(x)] = \frac{\partial}{\partial x} f(x)$$

Equation 52

$$x = ka$$

Equation 53

$$m = \frac{n_1}{n_{med}}$$
where $n_1$ is the real refractive index of the particle. The contrast ratio, $m$, is the ratio of the refractive index of the particle to that of the surrounding medium.

The magnitude of the scattered irradiance of a particle as a function of the scattering angle depends upon the polarization of the incident radiation relative to the scattering plane. For the case of polarization perpendicular to the scattering plane (i.e., the $s$ polarization), scattered irradiance $i_1$ as a function of angle is given by the expression:

**Equation 54**  
$$i_1 = |S_1(\theta)|^2$$

For the case of polarization parallel to the scattering plane (i.e., the $p$ polarization), scattered irradiance $i_2$ is given by the expression:

**Equation 55**  
$$i_2 = |S_2(\theta)|^2$$

The scattered irradiance associated with unpolarized or circularly polarized radiation is obtained by computing the mean of $i_1$ and $i_2$.

This discussion of Mie theory has focused primarily upon the case of a homogeneous sphere. These results can be readily extended to the case of an inhomogeneous sphere consisting of concentric shells with different optical properties. This is accomplished by expanding the fields within each coating layer in spherical harmonic basis functions (just as in the solid core of the coated sphere) and imposing the electromagnetic boundary conditions at both of the interfaces associated with each coating layer. The result is a modified pair of expressions for the scattering coefficients
$a_n$ and $b_n$ outside of the coated sphere, which are functions of the optical properties and thicknesses of the coating layers.¹

### 3.1.2 Far-Field Scattering Parameters

The most important angle-independent quantity relating to scattering efficiency of sphere is the scattering cross section, $C_{sca}$. Scattering cross section is the total power scattered by the sphere, divided by the incident intensity. It is expressed in units of area. If one imagines a spherical, mathematical surface with a radius very large compared to the radiation wavelength and centered at the particle, the scattering cross section can be visualized as the following surface integral taken over this far-field, mathematical surface:

$$
C_{sca} = \frac{\iiint i(\theta)d\Sigma}{i_0}
$$

where $i(\theta)$ is scattered intensity as a function of scattering angle, $d\Sigma$ is an infinitesimal element of surface area, and $i_0$ is the incident intensity. The far-field surface must be a large distance from the particle to ensure that evanescent fields in the vicinity of the particle do not reach the far-field surface. The scattering cross section can be computed from the scattering coefficients as:

$$
C_{sca} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) \left( |a_n|^2 + |b_n|^2 \right)
$$

The scattering cross section can be visualized as the geometric area of the incident plane wave which is scattered by the particle.
In general, the scattering cross section increases with increasing sphere radius. It is therefore useful to normalize the scattering cross section using the geometric properties of a particular sphere of interest. One means of normalization is to compute the ratio of the scattering cross section to the geometric cross section of the sphere. The result is the unitless scattering efficiency, $Q_{sca}$:

$$\text{Equation 58} \quad Q_{sca} = \frac{C_{sca}}{\pi a^2}$$

The scattering efficiency approaches zero as sphere radius approaches zero and approaches the value 2 as sphere radius approaches infinity. Between these two limits, $Q_{sca}$ can in principle attain arbitrarily large values for very high-index particles of optimal size for strong scattering, though in practice for non-absorbing materials of physically realistic refractive index, peak values in the resonant regime greater than 2 but less than 10 are observed. The scattering efficiency $Q_{sca}$ is an intuitive quantity which facilitates comparison of the scattering performance of particles with very different geometric or physical properties.

It is useful to normalize the scattering cross section in terms of the volume of a scattering particle. It is more natural on physical grounds to normalize scattering performance by volume, employing a geometric normalization which is three-dimensional, than by the two-dimensional cross-sectional area. Paint formulations and pigment costs, for example, are based upon pigment particle volume rather than upon particle cross sectional area. Therefore, it useful to evoke a third far-field scattering
parameter, the scattering coefficient, \( S \). \( S \) is defined as the scattering cross section of a particle divided by the particle volume:

Equation 59

\[
S = \frac{C_{\text{sc}}}{\left( \frac{4\pi a^3}{3} \right)} = \frac{3Q_{\text{sc}}}{4a}
\]

\( S \) is expressed in units of inverse length. The reader is cautioned that this \( S \) is not the same quantity as the \( S^* \) defined for particles or films in the discussion of Kubelka-Munk theory in Chapter 2.

The asymmetry parameter \( g \) is the average cosine of the scattering angle, weighted by scattered intensity. It is a unitless quantity. The asymmetry parameter provides important information about the relative importance of forward- and back-scattering by the spherical particle. Evoking the far-field spherical surface with the scattering particle at its center described in the case of the scattering cross section, the asymmetry parameter is defined as:

Equation 60

\[
g = \frac{\iint_{\Sigma} i(\theta) \cos \theta d\Sigma}{\iint_{\Sigma} i(\theta) d\Sigma}
\]

The asymmetry parameter can be computed from the scattering coefficients \( a_n \) and \( b_n \) as:

Equation 61

where the asterisk denotes the complex conjugate.
In the context of multiple scattering, where radiation encounters a large number of independently scattering particles while traversing an ensemble of such particles, the asymmetry parameter strongly affects the redirection of scattered radiation and therefore the scattering efficiency of the ensemble of particles as a whole. The scattering parameter $\sigma$ combines the asymmetry parameter and the scattering coefficient $S$ as follows:

Equation 62 \[ \sigma = S(1 - g) \]

Like the scattering efficiency $S$, the angle-weighted scattering coefficient $\sigma$ is expressed in units of inverse length. In the case of a semi-infinite film containing a large number of scattering particles, for example, the scattering coefficient $\sigma$ provides direct information about how effectively the ensemble back-scatters incident light through multiple scattering.\(^{17,18,2}\)

While it has been assumed in this discussion of far-field scattering parameters that the scattering particle is a sphere, the quantities $C_{\text{scat}}$, $Q_{\text{scat}}$, $S$, $g$, and $\sigma$ are all equally well defined for irregularly shaped particles.

### 3.2 Finite Element Time-Domain Method

The EMFlex time-domain finite element software for solving Maxwell’s equations is employed in much of the present research. In Section 3.2.1, the basis of its numerical implementation basis is presented. In Section 3.2.2, details of its application to problems of interest are described.
3.2.1 Numerical Implementation

The following description of the mathematical basis of the EMFlex code follows closely an unpublished report by Wojcik\textsuperscript{107}, one of the developers of the code. As described in Section 2.2.3.9, the finite element method allows piece-wise solution of Maxwell’s equations throughout a discretized computational volume containing scattering features. The partial differential equation which is solved is the combined form of Maxwell equations presented in Section 2.3.1:

\begin{equation}
\epsilon \frac{\partial^2 \vec{E}}{\partial t^2} + \sigma \frac{\partial \vec{E}}{\partial t} = -\frac{1}{\mu} \nabla \times \nabla \times \vec{E}.
\end{equation}

Forming the inner dot product of this equation with the arbitrary vector weighting function \( \vec{G} \) and integrating over the volume \( V \) of the computational volume yields the integral equation:

\begin{equation}
\iiint_V \vec{G} \cdot \left( \epsilon \frac{\partial^2 \vec{E}}{\partial t^2} + \sigma \frac{\partial \vec{E}}{\partial t} \right) \, dV = -\frac{1}{\mu} \iiint_V \vec{G} \cdot \left( \nabla \times \nabla \times \vec{E} \right) \, dV.
\end{equation}

Using a vector identity, the integrand of the right-hand side of Equation 64 can be rewritten as:

\begin{equation}
\vec{G} \cdot \left( \nabla \times \nabla \times \vec{E} \right) = \nabla \times \vec{E} : \nabla \times \vec{G} - \nabla \vec{G} \times \nabla \times \vec{E}.
\end{equation}

Substituting Equation 65 into Equation 64 and applying the divergence theorem to the second term on the right-hand side of Equation 64 gives:

\begin{equation}
\iiint_V \vec{G} \cdot \left( \epsilon \frac{\partial^2 \vec{E}}{\partial t^2} + \sigma \frac{\partial \vec{E}}{\partial t} \right) \, dV = -\frac{1}{\mu} \iiint_V \left( \nabla \times \vec{E} \cdot \nabla \times \vec{G} \right) \, dV - \frac{1}{\mu} \int_\Sigma \left( \vec{G} \cdot \hat{n} \times \nabla \times \vec{E} \right) \, d\Sigma.
\end{equation}
where \( \mathbf{n} \) is the outward unit vector normal to the surface of the computational volume. The second order spatial operator appearing in Equation 64 is thus replaced in Equation 66 by first order operators, making numerical implementation of this governing equation simpler.

The fields \( \mathbf{E} \) and \( \mathbf{G} \) are assumed to be separable in time and space, so that:

\[
\text{Equations 67} \quad \overrightarrow{E}(x,t) = S(x)\overrightarrow{f}(t) \quad ; \quad \overrightarrow{G}(x,t) = S(x)\overrightarrow{g}(t)
\]

where the same spatial dependence of the shape function \( S(x) \) is assumed for both \( \mathbf{E} \) and \( \mathbf{G} \). This is the Galerkin formulation in which the weighting and shape functions are taken to be the same and yields a symmetric system of linear equations in the finite element formulation. Substituting Equations 67 into the integrands of Equation 66 yields the differential equation:

\[
\text{Equation 68} \quad \overrightarrow{g}^T \left\{ M \frac{\partial^2 \overrightarrow{f}}{\partial t^2} + C \frac{\partial \overrightarrow{f}}{\partial t} - K \overrightarrow{f} - B \overrightarrow{f} \right\} = 0
\]

where the superscript \( T \) indicates the transpose and

\[
\text{Equation 69} \quad M \equiv \iiint_V (S^T \varepsilon S) \, dV \quad ; \quad C \equiv \iiint_V (S^T \sigma S) \, dV \quad ; \quad K \equiv \frac{1}{\mu} \iiint_V (\nabla \times S)^T (\nabla \times S) \, dV
\]

\( K, L, \) and \( M \) are symmetric coefficient matrices, and:

\[
\text{Equation 70} \quad B \equiv \frac{1}{\mu} \iiint_{\Sigma} \left( S^T \mathbf{n} \times \nabla \times S \right) d\Sigma
\]

is the coefficient matrix defined by the surface integral. Since \( \mathbf{g}(t) \) is an arbitrary function, Equation 68 can be rewritten as:
Equation 71  \[ M \frac{\partial^2 \vec{f}}{\partial t^2} + C \frac{\partial \vec{f}}{\partial t} = (K + B)\vec{f}. \]

It is this ordinary differential equation which is solved using the finite element approach by discretizing the computational volume, solving the integral equation within each element, and constructing the global system of linear equations in the unknown electric field \( f(t) \) at each node in the mesh. Rectangular solid volume elements, with eight corner nodes, are employed in EMFlex. There are therefore twenty-four unknown electric field components (three at each node) associated with each element in the finite element mesh. The interpolating shape function \( S(x) \) varies linearly within each element between the electric field values at each corner. In the time dimension, EMFlex uses the central difference approximation, which is second-order accurate, to compute the second derivative with respect to time:

Equation 72 \[ \frac{\partial^2 \vec{f}(t)}{\partial t^2} \approx \frac{\vec{f}(t + \Delta t) - 2\vec{f}(t) + \vec{f}(t - \Delta t)}{(\Delta t)^2}. \]

This is an explicit forward integration scheme.

In EMFlex finite element models, there are several different boundary conditions which can be assigned to each of the model walls. The absorbing boundary condition is intended to absorb all incident radiation at the wall, both scattered and non-scattered. The reflecting boundary condition assigns the properties of a perfect conductor to a model wall, resulting in complete reflection of all incident radiation. Symmetric and asymmetric boundary conditions can be used to impart lateral periodicity to models. Finally, the illumination boundary condition prescribes that only
scattered radiation is absorbed at a model wall, allowing non-scattered radiation to pass through. The illumination and absorbing boundary conditions can contribute to error at a model wall by causing a measure of spurious reflection of light back into the model. The illumination boundary condition is used in the finite element models throughout the present research.

In practice, an individual EMFlex finite element computation results in the steady-state properties of full electric field quantities (phase and amplitude) in the near-field surrounding the structure of interest. These near-field quantities can be expressed in terms of full, scattered, or reflected components. It is necessary to extrapolate these near-field quantities to far field in a second computational step to extract the far-field scattering parameters of interest. For this purpose, a mathematical surface (termed the Kirchoff box) is defined just inside the walls of the finite element model, on which the equivalent electric and magnetic currents $\mathbf{J}$ and $\mathbf{M}$ are computed from the tangential components of scattered electric and magnetic field. From these equivalent currents the scattered electric field at near field is extrapolated onto the surface of a far-field sphere having a radius which is much greater than the wavelength of light using the equivalence theorem. Extrapolation to far field eliminates evanescent electric field components which are present at near field so that only propagating electromagnetic waves contribute to the far-field result. The simulation of diffuse illumination is accomplished by superimposing the far-field scattered intensities computed from a series of individual computations in which the illumination directions have been varied.
step-wise over the full range of necessary orientations. The extrapolation of near-field intensities to far field is performed using the EMFlex post-processing software, Review.

3.2.2 Use of the EMFlex Software in Practice

The methodology used to run the EMFlex code is straightforward. The platform used for the EMFlex code is a Cray C-94 supercomputer. The platform used for the Review code is a Silicon Graphics, Inc. (SGI) Power Challenge mainframe computer. Individual EMFlex jobs are submitted to the Cray from the SGI in the form of text input decks. A typical EMFlex input deck is included in the Appendix. The EMFlex input deck contains parameters defining the geometry of the finite element model, the optical properties of the materials contained in the model, and parameters defining the illumination conditions. The geometric parameters of the finite element model include the physical dimensions of the Cartesian computational space (a rectangular solid in three-dimensional calculations), the number of finite elements along each edge of the model, and the size, shape, and position of particles embedded within the model. The illumination conditions include the free-space wavelength of the illuminating plane wave radiation, its propagation direction, its amplitude, and its polarization, along with the boundary condition implemented at each wall of the model.

Upon completion of a run on the Cray, a binary data block containing all of the user-requested near-field quantities (such as electric field amplitude, phase, and scattered intensity) is returned to the SGI for subsequent post processing. This post-
processing typically includes extrapolation of near-field intensities to the surface of a far-field sphere and computation of the far-field scattering parameters.

3.2.3 Computation of Far-Field Scattering Parameters

The computation of the scattering cross section $C_{sca}$ and the asymmetry parameter $g$ for a given microstructure using EMFlex is accomplished by numerical summations of scattered intensities on the surface of the far-field sphere. In practice the surface of this far-field sphere is discretized into $j$ surface area elements delineated by a spherical coordinate system with a user-defined mesh density in the two spherical angles phi and theta. In these computations, there is an established relationship between the spherical coordinate system of the far-field surface and the Cartesian coordinate system of the finite element model. The scattering cross section of a given microstructure is given by:

$$C_{sca} = \frac{\sum_j i(\theta_j) \cdot \Delta \Sigma_j}{i_0}$$

where $\theta$ is the scattering angle, $i(\theta_j)$ is the scattered intensity within surface element $j$, $\Delta \Sigma_j$ is the surface area of the surface element $j$, and $i_0$ is the incident radiation intensity in the finite element computation. The discretized expression in Equation 73 for the scattering cross section is analogous to the continuum expression given in Equation 56.

The asymmetry parameter $g$ is computed numerically on the surface of the far-field sphere through the summation:
The discretized expression in Equation 74 for the asymmetry parameter is analogous to the continuum expression given in Equation 60.

With the scattering cross section and asymmetry parameter computed in this manner for a given finite element computation, the scattering parameters $S$ and $\sigma$ can be computed, with knowledge the volume of scattering material contained in the finite element model.

3.2.4 Simulation of Random Illumination: The Illuminator

The general problem of interest in this research is the random illumination of a particular microstructure, producing an orientation-averaged result of its light scattering properties. This condition is appropriate to a film containing pigment particles, for example, which generally would have no particular orientation in the film relative to the incident light. Because the illumination conditions in an individual EMFlex computation prescribe the wavelength, polarization, and propagation direction of a plane wave of light, it is not possible to simulate random illumination with a single computation. Random illumination, however, can be simulated by superimposing far-field intensities from numerous individual EMFlex computations. To facilitate such a superposition scheme, a computational tools package called the Illuminator has been developed. The Illuminator creates and submits the individual job files constituting a random illumination computation to the Cray, performs extrapolation of near-field
scattering results to far field, and superimposes the individual far-field results to form images of scattering signatures. The Illuminator is an extensive script which is run by the Review software.

The individual steps of an Illuminator run are shown in the flow chart of Figure 6. As this flow chart indicates, the first step is to define the finite element model to be used in the Illuminator run. This model definition file, called the seed file, specifies the orientation of the Cartesian coordinate system used to define the model, the model dimensions, particle position(s) and shape(s), and the optical properties of the constituent materials of the model. A second definition file employed by the Illuminator is the control file. The Illuminator control file specifies the mesh density of the finite element grid (the number of finite element edge lengths per light wavelength in the model), the illumination wavelength, illumination directions (expressed in the spherical coordinate angles theta and phi), and the parameters controlling the extrapolation of near-field scattered intensities to far field. The control file also specifies more advanced options available in the Illuminator software, such as the ability to specify a series of jobs in which the particle size(s) in a model are systematically scaled.

There are two distinct coordinate systems employed in each Illuminator run. The first is the Cartesian coordinate system associated with the three-dimensional finite element model. The second is the illumination coordinate system. The illumination directions for an Illuminator run are expressed in spherical coordinates by specifying an overall range and angular increment for the angles theta and phi. Theta is the polar
angle, measured from the positive z axis of the Cartesian coordinate system; phi is the azimuthal angle measured counter-clockwise in the x-y plane from the positive x axis of the Cartesian coordinate system. The illumination conditions can be visualized by evoking the idea of the illumination sphere, an example of which is shown in Figure 7. The surface of this illumination sphere is divided into area elements determined by a regular increment (18°, in this case) of the two angles theta and phi. In the spherical illumination coordinate system, the individual illumination directions lie at the centers of the patches on the surface of the illumination sphere. One consequence of using spherical coordinates is that such a scheme leads to a higher density of illumination directions near the poles of the spherical coordinate system. If the mean scattering cross-section of the individual illuminations were computed in a non-weighted fashion, the resulting average scattering cross-section would be inappropriately biased toward the values associated with those illumination directions near the poles of the illumination coordinate system. To correct this effect, the Illuminator calculates an average scattering cross-section where the scattering cross-sections of the individual illuminations are weighted by the area of the corresponding area element on the surface of the illumination sphere. The illumination sphere should not be confused with the far-field extrapolation surface; the two are separate.

An important consideration in formulating an Illuminator control file is the spatial symmetry of the finite element model, since the presence of spatial symmetry elements can substantially reduce the number of illumination directions required to simulate random illumination. In the case of a finite element model geometry having
three mutually perpendicular mirror planes, for example, illumination over a single octant of the spherical coordinate system produces the complete scattering results. This reduces by a factor of eight the computational time required for the Illuminator run compared to a model requiring illumination over the full spherical coordinate system.

Once the Illuminator seed and control files have been defined, the Illuminator run is started on the SGI Power Challenge. In the first stage of an Illuminator run, as Figure 6 indicates, the individual jobs corresponding to the different illumination directions of a random illumination are created and submitted one by one to the Cray C-94. The Cray computes the full near-field scattering results at steady state for each individual job and returns the results to the SGI Power Challenge. Once all of these individual jobs have been computed on the Cray, the Illuminator scripts prompts the Review software to perform the extrapolation of near-field results to far field for each individual job using the parameters specified in the control file. The completion of these extrapolations to far field marks the end of an Illuminator run.
Figure 6. Flow chart showing the formulation and evaluation of light scattering problems using the Illuminator software.
Figure 7. A representation of the spherical illumination coordinate system used in Illuminator runs. In this case, there is an 18° increment in the spherical coordinate angles phi and theta between adjacent surface area elements. The individual illumination directions pass through the centers of the surface area elements.


Chapter 4. Performance of the Time-Domain Finite Element Method

This chapter describes the computational efficiency and accuracy of the finite element method. Section 4.1 presents the dependence of memory requirements and CPU times on the number of finite elements in EMFlex computations, along with the dependence of CPU times on the surface element density of the far-field extrapolation sphere. Section 4.2 considers the dependence of the accuracy of the finite element method upon selected model properties and upon the far-field extrapolation parameters.

4.1 Materials System of Interest

The materials system chosen for this set of studies is an isotropic sphere representing rutile titania embedded in a polymeric resin typical of paints, illuminated with 560-nm light (the center of the visible spectrum). The refractive indices of the sphere and the resin are 2.74 and 1.51, respectively, with zero absorption coefficient. These materials have been chosen for these studies because of the large refractive index mismatch between these two materials (making it a challenging system to model accurately) and the practical interest in this scattering system. The spherical particle shape has been chosen because comparison with the analytical solution from Mie theory can be used to determine the level of accuracy of the finite element computations. As noted throughout the sections below, most of the computations have been performed using a sphere diameter of 200 nm, which corresponds to the strongest resonance between the particle and the incident light. The resonant nature of this particle makes
this system especially challenging to model accurately using a numerical method, since steep gradients in electric field can be expected in the immediate vicinity of the particle. This resonance is illustrated in both Figure 8, which shows the scattering coefficient $S$ as a function of sphere diameter, and Figure 9, which shows the scattering coefficient $\sigma$ as a function of sphere diameter. Values of these parameters for the case of the 200-nm diameter sphere are marked with an “x” in each figure.

A finite element model of this 200-nm sphere is shown in Figure 10. The upper left panel of this figure shows a three-dimensional view of the particle (with the surrounding medium hidden), and the upper right panel shows a cross-sectional view of the model. The extra space below the sphere in the model was provided because it was suspected that interactions between the forward-scattered light and the lower model wall could produce errors (Section 4.2.4). The lower two panels show the variation in scattered light intensity with position through these same two views of the model. In this computation, the 560-nm light propagates in the +x direction (from top to bottom in Figure 10) and is polarized in the z direction. Fifteen wave cycles were allowed to propagate through the model in this computation. Shown in Figure 11 is a plot of electric field amplitude polarized in the z direction at the center of the spherical particle as a function of time, demonstrating convergence to steady state. This model contains 1.34 million cubic elements, each 3.6 nm on edge. The incident intensity of light in this model is unity. It is interesting to note that scattered intensities several times higher than this incident intensity are observed in the immediate vicinity of the particle in the lower two panels of the figure. This is typical of particles which are resonant with the
incident wavelength and larger particles. The distribution of scattered intensity in the cross-sectional view of the particle in indicates that most of the light is scattered in the forward direction; this is expected for particles which are not small compared to the light wavelength (i.e., outside the Rayleigh regime). For comparison with the finite element computation shown in Figure 10, an analogous result showing the same 200-nm sphere size but in a model containing only 168,000 elements is shown in Figure 12 exhibits a more noticeably rough surface than that shown in Figure 10, resulting from the coarser finite element mesh in the former case. In addition, comparison of the distribution of scattered light in these two figures indicates that there are quantitative differences in the maximum intensities in the near-field zone of the sphere.

Using the 200-nm sphere system described above as a basis, different series of finite element computations are performed in which particular parameters are systematically varied. These results are presented throughout this chapter. One set of computations can often serve more than one purpose. In the case of the investigation of the effect of finite element mesh density in the model, for example, the same set of results provides data for memory and CPU time requirements as a function of the number of volume elements in a model, in addition to the effect of finite element mesh density upon error.
Figure 8. Dependence of the scattering coefficient $S$ upon sphere diameter for the case of a sphere with $n = 2.74$ embedded in a resin with $n = 1.51$. The illumination wavelength is 560 nm.

Figure 9. Dependence of the angle-weighted scattering coefficient $\sigma$ upon sphere diameter for the case of a sphere with $n = 2.74$ embedded in a resin with $n = 1.51$. The illumination wavelength is 560 nm.
Figure 10. Finite element model of a 200-nm sphere with $n = 2.74$ embedded in a polymeric resin with $n = 1.51$. The 560-nm illuminating light propagates in the $+x$ direction and is polarized in the $z$ direction. This model contains 1,340,000 volume elements.
Figure 11. Time history of $z$-polarized electric field amplitude at the center of the sphere shown in the computation of Figure 10.
Figure 12. Finite element model of a 200-nm sphere with $n = 2.74$ embedded in a polymeric resin with $n = 1.51$. The 560-nm illuminating light propagates in the $+x$ direction and is polarized in the $z$ direction. This model contains 168,000 volume elements.
4.2 Computational Efficiency

4.2.1 Memory Requirements For Finite Element Computations

In this series of computations, the number of volume elements used in the construction of finite element models for the 200-nm titania sphere embedded in resin has been systematically varied. For the coarsest finite element mesh densities studied (having the fewest volume elements), the edge lengths of the finite element model have been extended a greater distance from the surface of the sphere to ensure an adequate number of elements between the sphere surface and the wall so as not to induce large errors in the computation (Section 4.3.5). The dependence of the Cray C-94 memory requirement in megawords (MW) upon the number of volume elements in each model is shown in Figure 13. (On the Cray C-94, a word is 64 bits, or eight bytes.) The memory requirement increases linearly with the number of volume elements in the finite element model; this is an important advantage of the time-domain finite element approach over many of the alternative numerical schemes described in Chapter 2 which exhibit higher-order dependence of memory requirement on volume elements. The memory requirement is an important property of an individual finite element computation, as the maximum memory available for routine use on this Cray C-94 is 40 MW. This memory limit constrains the maximum number of elements available for a computation to about 2,500,000, which in turn places an upper limitation upon the volume of material which can be modeled. The actual upper limit for the volume of material depends upon the radiation wavelength studied and the required level of
accuracy of the computation, since it is the relationship between element size and radiation wavelength that determines both the physical volume of the model and the expected level of error in the computation.

```
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<th>0.0</th>
<th>0.3</th>
<th>0.6</th>
<th>0.9</th>
<th>1.2</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Memory (MW)</td>
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<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>25</td>
</tr>
</tbody>
</table>
```

Figure 13. Dependence of Cray C-94 memory requirement upon the number of volume elements in the finite element model for the present series of EMFlex computations.

4.2.2 CPU Time Requirements For Finite Element Computations

The dependence of Cray C-94 CPU time upon the number of volume elements in a finite element model for the series of computations described in Section 4.1.1 is shown in Figure 14. As in the case of the memory requirement (Figure 13), CPU time shows a linear dependence upon the number of volume elements in the finite element model. This linear dependence is likewise an important advantage of the time-domain finite element approach over many of the alternative numerical approaches described in Section 2.3.3, such as the method of moments which exhibits a (N^2) dependence of CPU.
time upon the number of elements. It should be noted that the same number of wave cycles (15) were allowed to propagate in the finite element model in each of the computations in Figure 14. For fixed finite element model geometry, the Cray C-94 CPU time depends linearly upon the number of cycles allowed to propagate in a given computation. CPU times of 45-60 minutes are typical of individual finite element computations performed throughout this research. The vector nature of the Cray architecture offers a factor of 3-10 speed-up over conventional scalar workstations with the EMFlex code.

![Graph](image)

**Figure 14.** Dependence of Cray C-94 CPU time requirement upon the number of volume elements in the finite element model for the present series of EMFlex computations.

### 4.2.3 CPU Time Requirements For Far-Field Extrapolation

Once steady-state near-field quantities are computed using EMFlex in a finite element model, these fields are extrapolated to far field using the Review software. As
described in Section 3.2.3, the surface of the far-field sphere onto which near-field scattered intensities are extrapolated is divided into a number of surface elements according to a spherical coordinate system. In the present series of computations, the discretization in both angles theta and phi of the spherical coordinate system in the extrapolation step has been systematically varied. The angular discretizations investigated are 0.5, 1, 2, 3, 5, 10, and 15 degrees. The radius of the far-field sphere is 500 µm in all cases; the radius of the far-field sphere has no effect upon CPU time required for the extrapolation. The CPU time required on the SGI Power Challenge computer for a single far-field extrapolation is shown in Figure 15 as a function of the angular discretization on the surface of the far-field sphere. This data indicates that the required CPU time increases dramatically with increasing angular on the surface of the far-field sphere. Over six hours of CPU time are required for 0.5-degree angular discretization, while only about thirty minutes are required for 2-degree angular discretization.

The data showing CPU time dependence upon angular discretization in Figure 15 has been plotted as a function of the number of surface elements on the far-field sphere in Figure 16; the number of surface elements is proportional to the inverse square of the angular discretization. The plot of CPU time as a function of the number of surface elements shown in Figure 16 indicates that the dependence of CPU time upon the number of surface elements on the far-field sphere is of higher order than linear. The selection of angular discretization on the far-field surface affects CPU time strongly, and this selection must therefore be made with consideration of the effect of
angular discretization upon accuracy of the far-field result. This accuracy issue is described in Section 4.3.2.

\[\text{Figure 15. CPU time required for a single far-field extrapolation is shown as a function of the angular discretization on the surface of the far-field sphere.}\]

\[\text{Figure 16. CPU time required for a single far-field extrapolation is shown as a function of the number of surface elements on the far-field sphere.}\]
4.3 Computational Accuracy

4.3.1 Effects of Finite Element Mesh Density

The 200-nm titania sphere in polymeric resin is used here to determine the influence of finite element mesh density upon the accuracy of the time-domain finite element method. The size of the cubic volume elements in these computations is expected to exert a strong influence upon the accuracy of the results, since the ability to represent the geometries of curved particles such as spheres and to compute gradients in electric field are both controlled by the size of the rectangular solid volume elements. The most useful way to parameterize the finite element mesh density is to compare the edge length of cubic volume elements composing a finite element model to the wavelength of the electromagnetic radiation propagating in the model. Since the effective wavelength of radiation propagating in a dielectric material is inversely proportional to the refractive index of that material, it is the wavelength of a plane wave traveling through the material with the highest refractive index $n_{\text{max}}$ in the model that effective should be considered. The minimum effective wavelength $\lambda_{\text{min}}$ in the model is:

$$\lambda_{\text{min}} = \frac{\lambda_0}{n_{\text{max}}}$$

where $\lambda_0$ is the wavelength of the illuminating radiation in vacuum. In the present series of computations, the highest index material in the model is the scattering sphere with $n = 2.74$. The minimum wavelength of the 560-nm light in these computations is
therefore $\lambda_{\text{min}} = 560 \text{ nm}/2.74 = 204 \text{ nm}$. The number of cubic volume elements per minimum wavelength in the model is given by the unitless quantity $\rho$:

$$\textbf{Equation 76} \quad \rho = \frac{\lambda_{\text{min}}}{l_{\text{edge}}}$$

where $l_{\text{edge}}$ is the edge length of the cubic volume elements in the model. In the case of the finite element models shown in Figure 10 and Figure 12, the values of $\rho$ are 68 and 20, respectively.

The values of $\rho$ investigated here are 10, 15, 20, 25, 30, 35, 45, 55, and 68. The sphere diameter of 200 nm was used in each computation, and the edge length of the finite element model were varied, when necessary, in order to maintain at least ten elements between the sphere surface and the nearest model walls. In the extrapolation to far field, the radius of the far-field sphere was 500 $\mu$m and the angular discretization on the far-field sphere surface was 3 degrees in all cases. The scattering cross section was computed for each case and compared with the exact result from Mie theory. The resulting error is plotted in Figure 17 as a function of the finite element mesh density $\rho$. As expected, the error increases with decreasing $\rho$, with an error less than 1% for $\rho = 68$ and an error greater than 8% for $\rho = 10$. Finite element mesh densities with $\rho \geq 20$ are used in all of the computations described in subsequent chapters of this dissertation, and $\rho \geq 40$ in most cases. These resolutions in the finite element mesh ensure that maximum expected errors are limited to the values in Figure 17.
Evaluations of computational error in many systems the 200-nm titania sphere in resin one chosen for the data in Figure 17 have confirmed that the values shown in this figure represent a reasonable upper bound on computational error. Knowledge of these error levels is critical, since it provides a basis for differentiating the real, microstructural influences upon computed scattering properties from numerical error. For example, if a computation on the effects of particle agglomeration with $\rho = 40$ exhibits a 30% change in scattering cross section relative to the primary particles, this change can be attributed with confidence to the microstructural influence rather than to numerical error.

![Graph](image)

Figure 17. Error in scattering cross section compared to the exact result from Mie theory as a function of $\rho$, the number of volume elements in a model per minimum wavelength of the 560-nm light propagating in the finite element models.
4.3.2 Effects of Mesh Density on Surface of Far Field Sphere

In Section 4.2.3, the effects of angular discretization on the surface of the far-field sphere upon the CPU time required for extrapolation of fields from near to far field were described. Here, the errors in scattering cross section for that same series of computations are compared to the exact result from Mie theory. These results are plotted in Figure 18 as a function of angular discretization on the far-field sphere surface. As expected, computational error increases with decreasing angular resolution. The error increases non-linearly with angular discretization, with an error of ~0.7% for all values less than or equal to 3 degrees. For values greater than 3 degrees, error increases rapidly with increasing angular discretization. As shown in Figure 15, the CPU time required for extrapolation decreases very rapidly with increasing angular discretization on the surface of the far-field sphere; there is therefore a trade-off between increased accuracy and increased CPU time in extrapolation of near-field results to far field. This trade-off is well-balanced for the angular discretization 2-3 degrees, which is the range of values typically used in this research. Investigation of error as a function of the illumination angle have confirmed that these values yield good accuracy while requiring reasonable CPU times for the computation.
4.3.3 Effects of Far-Field Sphere Radius

In order to determine the effects of the far-field sphere radius upon computational error, the fields in the finite element model shown in Figure 10 have been extrapolated to far-field sphere surfaces having radii of 2, 5, 10, 50, and 500 µm. The angular discretization in the two spherical coordinate system angles was 3 degrees in all cases. The resulting error compared to the exact solution known from Mie theory is plotted as a function of far-field sphere radius in Figure 19. These data indicate that the far-field sphere radius affects error only in the limit of very small extrapolation radii. In the case of small extrapolation radii, evanescent components of the scattered light still contribute to intensity on the surface of the extrapolation surface. This is an important result, for it provides direct information about the length scale over which...
near-field optical interactions in this system are important. For radii greater than or equal to 10 \( \mu \text{m} \), there is no dependence of error upon the extrapolation radius. In all cases, the CPU time required for extrapolation was independent of the extrapolation radius. Based upon the results shown in Figure 19, a far-field sphere radius of 500 \( \mu \text{m} \) is used in all subsequent far-field extrapolations in this research.

![Graph](image)

**Figure 19.** Error in scattering cross section compared to the exact result from Mie theory as a function of far-field sphere radius.

4.3.4 Effects of Kirchoff Box Placement in the Model

Using the model shown in Figure 10, the position of the Kirchoff box surrounding the scattering sphere in this model has been systematically varied to determine its effects upon computational error. The Kirchoff box is the mathematical surface on which equivalent electric and magnetic currents are computed for subsequent extrapolation of near-field results to far field (Section 3.2.1). The Kirchoff box surface
must be sufficiently displaced from the particle surface (where electric field gradients are potentially greatest) and from the model walls (where electric field values may be spuriously influenced by the boundary conditions). The usual placement of the Kirchoff box is just inside the walls of the model but with sufficient space between it and the wall to prevent boundary condition effects from introducing errors into the extrapolation.

Using the model shown in Figure 10, the Kirchoff box was placed precisely half-way between each wall of the model and the surface of the sphere. The error in the scattering cross section for this calculation (compared to the exact solution known from Mie theory) was 0.76%. In subsequent calculations, the six sides of the Kirchoff box were progressively moved closer to the surface of the spherical particle. With just two elements separating the Kirchoff box from the sphere surface on all six sides, the error in scattering cross section was 0.79%, indicating no deviation from the previously cited result. With the Kirchoff box just one element away from the sphere surface, however, the error in scattering cross section increased to 4.3%, suggesting that the presence of strong electric field gradients immediately at the sphere surface caused significant error in the extrapolation operation. The Kirchoff box was then moved progressively closer to the walls of the model from the half-way point between the sphere and the model walls. With the Kirchoff box positioned two elements away from the model walls on all six sides, the error in scattering cross section was 0.75%, in good agreement with case where the Kirchoff box was farther removed from the model wall. With the Kirchoff box just one element away from the model wall, however, the error jumped to 186%, a
result of errors in electric field vectors and gradients produced by the boundary conditions at the model walls.

The results described in this section indicate that the positioning of the Kirchoff box can affect the accuracy of these finite element calculations. No significant problems are anticipated, however, provided that the sides of the Kirchoff box are several elements removed from both the surfaces of the scattering particle and the model walls.

4.3.5 Effects of Particle Position Relative to Model Walls

Illumination boundary conditions (Section 3.2.1), which are intended to absorb only scattered radiation, are used at each of the six model walls of finite element models throughout this research. Since scattered light can be spuriously reflected back into the model at the walls due to the imperfection of the boundary condition, increased error could be expected as the intensity of scattered radiation encountering the walls increased. To investigate these effects, the 200-nm titania sphere shown in Figure 10 was displaced from the top edge of the model to the bottom edge over a series of four computations. Figure 20 shows the steady-state scattered electric field intensities on cross-sectional slices through the centers of these four models. The 560-nm light propagates in the +x direction in each case. It is evident in Figure 20 that the forward scattered light interacts more strongly with the bottom wall of the model as the sphere moves closer to it, with the extreme case appearing in the bottom right panel of the
Figure. The distances between the bottom surface of the sphere and the bottom of the model in these four models are listed in Table 1.

Table 1 summarizes the results of extrapolating the near-field scattering results shown in Figure 20 to far field. The results of this extrapolation have been compared to the exact scattering cross section known from Mie theory; the errors associated with those computations are presented in Table 1. Interestingly, the error in scattering cross section decreases systematically as the scattering sphere is moved closer to the bottom wall of the model (or, alternatively, away from the top of the model). This observation was surprising; it was expected that increased interaction of forward-scattered light with the bottom wall of the model would cause increased error. The results of Table 1 provide no evidence that such a problem arose in these computations. An important result the data in Table 1 is that there is no evidence that the interaction between the forward scattered light and the model wall has caused the computation to fall into severe error. This result is encouraging, since it suggests that it is not necessary to provide large volumes of surrounding medium in the forward-scattering direction, allowing the implementation of models containing fewer volume elements and therefore requiring shorter CPU times for computation. It is possible that the increased error associated with longer distances between the sphere and the bottom wall of the model is a result of resonance between forward-scattered light and the bottom model wall. These effects could also occur in the back-scattered direction (i.e., between the top of the sphere and the top model wall in Figure 20), but they would be substantially weaker since significantly less light is back-scattered than forward-scattered.
Figure 20. Cross-sectional slices through the centers of four finite element models in which the spacing between the 200-nm sphere and the bottom wall of the model has been systematically varied. Scattered light intensity is shown in each case.
Table 1. Error in scattering cross section as a function of separation distance between the bottom of the sphere and the bottom wall of the model. The corresponding models are shown in Figure 20.

<table>
<thead>
<tr>
<th>Sphere-Bottom Wall Distance (nm)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>185</td>
<td>1.9</td>
</tr>
<tr>
<td>150</td>
<td>0.74</td>
</tr>
<tr>
<td>85</td>
<td>0.21</td>
</tr>
<tr>
<td>20</td>
<td>0.02</td>
</tr>
</tbody>
</table>

4.3.6 Effects of Model Dimensions Compared to Light Wavelength

In addition to Kirchoff box and model wall placement, the edge length of a finite element model compared to the radiation wavelength can have significant impact upon computational error. Figure 21 shows a finite element model of a 40-nm titania sphere with refractive index $n = 2.74$ embedded in the polymeric resin with refractive index $n = 1.51$. As in all previous computations in this chapter, the wavelength of the incident light is 560 nm. This represents a non-resonant case in the Rayleigh scattering regime. Referring to the plot of the scattering coefficient $S$ as a function of sphere diameter shown in Figure 8, the 40-nm sphere diameter is very weakly scattering compared to the 200-nm sphere diameter. The edge length of the model shown in Figure 21 is 400 nm, and light propagates in the $+x$ direction. The two panels of Figure 21 showing near-field scattered intensity indicate that the particle scatters light nearly isotropically rather than in the forward direction, which is expected in the Rayleigh regime. To investigate
the effects of model size upon accuracy of these finite element computations, the edge length of the cubic model in this series of computations was systematically varied between 100 and 400 nm, without changing the edge length of the cubic volume elements composing the model. The scattering sphere was located at the center of the model in all cases.

The columns of Table 2 show the edge length of the model, the optical length of the model, and the percent error in scattering cross section versus the known result from Mie theory for each case. The optical length of the model, which is defined here as the number of wavelengths of light which would exist along the linear path from the top to the bottom of the model which passes through the center of the sphere. Since the refractive indices of the sphere and the surrounding medium are both greater than unity, the wavelength of radiation propagating in these materials is compressed. The optical length is the sum of the individual propagation distances through the different media present in the model multiplied by their respective refractive indices, divided by the free wavelength of the incident light:

\[ l_{\text{opt}} = \left( l_1 n_1 + l_2 n_2 + \ldots \right) / \lambda_0 \]

For example, in the case of the finite element model in Figure 21 with 400-nm edge length, a line passing from the top of the model to the bottom and passing through the center of the 40-nm sphere encounters 40 nm of material with \( n = 2.74 \) (the sphere) and 360 nm with \( n = 1.51 \) (the surrounding medium). The optical length is therefore computed as:
Equation 78 \[ l_{opt} = \left[ \frac{(40\text{nm} \cdot 2.74 + 360\text{nm} \cdot 1.514)}{560\text{nm}} \right] = 1.16. \]

As Table 2 indicates, the error in scattering cross section is strongly dependent upon the edge length of the model. For models smaller than 400 nm on edge, error increases abruptly from roughly 1% to the range 17-41%. These effects are attributed to the size of the model relative to the light wavelength. In the case of models which are so small compared to the light wavelength that the optical length is less than unity, the problem of not developing a steady-state, propagating wave in the model arises. Instead of at least one full wavelength of light propagating through the model, electric field amplitudes in the model can fluctuate unstably in response to the fluctuating electric field of the incident radiation, to which most of the model is at once subject.

The same analysis shown in Table 2 has also been applied to the problem of the more resonant 200-nm sphere described in the preceding section. In this series of experiments, the 200-nm sphere with \( n = 2.74 \) has been placed at the center of a cubic model with a surrounding medium with \( n = 1.51 \) and the edge length of the model systematically decreased until it was in close proximity to the surface of the particle. The results of this series of experiments, shown in Table 3, support the idea that models must be sufficiently large to ensure that the optical length of the model is greater than unity in order to avoid large errors in scattering cross section in these finite element computations. Comparing results from Table 2 and Table 3, it appears that an optical length of 1.2 is sufficient to ensure minimal computational errors for the materials employed in these two series of computations.
Figure 21. Finite element model of a 40-nm sphere with $n = 2.74$ embedded in a polymeric resin with $n = 1.51$. The 560-nm illuminating light propagates in the +x direction and is polarized in the z direction.
Table 2. Error in scattering cross section of finite element calculations in which the model edge length was systematically varied. All calculations are for the case of a 40-nm sphere at the center of a cubic model.

<table>
<thead>
<tr>
<th>Model Edge Length (nm)</th>
<th>Optical Length</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.4</td>
<td>41</td>
</tr>
<tr>
<td>200</td>
<td>0.6</td>
<td>26</td>
</tr>
<tr>
<td>300</td>
<td>0.9</td>
<td>17</td>
</tr>
<tr>
<td>350</td>
<td>1.0</td>
<td>30</td>
</tr>
<tr>
<td>400</td>
<td>1.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 3. Error in scattering cross section of finite element calculations in which the model edge length was systematically varied. All calculations are for the case of a 200-nm sphere at the center of a cubic model.

<table>
<thead>
<tr>
<th>Model Edge Length (nm)</th>
<th>Optical Length</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>234</td>
<td>1.07</td>
<td>4.7</td>
</tr>
<tr>
<td>254</td>
<td>1.12</td>
<td>1.9</td>
</tr>
<tr>
<td>272</td>
<td>1.17</td>
<td>0.94</td>
</tr>
<tr>
<td>300</td>
<td>1.25</td>
<td>0.97</td>
</tr>
</tbody>
</table>
4.3.7 Effects of Strong Resonance: High-Index Spheres in Vacuum

As the mismatch between the refractive index of a sphere and the medium in which it is embedded is increased, the maximum scattering efficiency which is attainable increases. This is illustrated in the following example calculated using Mie theory. Figure 8 shows a plot of scattering coefficient $S (\mu m^{-1})$ versus diameter for the case of a sphere with refractive index $n = 2.74$ embedded in a medium with $n = 1.51$. The maximum value observed, representing the most resonant condition, is $S \approx 26 \mu m^{-1}$ for the sphere diameter 200 nm. Figure 22, in comparison, shows a plot of $S$ versus diameter for the case of a sphere with $n = 3.0$ embedded in a medium with $n = 1.0$ (e.g., air or vacuum). The maximum value observed in this case is $S \approx 68 \mu m^{-1}$ for the sphere diameter 177 nm, a substantially greater value than the previous case considered. This higher value implies much greater scattered intensities and electric fields gradients at near field. These make this highly resonant system more susceptible to errors associated with the mesh density and its ability to describe sharp gradients accurately.

To quantify the computational error of the time-domain finite element approach in highly resonant cases, the three sphere diameters marked with “x” in Figure 22 have been investigated. The point corresponding to the first resonant peak in this figure (diameter 0.177 μm) is the most strongly resonant condition and therefore the most difficult to model accurately using the finite element approach. The other two points, corresponding to sphere diameters 0.16 and 0.22 μm, are not as strongly resonant and lower numerical errors are expected in these cases.
The results of these calculations are summarized in Table 4. The errors associated with the calculations for the less resonant cases (sphere diameters 0.16 and 0.22 µm) are both less than 1%, indicating very close agreement with the known solutions from Mie theory. The error associated with the strongly resonant case (sphere diameter 0.177 µm), on the other hand, is 6.4%, deviating substantially from the exact solution. This series of calculations demonstrates that error in the time-domain finite element approach depends upon the degree of resonance in a specific calculation as well as the factors identified above. It should be noted that the extreme contrast ratio of $m = 3.0$ between the sphere and the surrounding medium in the case studied here exceeds any which is encountered in practice; there are no known, non-lossy dielectric materials with refractive index as high as 3.0. The calculations described in this section are therefore non-physical but nevertheless highlight the effects of resonance upon computational accuracy of the finite element method.
Figure 22. The scattering coefficient $S$ ($\mu m^{-1}$) as a function of sphere diameter for the case of a sphere with $n = 3.0$ in a medium with $n = 1.0$. This represents a more resonant system than can be achieved in practice, since no known, non-lossy material exhibits such a high refractive index in the visible spectrum.

<table>
<thead>
<tr>
<th>Sphere Diameter (nm)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>0.64</td>
</tr>
<tr>
<td>177</td>
<td>6.4</td>
</tr>
<tr>
<td>220</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 4. Error in scattering cross section as a function of sphere diameter for the three cases indicated on the plot in Figure 22.
4.4 Guidelines For Building Robust Finite Element Models

The observations of the present chapter may be used to formulate a set of simple guidelines for the construction of robust finite element models for the EMFlex software. These guidelines are designed to minimize the error of the finite element. They are:

1. The optical length (Equation 77) of the finite element model edges should be at least 1.2 wavelengths.

2. The finite element mesh should be as fine as memory limitations allow.

3. The scattering microstructure should be positioned at the center of the model.

4. The scattering microstructure should be at least eight elements from any model wall.

5. The Kirchoff surface should be placed at least three elements from any model wall and the scattering microstructure.

6. The surface of the far-field extrapolation surface should be placed a very large optical distance from the finite element model.

7. The angular mesh on the surface of the far-field extrapolation surface should be as fine as possible to ensure minimal error; CPU time restrictions are the limitation here.
Chapter 5. A Potpourri of Pigment Particles

In this chapter, the light scattering properties of three different white pigment systems are determined using computational modeling. In Section 5.1, Mie theory computations are performed for the case of core-shell composite pigment architectures for the case of coated spheres. In this study, the average index approximation for rutile titania is used; titania is modeled as an optically isotropic material. This assumption is justified, since the most dramatic changes in scattering behavior arise from the presence of the second material in the coated particle. In Section 5.2, the time-domain finite element approach is used to determine the light scattering behavior of optically anisotropic spheres of rutile titania. These results are compared to the average index and weighted sum approximations to determine their ability to describe the scattering efficiency of rutile titania. Finally, in Section 5.3, the light scattering properties of a morphological rutile titania particle are computed using the time-domain finite element method. These results are compared to the scattering performance of the equivalent-volume sphere under both the average index and weighted sum approximations. In addition, the scattering data are used to calculate equivalent spherical diameters in order to highlight the difficulties in particle size analysis which can arise in modeling complex particle shapes as simple spheres.
5.1 Core-Shell Pigment Particles

5.1.1 Introduction

One of the largest market segments for titania white pigment is the paper industry. Since titania is more expensive than pulp and the other mineral pigments which are used in paper formulations, such as kaolin clay and calcium carbonate, formulators of paper systems attempt to use titania as efficiently as possible. In paper applications, it is normally most cost-effective to optimize the content of the non-titania components and then add titania as required to achieve target opacity. Formulation strategies for optimization of both paper furnish and coating formulations have been proposed by Houle1 and Kwoka.2,3,4

Recently, it has been proposed that the scattering efficiency of white pigment can be improved by coating spherical silica particles with a titania shell.22,23,24 The lower titania content of such particles suggests that they could potentially provide better value versus pure titania pigments. To address this issue, the light scattering properties of model core-shell pigments have been determined using a computational approach. Results are presented below for the general case of a titania shell over cores with refractive index varying from 1.0 (hollow titania spheres) up to 2.74 (solid titania spheres). This is followed by a comparison of the scattering performance of titania-coated silica versus pure titanium dioxide.
5.1.2 Scattering Properties of Titania-Coated Core-Shell Pigments

A schematic diagram of the configuration for the titania-coated core-shell particles is shown in Figure 23. All critical parameters are indicated. The core is a sphere of diameter $D_C$. The titanium dioxide coating forms a shell with outside diameter $D_T$. The reported calculations include particles with shell diameters up to 1 µm and consider the full range of 100% titania (i.e., $D_C = 0$) to 100% core material (i.e., $D_C = D_T$). In the case of a silica core, for example, it is not practical to deposit more than 40 weight percent titania on the core. Since the volume percent titania is related to the cube of $D_C/D_T$ and since titania is more dense than silica, this composition corresponds to a thin shell around the silica core, with a shell diameter only 10% larger than the core. For clarity, the schematic diagram in Figure 23 illustrates a particle with a shell diameter about 20% larger than the core diameter. This represents an impractical case with a titania content of 64 wt %. For practical cases, the thickness of the titania layer would be much thinner than illustrated.
Figure 23. Schematic representation of titania coated on a core particle of lower refractive index.

The other key parameters in Figure 23 are the refractive indices of the component materials. The value of 2.74 for titania is the average refractive index at the center of the visible spectrum. The refractive index of the core is an independent variable. A core refractive index of 1.0 (air) represents a hollow titania shell, while a core index of 1.46 represents titania-coated silica. A core with refractive index equal to that of rutile titania represents a solid rutile particle. The refractive index for the surrounding medium in a paper system is more difficult to assign. The value of 1.45 used in these calculations is the average refractive index of a representative paper coating composed of a mixture of clays and calcium carbonate (refractive index 1.6), starch or latex binders (refractive index 1.5), and air voids (refractive index 1.0). Uncoated papers are composed of cellulose fiber (refractive index 1.45), clays, calcium
carbonate, and air voids. A refractive index lower than 1.45 should be used to represent the surroundings for titania in filled sheet applications.

### 5.1.2.1 Refractive index of medium at 1.45

A plot of the angle-weighted scattering coefficient $\sigma$ for the general case of rutile titania-coated cores in a paper coating or cellulose matrix is shown in Figure 24. The results were calculated for the light wavelength 560 nm, the center of the visible spectrum. This is the wavelength where the human eye is most sensitive and close to the center of the wavelength bands used for measurement of paper opacity. Absolute values of scattering coefficients are dependent on wavelength, but results calculated at 560 nm provide a sound representation of the light scattering properties that affect opacity.

For the particles in Figure 24, the ratio of the core diameter to total diameter, $D_c/D_T$, is fixed at 0.9. The three-dimensional plot shows the scattering efficiency for particles with outer diameter, $D_T$, from 0.0 to 1 $\mu$m. Each contour line represents the dependence of $\sigma$ on diameter for a given core refractive index. The refractive index of the core material is incremented by 0.035 with each contour line and ranges from 1.0 (air) to 2.74 (rutile). The global maximum of this plot, indicating the optimally scattering particle structure, corresponds to a solid rutile particle (core and shell refractive index both equal to 2.74) with of diameter 0.2 $\mu$m.

In the case of titania-coated silica, the core index is 1.46. The data in Figure 25 are plotted as a function of the diameters of the silica core and the titania shell
diameters, both of which vary in the range 0.0–1.0 µm. Each contour line represents a 0.002 µm increment of outer shell diameter. As in Figure 24, the global maximum corresponds to a solid rutile sphere (i.e., silica core diameter equal to zero). Variation of the core and shell diameters results in the undulating series of local minima and maxima in Figure 25. The greatest local maximum corresponding to a sphere having substantial silica content occurs at a titania shell diameter of about 0.35 µm, with a silica core diameter of about 0.2 µm. The σ value associated with this coated silica particle is only about 64% that of the optimized solid rutile sphere.
Figure 24. Scattering coefficient $\sigma$ ($\mu$m$^{-1}$) versus coated particle diameter and refractive index of the core material for titania-coated particles with coating thickness equal to 10% of the particle radius.

Figure 25. Scattering coefficient $\sigma$ ($\mu$m$^{-1}$) versus silica core diameter and titania shell diameter for a coated particle. The global maximum of this plot corresponds to a solid titania sphere of 0.2 $\mu$m diameter.
For greater clarity, five contours have been extracted from the three-dimensional plot in Figure 25 and shown in the two-dimensional plot of Figure 26. This figure shows $\sigma$ as a function of silica core diameter for spheres having five different titania shell diameters. The sphere with titania shell diameter 0.20 $\mu$m is that which exhibits the highest $\sigma$ value associated with solid titania (silica core diameter equal to zero). There is an obvious decrease in $\sigma$ with increasing silica core diameter. Many of the titania-coated silica particles nearly match the scattering efficiency of the pure titania particles with the same outside diameter, but each is deficient relative to pure titania at its optimum diameter. For example, in the case of particles with titania shell diameter 0.5 $\mu$m, the scattering coefficient is nearly constant as the silica core is increased from 0 to 0.4 $\mu$m. The scattering coefficient of this set of particles is 70% below that of the optimized solid titania particle. A sphere with titania shell diameter 0.35 $\mu$m is the particle which exhibits the highest $\sigma$ value among those spheres containing a substantial amount of silica (silica core diameter 0.2 $\mu$m). This core-shell particle has $D_C/D_T = 0.2/0.35 = 0.57$ and a titania content of 89 weight percent, which means that the titania coating is impractically thick from a synthesis standpoint. All other silica-containing particles exhibit even lower $\sigma$ values than those having titania shell diameters of 0.35 and 0.5 $\mu$m.

As noted previously, physically realizable core-shell architectures are limited to those with a titania shell thickness that is less than or equal to 10% of the outer particle diameter ($D_C/D_T = 0.9$). This limiting case has been plotted in Figure 27, which shows $\sigma$
as a function of sphere diameter both for solid titania and for coated particles with $D_C/D_T = 0.9$. The results for the two structures are strikingly different; the maximum $\sigma$ value achieved by a solid titania sphere is $10.5 \ \mu m^{-1}$, while the maximum value achieved by the silica-coated particle is only about $1.7 \ \mu m^{-1}$. The two curves are approximately equal for particle diameters greater than $\sim 0.7 \ \mu m$. The resonant peaks observed in Figure 27 for the pure rutile particles are an artifact the high spatial symmetry of a sphere. In practice, these surface wave resonances are not experimentally observed even for particles with narrow size distributions.$^5$

![Figure 26. Scattering coefficient $\sigma$ for five coated particles with different outside diameters.](image)
Figure 27. Scattering coefficient $\sigma$ versus particle diameter for a solid titania sphere and a titania-coated silica particle with coating thickness equal to 10% of the particle radius.

The Mie theory computations presented here describe the light scattering properties of an isolated spherical particle and cannot be applied to systems in which the crowding effect is important. However, crowding can be viewed as agglomeration of individual particles into clusters. If the scattering properties of these clusters could be reasonably approximated by computing the scattering properties of equivalent-volume spheres, the data in Figure 27 at higher diameters suggest that optimized rutile particles will show more loss due to crowding than particles of titania-coated silica. This effect will not apply for most paper applications where titania concentrations are below ~15% by volume.

The incentive for depositing titania coatings on a low density and inexpensive core material like silica is to attempt to increase the light scattering efficiency per pound of pigment or to reduce the price of the pigment. The scattering coefficients in Figure
24–Figure 27 can be divided by the density of the coated particle, thereby expressing $\sigma$ on a weight basis (m$^2$/g). Using specific gravities of 2.2 g/ml for silica and 4.26 g/ml for rutile titania, the data in Figure 25 were normalized by dividing by the density of the particle; these results are shown in Figure 28. While this normalization scheme has the effect of slightly increasing the effective $\sigma$ values of those particles containing silica, the global maximum in Figure 28 nevertheless corresponds to a solid titania sphere, with no silica present, as in Figure 24–Figure 27.

It is also of interest to normalize the light scattering data in Figure 25 by dividing the $\sigma$ values by the weight fraction of titania present in the particle. This normalization scheme reveals the relative scattering efficiency for the limiting case where the value of the titania-coated silica pigment is assessed only by its titania content. The results of this normalization scheme are shown in Figure 29. This data does not include the diverging $\sigma$ values which occur for those cases where the titania coating thickness approaches zero. Even with this normalization scheme, the global maximum in Figure 29 corresponds to a solid titania sphere, with no silica present.
Figure 28. Scattering coefficient $\sigma$ divided by the density of the coated particle. The global maximum of this plot corresponds to a solid titania sphere with no silica present.

Figure 29. Scattering coefficient $\sigma$ divided by the weight fraction of titania present in each coated particle. The global maximum of this plot corresponds to a solid titania sphere with no silica present.
Finally, the light scattering performance of the silica-titania core-shell pigments can be compared to a heterogeneous mixture of the two pure pigments to determine whether any synergy results for the coated particles. For the titania-coated silica particles in Figure 27, $D_{C}/D_{T}$ is 0.9 which corresponds to 27.1 volume percent titania. The highest $\sigma$ value of $1.70 \, \mu m^{-1}$ occurs for the titania-coated silica at the diameter $0.687 \, \mu m$. For pure rutile, the optimal $\sigma$ value of $10.574 \, \mu m^{-1}$ occurs at the diameter $0.20 \, \mu m$. For pure silica, the optimal $\sigma$ value for pure silica is very low because the refractive index is close to that of the medium; the optimum occurs at the diameter $0.20 \, \mu m$ but is only $\sigma = 0.0005 \, \mu m^{-1}$. For a heterogeneous mixture of optimized rutile and silica spheres, the scattering coefficient $\sigma_{\text{mix}}$ is calculated using volume fraction, $\phi$ of each component:

$$\text{Equation 79} \quad \sigma_{\text{mix}} = \phi_{\text{TiO}_2} \sigma_{\text{TiO}_2} + \phi_{\text{SiO}_2} \sigma_{\text{SiO}_2}$$

For the core-shell particle containing 27.1 volume % titania, $\phi_{\text{TiO}_2}$ is 0.271 and $\phi_{\text{SiO}_2}$ is 0.729. Therefore, $\sigma_{\text{mix}}$ for the mixture of titania and silica spheres computed from Equation 79 is $2.866 \, \mu m^{-1}$, which is 1.7 times greater than the scattering coefficient for the same volumes of titania and silica in the optimized core-shell structure. Similar evaluations of other combinations of $D_{C}$ and $D_{T}$ for silica and titania also reveal no evidence of synergy in the scattering properties of the core-shell structures.

5.1.2.2 Refractive index of medium at 1.0 (air)

White pigment particles in filled paper applications are not surrounded only by cellulose (refractive index 1.45) but instead by both cellulose and air. To address this
point, these calculations have been modified by changing the index of refraction of the surrounding medium from 1.45 to 1.0, that of air. With a surrounding matrix of air, the difference in $\sigma$ between the optimized titania sphere and titania-coated silica spheres is even more pronounced. Figure 30 shows a plot of $\sigma$ versus silica core diameter for the five core-shell particles shown in Figure 26. The $\sigma$ value for a solid titania sphere with diameter $0.20 \mu m$ in Figure 30 is $\sigma \approx 28 \mu m^{-1}$, while the value for a titania-coated silica sphere with outer diameter $0.35 \mu m$ and silica core diameter $0.3 \mu m$ is $\sigma \approx 10 \mu m^{-1}$. This difference is much more pronounced than the values observed in Figure 26. Since pure rutile particles outperform titania-coated silica particles in both a cellulose matrix and an air matrix, it can be concluded that rutile particles are also more efficient in porous paper substrates, in which the medium surrounding the particles is a mixture of cellulose and air.
Figure 30. Scattering coefficient $\sigma$ for the five particles shown in Figure 26, with the cellulose surrounding medium replaced by air (refractive index 1.0 instead of 1.45).

5.2 Anisotropic Spheres of Rutile Titania

5.2.1 Introduction

Attempts to use Mie theory to predict the light scattering properties of a rutile titania particle require approximation to address the optical anisotropy of the crystal. Rutile titania is uniaxial, exhibiting its ordinary refractive index for light polarized parallel to either the $a$ or $b$ axis of the crystal and its extraordinary refractive index for light polarized parallel to the $c$ axis. In this section, the light scattering properties of optically anisotropic spheres of rutile titania have been computed directly for the first time using the time-domain finite element approach.
As described in Section 2.2.1, two methods for approximating rutile as an isotropic material have been proposed in the literature. One approach has been to compute the mean of the refractive indices along the three crystal axes at the light wavelength of interest\(^\text{18}\) and subsequently apply Mie theory to compute far-field scattering parameters. This is the average index approximation. For the light wavelength 560 nm, the average refractive index of rutile titania is 2.74. In these computations, the refractive index of the surrounding medium is 1.51, representing a typical paint resin. The results of Mie theory computations for the scattering coefficient \(S\) using the average index approximation are shown in Figure 31 as a plot of \(S\) versus sphere diameter. The greatest \(S\) values occur for sphere diameters in the range 0.18-0.30 \(\mu\)m, with a maximum value of \(S = 27.74 \text{ \(\mu\)m}^{-1}\) for the diameter 0.272 \(\mu\)m. Likewise, the results of Mie theory computations for the angle-weighted scattering coefficient \(\sigma\) using the average index approximation are shown in Figure 32. The maximum value of the angle-weighted scattering coefficient \(\sigma = 12.17 \text{ \(\mu\)m}^{-1}\) occurs for the sphere diameter 0.20 \(\mu\)m.

A second method for approximating the scattering behavior of rutile titania using isotropic materials has been to compute separately far-field scattering parameters for an isotropic sphere having the ordinary and extraordinary refractive indices of rutile titania, and subsequently compute the weighted sum of these separate far-field results.\(^\text{17,18}\) The weighted sum consists of two-thirds the result for the ordinary refractive index plus one-third the result for the extraordinary refractive index. This is the weighted sum approximation. The results of Mie theory computations for the
scattering coefficient $S$ using the weighted sum approximation are shown in Figure 33 with $S$ plotted as a function of sphere diameter. This result exhibits less pronounced resonant peaks in $S$ than the analogous plot generated using the average index approximation shown in Figure 31. This is expected, since the resonant peaks in the two individual curves used to form the weighted sum are systematically offset from one another. The maximum $S$ values for the weighted sum approximation occur in the range 0.18–0.3 µm, as with the average index approximation. The maximum value $S = 25.08$ µm$^{-1}$ occurs for the diameter 0.270 µm, about 10% lower than the maximum value $S = 27.74$ µm$^{-1}$ observed in the case of the average index approximation. The angle-weighted scattering coefficient $\sigma$ using the weighted sum approximation is shown in Figure 34. This curve is in close agreement with that computed using the average index approximation, shown in Figure 32. In the case of the weighted sum approximation, the maximum value of the angle-weighted scattering coefficient $\sigma = 11.71$ µm$^{-1}$ occurs for the sphere diameter 0.204 µm, about 4% lower than the maximum value of the angle-weighted scattering coefficient $\sigma = 12.17$ µm$^{-1}$ observed in the case of the average index approximation.

The average index and weighted sum approximation results shown in Figure 31–Figure 34 will be used as bases for comparison with results for anisotropic spheres of rutile titania computed using the time-domain finite element method. Results obtained using the finite element method contain the effects of the optical activity of the uniaxial crystal, unlike the results of the average index or weighted sum approximations based upon scattering by isotropic spheres.
Figure 31. Scattering coefficient $S$ versus sphere diameter for an optically isotropic sphere from Mie theory, using the average index approximation.

Figure 32. Angle-weighted scattering coefficient $\sigma$ versus sphere diameter for an optically isotropic sphere from Mie theory, using the average index approximation.
Figure 33. Scattering coefficient $S$ versus sphere diameter for an optically isotropic sphere from Mie theory, using the weighted sum approximation.

Figure 34. Angle-weighted scattering coefficient $\sigma$ versus sphere diameter for an optically isotropic sphere from Mie theory, using the weighted sum approximation.
5.2.2 Scattering By Anisotropic Spheres of Rutile Titania

The light scattering properties of anisotropic, high-index spheres assigned the optical constants of rutile titania with diameters in the range 50–350 nm have been computed using the finite element method. The light wavelength used in these computations is 560 nm. At this wavelength, the ordinary refractive index of rutile titania is 2.64, while the extraordinary index is 2.94. The spatial symmetry elements of an anisotropic, uniaxial sphere include an equatorial mirror plane and a cylindrical rotation axis perpendicular to this mirror plane. (In this description, the optic axis is parallel to the cylindrical rotation axis.) The complete light scattering behavior of such a system can therefore be determined through a series of illuminations along any arc connecting one pole of the sphere to the equator. Six different illumination directions are used for each sphere, at the equally spaced angles 7.5°, 22.5°, 37.5°, 52.5°, 67.5°, and 82.5° relative to the optic axis. Two mutually perpendicular polarizations (parallel and perpendicular to the optic axis of the sphere) are used for each illumination direction, resulting in a total of 12 individual illuminations per sphere. The far-field scattering parameters $S$ and $\sigma$ are computed for each sphere by computing the averages of these two quantities, weighting the individual results by the probabilities of their occurrence under conditions of random illumination (Section 3.2.4). As a result of the cylindrical rotation axis parallel to the optic axis of these spheres, illumination directions nearly perpendicular to the optic axis are significantly more probable than those nearly parallel to the optic axis.
The finite element models for each of the spheres studied consist of a spherical particle at the center of a cubic finite element model. In each case, the sphere is surrounded by an optically isotropic medium with refractive index \( n = 1.51 \), representative of an acrylic, alkyd paint resin. The finite element mesh density differs from model to model but is typically \( \rho = 50-60 \) elements per wavelength in the highest index material in the model. In the case of the 0.2-\( \mu \)m sphere, for example, the cubic element edge length is 3.87 nm. Accuracy analysis of the time-domain finite element approach (Chapter 4) suggests that the numerical error associated with each of the calculations in this study should be less than 2%.

The full near-field results of a finite element computation performed on the anisotropic titania sphere with diameter 0.2 \( \mu \)m are shown in Figure 35. The upper left panel of the figure shows a three dimensional view of the sphere (with the surrounding medium removed for clarity), and the upper right panel shows a cross-sectional slice through the center of the finite element model. The lower two panels show steady-state scattered intensities in the views shown in the two panels above. In this computation, the incident light propagates in the +x direction, and its polarization is parallel to the y direction. The incident intensity of the light is equal to unity. The scattered intensities observed in the model are as much as 4.3 times greater than the incident intensity.

Using the methodology described above, the far-field parameters \( S \) and \( \sigma \) have been computed for a series of anisotropic spheres of rutile titania with diameters in the range 0.05-0.35 \( \mu \)m. Results for the scattering coefficient \( S \) are summarized in Table 5 and plotted versus sphere diameter in Figure 36 (solid circles). These data exhibit a
sharp increase in $S$ as the sphere diameter is increased through the Rayleigh scattering regime from 0.05-0.2 $\mu$m, beyond which resonant peaks are observed with increasing diameter. Results for the angle-weighted scattering coefficient $\sigma$ are likewise summarized in Table 5 and plotted versus sphere diameter in Figure 37 (solid circles). The $\sigma$ data exhibit the same sharp increase the sphere diameter increases from 0.05-0.2. For sphere diameters greater than 0.2 $\mu$m, the $\sigma$ data in Figure 37 decrease without the same pronounced resonant peaks observed in the $S$ data in Figure 36.
Figure 35. Finite element model and scattered intensities for a 0.2-\(\mu\)m anisotropic sphere of rutile titania. The 560-nm radiation propagates in the +x direction, with unit incident intensity. Polarization is parallel to the y direction.
Figure 36. The scattering coefficient $S$ as a function of sphere diameter computed using the finite element method (solid points) for anisotropic spheres of rutile titania with $n = 2.74$ embedded in a medium with $n = 1.51$. The illumination wavelength is 560 nm. The long dashed curve corresponds to the average index approximation, while the dotted curve corresponds to the weighted sum approximation.

Figure 37. The angle-weighted scattering coefficient $\sigma$ as a function of sphere diameter computed using the finite element method (solid points) for anisotropic spheres of rutile titania embedded in a medium with $n = 1.51$. The illumination wavelength is 560 nm. The long dashed curve corresponds to the average index approximation, while the dotted curve corresponds to the weighted sum approximation.
Table 5. Scattering coefficients $S$ and $\sigma$ computed for anisotropic spheres of different diameter using the finite element approach.

<table>
<thead>
<tr>
<th>Diameter ($\mu$m)</th>
<th>$S$ ($\mu$m$^{-1}$)</th>
<th>$\sigma$ ($\mu$m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>0.587</td>
<td>0.564</td>
</tr>
<tr>
<td>0.100</td>
<td>4.52</td>
<td>3.79</td>
</tr>
<tr>
<td>0.150</td>
<td>12.50</td>
<td>7.03</td>
</tr>
<tr>
<td>0.175</td>
<td>20.06</td>
<td>8.82</td>
</tr>
<tr>
<td>0.187</td>
<td>23.94</td>
<td>11.73</td>
</tr>
<tr>
<td>0.200</td>
<td>25.62</td>
<td>12.34</td>
</tr>
<tr>
<td>0.212</td>
<td>22.27</td>
<td>11.30</td>
</tr>
<tr>
<td>0.225</td>
<td>21.01</td>
<td>10.37</td>
</tr>
<tr>
<td>0.250</td>
<td>22.17</td>
<td>9.41</td>
</tr>
<tr>
<td>0.275</td>
<td>25.83</td>
<td>9.68</td>
</tr>
<tr>
<td>0.300</td>
<td>22.10</td>
<td>9.07</td>
</tr>
<tr>
<td>0.325</td>
<td>18.89</td>
<td>9.43</td>
</tr>
<tr>
<td>0.350</td>
<td>18.91</td>
<td>8.44</td>
</tr>
</tbody>
</table>
5.2.3 Angle and Polarization Dependence of Scattering by an Anisotropic Titania Sphere

An essential difference between radiation scattering by an optically anisotropic sphere versus an optically isotropic sphere is the dependence of the far-field scattering properties upon illumination direction and polarization. This orientation dependence results from the optical activity of the optically anisotropic sphere. In addition, an optically anisotropic sphere exhibits polarization dependence in its far-field scattering parameters for a given illumination direction, with the exception of the special case where the incident radiation propagates parallel to the optic axis of the sphere. These effects have been observed in the scattering properties of each of the anisotropic spheres studied here. The combined effects of the direction of light incidence and polarization upon scattering properties for the case of the 0.2-µm sphere are shown in Figure 38. Plotted in this figure is the scattering coefficient $S$ versus the angle of light incidence for polarization both parallel to (filled circles) and perpendicular to (hollow circles) the optic axis of the sphere; the angle of incidence is measured between the propagation direction of the incident light and the optic axis. The curves in Figure 38 converge to the same values at low angles of incidence; this is expected, since both polarizations of light incident at low angles encounter primarily the ordinary refractive index of the crystal. As the angle of incidence increases, the scattering coefficient associated with polarization parallel to the sphere optic axis increases markedly as the light increasingly encounters the higher, extraordinary index of the rutile crystal. For polarization
perpendicular to the optic axis, however, no component of the incident light is exposed to the extraordinary refractive index of the crystal, resulting in no dependence of $S$ upon the angle of incidence. The scattering coefficient $S$ for unpolarized light incident for any of the angles shown in Figure 38 can be computed by averaging the $S$ values associated with the two orthogonal polarizations.

![Graph showing scattering coefficient $S$ as a function of angle of incidence](image)

**Figure 38.** Scattering coefficient $S$ as a function of the angle of incidence (relative to the optic axis) for the 0.2-µm anisotropic sphere of rutile titania. Hollow circles are for polarization perpendicular to the optic axis of the sphere; filled circles are for polarization coplanar with the optic axis.

5.2.4 On the Validity of the Average Index and Weighted Sum Approximations

A question of central interest in this study is to what degree the average index and weighted sum approximations described in Section 5.2.1 succeed in predicting the far-field scattering parameters associated with the anisotropic spheres investigated here.
Agreement in the scattering coefficient $S$ between the results computed using the finite element method (solid circles) and both the average index (dashed curve) and the weighted sum (dotted curve) approximations is shown in Figure 36. In both cases, agreement between the finite element method results for anisotropic spheres and the approximate approaches is very good for diameters 0.18 $\mu$m and smaller. The weighted sum approximation underestimates the first resonant peak in the finite element results (0.2–$\mu$m sphere), though the average index approximation accurately matches this peak value. For diameters greater than 0.2 $\mu$m, differences of up to 10% occur between the two approximations and the finite element results. The three data sets in Figure 36 suggest that the periodicity of the resonant peaks in the finite element results is longer than in either of the two approximations. It has been suggested that such resonant peaks arise from resonant surface waves on a sphere;\textsuperscript{2} it is therefore reasonable that the different symmetry of an anisotropic sphere compared to an isotropic should result in a quantitatively different behavior of such resonances. It is not clear why the period of the resonant peaks associated with anisotropic spheres are longer than either of the two approximations based upon isotropic spheres. Comparison of the average index and weighted sum approximation data sets in Figure 36 indicate that the main difference between the two is that the resonant peaks in the weighted sum approximation are less sharp. That approximation is a weighted superposition of two curves which are slightly offset with respect to sphere diameter, resulting in averaging of the resonant peaks.

The agreement in the angle-weighted scattering coefficient $\sigma$ between the finite element method (solid circles) and both the average index (dashed curve) and weighted
sum (dotted curve) approximations are shown in Figure 37. In analogy with results for
the scattering coefficient $S$ in Figure 36, agreement between the finite element data and
both approximations is very good for diameters less than 0.18 $\mu$m. For sphere
diameters greater than this value, the data sets contain the same resonant features, with
the period of the resonant peaks for the finite element data again being greater than that
of the average index approximation. In both $S$ and $\sigma$, the maximum values in the
average index approximation (sphere diameter $\sim$0.2 $\mu$m) are in very good agreement
with the finite element data. The most significant disagreement between the weighted
sum approximation and the finite element data occurs around the primary resonant
peak, around 0.2 $\mu$m. The average index approximation more accurately fits this first
resonant peak than the weighted sum approximation in both $S$ and $\sigma$.

The statistical quantity $\chi^2$ has been computed as a means to quantify the ability
of both the average index and weighted sum approximations to predict the results for $S$
and $\sigma$ of anisotropic spheres obtained using the finite element method. The complete
data sets in Figure 36 and Figure 37 were used. The quantity $\chi^2$ has been computed as

$$\chi^2 = \sum_{k=1}^{n} \frac{(O_k - E_k)^2}{E_k}$$

where $n$ is the number of data points (thirteen, in this case), $O_k$ is the value of $S$ or $\sigma$
computed for a given sphere diameter using either the average index or weighted sum
approximations, and $E_k$ is the value of $S$ or $\sigma$ computed for the sphere diameter using
the finite element method. The values of $\chi^2$ computed for the average index and
weighted sum approximations are summarized in Table 6 for both quantities $S$ and $\sigma$. The value of $\chi^2$ is significantly smaller than the number of data points for each data set, indicating a very good statistical fit in each case. For both $S$ and $\sigma$, the weighted sum approximation exhibits slightly lower $\chi^2$ values than the weighted sum approach, but this can be reversed by selectively omitting certain discrete data points from the data sets, indicating no clear advantage to either approach from the statistical standpoint.

While both the average index and weighted sum approximations are in good statistical agreement with the results of finite element computations for anisotropic spheres, there are possible advantages associated with each for a given circumstance. The average index approximation offers the advantage of explicitly defining a single refractive index for the material, therefore requiring only a single set of computations to obtain far-field results. The weighted sum approximation offers the advantage of smoothing out the sharp resonant peaks associated with particular sphere diameters in Mie theory computations, artifacts of the high symmetry of a sphere which in practice are not observed in light scattering by real systems of multiple particles.

| Table 6. Values of $\chi^2$ (Equation 80) associated with $S$ and $\sigma$ values for the average index and weighted sum approximation, compared to anisotropic sphere scattering data generated using the finite element approach. |
|---|---|---|
| **Average Index Approximation** | $S$ | 0.71
| | $\sigma$ | 0.44 |
| **Weighted Sum Approximation** | $S$ | 0.60
| | $\sigma$ | 0.33 |
5.3 **Scattering by a Morphological Rutile Titania**

5.3.1 **Introduction**

A fundamental goal of both consumers and manufacturers of rutile titania pigment is to maximize the light scattering efficiency of the pigment in end use. The achievement of this goal requires quantitatively identifying, and subsequently controlling, the factors which impact the light scattering efficiency of rutile titania powders. This light scattering efficiency is controlled by a number of factors, including the particle size distribution, the degree of particle agglomeration, and the degree of optical interaction between neighboring particles in a pigmented microstructure. However, the quantitative influence of each of these factors upon the scattering efficiency of rutile titania is not fully understood, due in large part to the difficulty of controlling laboratory experiments to the degree that the effect of each can be studied independently.\(^5,6\)

Due to these inherent experimental challenges, theoretical modeling attempts have been made to understand light scattering properties of rutile titania. These efforts have typically relied upon Mie theory, which provides an exact treatment of the light scattering properties of a single, optically isotropic sphere.\(^1,2,48\) Examples of such studies include investigation of the theoretical scattering efficiency of rutile titania versus that of air voids,\(^17\) the crowding effect in highly loaded films,\(^25,26,28,7\) and the application of a multiple scattering model to predict the light scattering efficiency of
In reality, individual rutile titania particles exhibit both optical anisotropy and complex shapes. In addition, pigmented films typically contain multiple-particle aggregates in which near-field optical interactions between neighboring particles play a critical role. Mie theory is therefore not capable of rigorously describing the light scattering properties of realistic rutile titania particle shapes and microstructures. To illustrate this point, a high-resolution scanning electron micrograph of a commercial rutile titania pigment powder is shown in Figure 39. Both the characteristic, non-spherical shape of the primary particles and particle aggregation are apparent in the micrograph.

![Figure 39. High resolution scanning electron micrograph of rutile titania particles, showing their characteristic, morphological shapes. (Micrograph courtesy E.D. Boyes, DuPont Central Research and Development.)](image)
5.3.2 Scattering by a Morphological Rutile Particle

Here, the time-domain finite element approach has been applied to the case of 560-nm light scattering by a single, morphological rutile titania particle. This particle, shown in the upper panels of Figure 40, has a width 0.175 µm and a tip-to-tip length of 0.35 µm. The shape and size of this particle is representative of rutile titania pigment and has been chosen to illustrate the scattering properties of a typical pigment particle. In contrast to the finite element computations performed for the case of a single sphere in the Section 3 of this study, this rutile particle has been assigned the appropriate anisotropic optical constants. As in the calculations described above, the particle is surrounded by a medium with refractive index $n = 1.51$, representative of an acrylic resin. This model contains ~1.6 million cubic elements, 3.6 nm on edge. This corresponds to a finite element mesh density of $\rho = 50$ elements per light wavelength in the model. The upper left panel of Figure 40 shows a three-dimensional view of the sphere with the surrounding medium hidden; the cubic elements which compose the particle are visible. The upper right panel shows a cross-sectional view of the finite element model, including the particle and the surrounding medium. In this case, light is propagating in the finite element model with components in both the +x and +z directions with unit incident intensity. The lower two panels of Figure 40 show scattered intensities in the geometric domains displayed in the corresponding upper panels. As in the case of the spherical particle shown in Figure 10, scattered intensities in the near field can be several times greater than the incident intensity.
In general, the rutile titania particles in a paint film are randomly oriented. In order to determine the light scattering properties of the morphological, anisotropic rutile particle shown in Figure 40 under conditions of diffuse illumination, a set of individual finite element computations with different angles of light incidence are performed. Two individual plane waves having mutually perpendicular polarizations are used for each illumination direction. To determine far-field scattering properties under conditions of random illumination, far-field intensities for the individual illuminations are superimposed. The presence of four different mirror planes in the spatial symmetry of the rutile particle shown in Figure 40 requires that only one half-octant of the particle be illuminated to determine the full light scattering properties of the particle. In the present case, fifteen different illumination directions were employed over one half-octant of the particle, which is equivalent to one hundred eighty illumination directions over the entire particle. Using the finite element method, the far-field scattering parameters $S = 23.97 \, \mu m^{-1}$ and $\sigma = 10.07 \, \mu m^{-1}$ have been computed for the rutile particle shown in Figure 40.
Figure 40. Finite element model and near field scattering results for an anisotropic, morphological rutile particle with a width of 0.175 µm, and a length of 0.35 µm in $n = 1.51$ resin; the light wavelength is 560 nm.
5.3.3 Discussion

5.3.3.1 Scattering Coefficients of the Morphological Rutile Particle

It is of interest to compare the far-field scattering parameters $S$ and $\sigma$ computed for the rutile particle to those from Mie theory for the sphere with equivalent volume, using both the average index and weighted sum approximations. The volume of the rutile particle shown in Figure 40 is $7.77 \times 10^{-3} \, \mu m^3$, corresponding to an equivalent spherical diameter of $0.246 \, \mu m$. Such comparisons provide a sense of the adequacy of Mie theory to describe the optics of realistic rutile particles. Table 7 shows the results of this comparison, with $S$ and $\sigma$ values shown for the finite element computation for the rutile particle and for the equivalent volume sphere computed using both the average index and weighted sum approximations. For the average index approximation, the $S$ result is 1.4% lower than the finite element result, and the angle-weighted scattering coefficient $\sigma$ result is 4.6% higher than the finite element result. For the weighted sum approximation, the $S$ result is 6.4% lower than the finite element result, and the angle-weighted scattering coefficient $\sigma$ is in agreement with the finite element result. For this particular rutile particle, at least, the scattering properties of the equivalent volume sphere computed using the two approximations and Mie theory are within ~5% of the finite element result.
5.3.3.2 Mie Theory in Particle Size Analysis by Light Scattering

It is common practice in particle sizing methods based upon light scattering to use Mie theory to compute particle size distributions for particles which are in reality non-spherical. In these methods, the light scattering properties of a system are used to determine equivalent spherical particle sizes by fitting scattering data to a size distribution. It is therefore of considerable interest to compare the results of the finite element calculations on systems containing realistically shaped rutile particles to the results of Mie theory. This can be achieved by back-calculating equivalent spherical diameters corresponding to the morphological rutile particle based upon the scattering parameters $S$ and $\sigma$ rather than upon particle volume (as in Table 7).

Using the results $S = 23.97 \, \mu m^{-1}$ and $\sigma = 10.07 \, \mu m^{-1}$ for the isolated rutile particle shown in Figure 40, the Mie theory results shown in Figure 31–Figure 34 have been used to compute the spherical diameters exhibiting these same far-field scattering parameters. These results are shown in Table 8. For both the average index and weighted sum approximations, four different spherical diameters correspond to matching $S$ values, and two different spherical diameters correspond to matching angle-weighted scattering coefficient $\sigma$ values. The multiple sphere diameters corresponding to the single $S$ and $\sigma$ values associated with this particle result from multiple occurrences of these values in the curves shown in Figure 31–Figure 34. These results highlight the potential ambiguity in using Mie theory to impute equivalent spherical diameters to non-spherical particles based upon far-field scattering properties.
Table 7. Comparison between the far-field scattering coefficients for the single rutile particle and the equivalent volume sphere, using both the average index and weighted sum approximations.

<table>
<thead>
<tr>
<th></th>
<th>$S$ (μm$^{-1}$)</th>
<th>$\sigma$ (μm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anisotropic Rutile Particle w=0.175 μm, Aspect Ratio 2</td>
<td>23.97</td>
<td>10.07</td>
</tr>
<tr>
<td>Equivalent-Volume Sphere $n = 2.74$</td>
<td>22.44</td>
<td>10.07</td>
</tr>
<tr>
<td>Equivalent-Volume Sphere Weighted Sum of $n = 2.64$ and $n = 2.94$ Results</td>
<td>23.64</td>
<td>10.54</td>
</tr>
</tbody>
</table>

Table 8. Diameters of spheres exhibiting the same far-field scattering coefficients as the single rutile particle, using both the average index and weighted sum approximations.

<table>
<thead>
<tr>
<th></th>
<th>$S$ Basis</th>
<th>$\sigma$ Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent Spherical Diameter $n = 2.74$</td>
<td>0.186 μm or 0.212 μm or 0.254 μm or 0.293 μm</td>
<td>0.183 μm or 0.247 μm</td>
</tr>
<tr>
<td>Equivalent Spherical Diameter Weighted Sum of $n = 2.64$ and $n = 2.94$ Results</td>
<td>0.190 μm or 0.204 μm or 0.248 μm or 0.287 μm</td>
<td>0.179 μm or 0.261 μm</td>
</tr>
</tbody>
</table>


Chapter 6. Clusters of Latex Spheres: A Low-Contrast System

This chapter describes the light scattering properties of clusters of latex particles in water studied using the time-domain finite element method. Using synthesis methods such as emulsion polymerization, polymeric materials can be formed as sub-micron latex particles which are spherical in shape and can be nearly monodisperse in size. The use of latex particles is widespread in polymer processing, since these materials can be readily dispersed in liquids and subsequently formed into complex shapes. Latex particles can be stabilized in water, allowing the elimination of potentially flammable and toxic volatile organic solvents from the processing of the sol. This valuable attribute of latices has created a very large market for latex-based paint systems. The near monodispersity and controllable dispersion characteristics of latex systems makes them ideal for model studies of particle agglomeration dynamics in liquid suspensions. These agglomeration characteristics can be studied by microscopy, rheological measurements, and light scattering techniques.

In Section 6.1, the general scattering properties of the materials system of interest are described. In Section 6.2, the effects of latex particle agglomeration upon the scattering properties of the system are described. In Section 6.3, the length scale over which near-field optical interactions between neighboring latex particles are determined. The computational results presented in this chapter are placed within the context of scattering efficiency and hiding power. The latex system studied here is of particular interest because it is a widely used system with low optical contrast,
providing a valuable basis for comparison with the results for clusters of white pigment particles with high optical contrast described in Chapter 7.

6.1 Materials System of Interest

The system of interest in the present work is a latex material with refractive index \( n = 1.50 \) in a water medium with refractive index \( n = 1.33 \). The illuminating wavelength is 488 nm, a commonly used argon ion laser wavelength. A plot of the scattering coefficient \( S \) versus diameter for a single sphere calculated using Mie theory for these conditions is shown in Figure 41. The sphere diameter producing the maximum \( S \) value is 1.4 µm. The low optical contrast of this system produces significantly lower \( S \) values (one order of magnitude) than the high-contrast pigment particle systems studied in the previous chapter. A plot of the angle-weighted scattering coefficient \( \sigma \) versus sphere diameter calculated using Mie theory for the latex system is shown in Figure 42. The sphere diameter producing the maximum \( \sigma \) value is 0.18 µm. This value is significantly smaller than the 1.4 µm diameter producing the maximum \( S \) value in Figure 41. This result indicates that the quantity \((1-g)\), where the asymmetry parameter \( g \) is the average cosine of the scattering angle, decreases sharply with increasing sphere diameter in the sub-micron size range. That is, there is a rapid transition from isotropic to forward scattering as the latex particle size increases beyond the Rayleigh regime. The primary particle size studied here is 200 nm, a representative latex particle diameter. This sphere diameter is indicated in the plots of Figure 41 and Figure 42 with an “x”; this particle size provides an especially interesting case since it is
sub-optimal for the scattering coefficient $S$ and very nearly optimal for the angle-weight scattering coefficient $\sigma$.

The light scattering properties of a single 200-nm latex sphere in water has been computed using the time-domain finite element method. Shown in Figure 43 are the model geometry and near field scattered intensities for this computation. The 488-nm light propagates in the $+x$ direction and is polarized in the $z$ direction. The top two panels of this figure show a three-dimensional view of the scattering sphere and a cross-sectional slice through the center of the model, respectively. The bottom two panels of this figure show the near-field scattered intensities as a function of position in the geometries shown in the top two panels. In contrast with the titania sphere in resin shown in Figure 10, the latex sphere shown in Figure 43 exhibits scattered intensities in the near field which are much smaller than the unit intensity of the incident light. This is a result of the relatively low optical contrast of the latex system. The distribution of scattered light in Figure 43 shows that most of the light is scattered in the forward direction, with two lobes of concentrated light on the forward-scattering hemisphere of the particle. The computed values of the scattering coefficients $S$ and $\sigma$ from the results shown in Figure 43 are within 0.8% and 0.9% of the exact results computed from Mie theory, respectively, showing close agreement.
Figure 41. The scattering coefficient \( S \) as a function of sphere diameter for a latex particle with \( n = 1.50 \) in a water medium with \( n = 1.33 \). The illuminating light wavelength is 488 nm. The 200-nm sphere diameter studied in this chapter is marked with an “x.”

Figure 42. The angle-weighted scattering coefficient \( \sigma \) as a function of sphere diameter for a latex particle with \( n = 1.50 \) in a water medium with \( n = 1.33 \). The illuminating light wavelength is 488 nm. The 200-nm sphere diameter studied in this chapter is marked with an “x.”
Figure 43. Finite element model for a 200-nm latex sphere with $n = 1.50$ in a water medium with $n = 1.33$. The illuminating wavelength is 488 nm, and light propagates in the $+x$ direction.
6.2 Light Scattering by Latex Sphere Clusters of Increasing Size

A series of computations has been performed using the time-domain finite element method to determine the light scattering properties of particle clusters containing increasing numbers of the 200-nm primary particle shown in Figure 43. Cluster sizes investigated consisted of 2, 3, 6, 7, 8, 13, 27 and 64 primary particles. The packings of these particles are not identical in each case; instead, the highest-symmetry arrangements have been selected. For example, the clusters of 8, 27, and 64 spheres share a simple cubic packing, while the cluster of 13 spheres has a face-centered cubic packing. The geometries of the clusters containing 3, 7, 13, and 27 spheres are shown in Figure 44 as examples of the cluster packings. In each computation, random illumination conditions are simulated using the Illuminator software, yielding orientation-averaged scattering coefficients along with the individual scattering results for each illumination direction and polarization.

Near-field optical interactions between the latex spheres in these clusters can be expected to occur and thus produce light scattering properties which differ from those of the isolated, 200-nm latex primary particle which composes each cluster. The finite element method permits direct visualization of these near-field interactions. Shown in Figure 45 are geometric views of the cluster containing seven 200-nm latex particles and the distribution of scattered light intensity in the near field. The top two panels of this figure show a three-dimensional view of the spheres and a cross-sectional slice through the center of the model, while the bottom two panels show the distribution of
scattered light through these two geometric views. The geometry of this model consists of a central sphere surrounded by two neighboring spheres along each of the three axes of the Cartesian coordinate system. As in all of the sphere clusters constructed in this study, the spheres are in hard contact with their neighbors. The 488-nm light propagates in the +x direction in the computation shown in Figure 45. The lower two panels of Figure 45 demonstrate clearly that near-field scattered light in the seven-sphere cluster is not distributed evenly among the seven primary particles in the cluster as would be the case in the limit of single scattering. Instead, the greatest intensity of scattered light is in the forward-scattering hemisphere of the cluster. This result is significant and illustrates a phenomenon which is observed in all computations performed on these latex sphere clusters: a cluster of latex spheres scatters light as a single entity rather than as a collection of independent particles. This fact lies at the root of the dramatic effects of sphere clustering upon light scattering which are described in this and the following sections of this chapter.

The effects of latex particle clustering upon the scattering coefficient $S$ are shown in Figure 46 with $S$ plotted as a function of the number of spheres contained in a cluster. There is a steady increase in $S$ as additional particles are added to the cluster. A discontinuity occurs for the case of the seven-sphere cluster; this is likely due to the relatively low packing density of this cluster (see Figure 45) compared to the others. The $S$ results shown in Figure 46 indicate that the efficiency of light scattering by these latex clusters increases on a volume-normalized basis with increasing numbers of primary particles in a cluster. The value of $S$ for a six-sphere cluster is two times that
associated with a single latex primary, for example, and the value for a sixty-four-sphere cluster is nearly four times that associated with the isolated primary.

The quantity \((1-g)\) is plotted in Figure 47 as a function of the number of latex spheres in a cluster. The data indicate a sharp decrease in this term as cluster size increases, corresponding to a decrease in the fraction of light deflected away from the forward-scattered direction. This decrease in \((1-g)\) is the opposite of the trend observed in the scattering coefficient \(S\). That is, while clustering of greater numbers of the 200-nm latex spheres causes increased scattered intensity on a volume-normalized basis, this additional scattered intensity is directed more strongly in the forward direction. The opacifying efficiency of these clusters in an aqueous dispersion depends upon the angle-weighted scattering coefficient \(\sigma\), which is the product of \(S\) and \((1-g)\). The opposite trends observed in \(S\) and \((1-g)\) indicate that the dependence of \(\sigma\) upon the number of spheres in a cluster is less strong than the case of either \(S\) or \((1-g)\).

The effects of latex particle clustering upon the scattering coefficient \(\sigma\) are shown in Figure 48 with \(\sigma\) plotted as a function of the number of spheres contained in a cluster. In contrast to the results of Figure 46 for the scattering coefficient \(S\), the plot in Figure 48 in general shows a steady, but only slight, decrease in \(\sigma\) with increasing numbers of latex spheres in a cluster. The global maximum in the data corresponds to the case of a two-sphere cluster, exhibiting a \(\sigma\) value which is 5% greater than that of the isolated latex primary. For larger clusters, there is little change in the data between the cases of 13-, 27-, and 64-sphere clusters. The cluster of thirteen particles exhibits a
\(\sigma\) value which is 25\% lower than that associated with the isolated latex primary, and the cluster of sixty-four primary particles exhibits a value which is about 15\% lower than the isolated latex primary. It can be concluded that, in general, clustering of these latex spheres over the size range investigated here results in poorer scattering efficiency for a dispersion of these particles compared to the case where no particle agglomeration is present.
Figure 44. Finite element models of latex sphere clusters containing 3, 7, 13, and 27 spheres.
Figure 45. Finite element model of a cluster of seven 200-nm latex spheres $n = 1.50$ in a water matrix with $n = 1.33$. The 488-nm illuminating light propagates in the +x direction and is polarized in the z direction.
Figure 46. The scattering coefficient $S$ as a function of the number of 200-nm latex particles composing a particle cluster under conditions of random illumination.

Figure 47. The quantity $(1-g)$ as a function of the number of 200-nm latex spheres composing a particle cluster under conditions of random illumination.
6.3 Near-Field Interactions Between Neighboring Latex Particles

In the previous section, it has been demonstrated that clusters of 200-nm latex spheres can exhibit substantially different scattering efficiencies than the individual primary particles composing them. That result calls into question of the length scale of interparticle separation over which near-field interactions between the particles are important. In this section, this question is investigated in model systems containing a small number of 200-nm latex particles illuminated with 488-nm light. These model systems are based upon the geometry of the seven-sphere cluster shown in Figure 45; the spacing between the central sphere and the six surrounding spheres are uniformly varied from one computation to the next. In the case of a 0.4-µm interparticle separation, for example, each of the six surrounding spheres is positioned to have a 0.4-
µm surface-to-surface interparticle separation from the central sphere. The resulting shape of the cluster is therefore an octahedron for each interparticle separation distance investigated. Conditions of random illumination are simulated for each separation distance using the Illuminator software, and scattering efficiencies are computed on an orientation-averaged basis as in Section 6.2.

The geometry of the model with 0.4-µm surface-to-surface interparticle separation distance is shown in Figure 49. The upper two panels of this figure show a three-dimensional view of the latex spheres and a cross-sectional slice through the center of the finite element model. Five of the spheres in the seven-sphere cluster are bisected by this cross-sectional slice; the other two particles are positioned in the +z and –z directions in the model (out of the page, and into the page, respectively). Shown in the lower two panels are the distributions of near-field scattered light intensity on the surfaces of the seven spheres and through the cross-sectional slice through the center of the model. The incident 488-nm light is polarized in the z-direction in this computation and propagates in the +x direction in the model. There are several interesting features in the distributions of scattered light intensity in the near field for this computation. First, it is clear in both the surface and cross-sectional views that each of the seven individual latex spheres do not exhibit the same distribution of scattered light on their surfaces or through their cross-sections. Instead, the two spheres positioned in the forward scattering (+x) direction appear to have greater scattered intensities in their immediate vicinity than the other spheres in the cluster. This suggests that at this 0.4-µm separation, the seven particle are interacting optically in the near field rather than
scattering independently. This interaction is evident in the scattered intensity distribution in the cross-sectional slice through Figure 49, in which faint scattered intensity is visible in the spaces between the five particles visible in that view. It is also interesting to compare the results for 0.4-µm interparticle separation distance in Figure 49 with those for the touching spheres in Figure 45. It is evident that while the seven spheres separated by 0.4 µm do not scatter light independently, the distribution of scattered light between those spheres is more even than the distribution of scattered light in the cluster of touching spheres. That is, these near-field results suggest that the light scattering properties of the cluster with 0.4-µm interparticle separation should be much closer to the result for seven isolated spheres than the case of the cluster of seven touching spheres.

The dependence of the scattering coefficient $S$ upon surface-to-surface interparticle separation distance for the clusters of seven latex spheres is shown in Figure 50. The dashed line in this plot corresponds to the $S$ value associated with a single, isolated 200-nm latex primary particle. Deviations from this dashed line are the result of near-field interactions between neighboring spheres in the clusters. At the maximum interparticle separation distance studied, 0.6 µm, the $S$ value exhibited by the seven-sphere cluster is only 5% greater than that of a single 200-nm latex primary particle. The data in Figure 50 indicate a steady increase in $S$ as the interparticle spacing between the spheres in the cluster decreases to zero. For the case of zero interparticle separation distance (touching spheres, Figure 45), the value of $S$ is 0.88 µm$^{-1}$, which is 80% greater than the value associated with a single primary particle.
The interparticle separation distance at which the seven-sphere cluster exhibits an $S$ value more than 10% greater than that of an isolated 200-nm primary particle is 0.35 $\mu$m, which is very close to the effective wavelength of the 488-nm light in water with $n = 1.33$ refractive index.

The quantity $(1-g)$ is plotted in Figure 51 as a function of interparticle separation distance between the seven-sphere clusters. The dashed line in the plot indicates the value associated with a single 200-nm latex primary particle. As in the case of particle agglomeration investigated in Section 6.2, the quantity $(1-g)$ exhibits the opposite trend from the scattering coefficient $S$, decreasing sharply as the interparticle separation distance approaches zero. That is, as the seven spheres in these clusters approach each other and interact more strongly optically, the total amount of light scattering increases but this scattered intensity is directed more strongly in the forward direction. The value of $(1-g)$ for the case of touching spheres is 46% lower than that of a single 200-nm latex primary particle.

The dependence of the angle-weighted scattering coefficient $\sigma$ upon interparticle separation distance in the seven-sphere clusters is shown in Figure 52. As in Figure 50 and Figure 51, the dashed line in this figure corresponds to the value associated with a single 200-nm latex primary particle. The data indicate a relatively weak dependence of $\sigma$ upon interparticle separation distance, compared to either $S$ or $(1-g)$. The value associated with zero interparticle separation is just 5% less than that associated with a single 200-nm latex primary particle. In contrast to the data for $S$ and $(1-g)$, the $\sigma$ data
oscillate about the value associated with the single latex primary particle, exceeding it by about 3% with a 0.25-µm interparticle separation distance. The data appears to have an oscillatory character, but the amplitude of this oscillation is not large compared to the 1-3% error level expected in these computations.
Figure 49. Finite element model of a cluster of seven 200-nm latex spheres $n = 1.50$ in a water matrix with $n = 1.33$. The surface-to-surface interparticle spacing is 0.4 µm. The 488-nm illuminating light propagates in the $+x$ direction and is polarized in the $z$ direction.
Figure 50. Dependence of the scattering coefficient $S$ upon surface-to-surface interparticle separation distance for the clusters of seven latex spheres. The dashed line corresponds to the value associated with a single 200-nm latex primary particle.

Figure 51. Dependence of the quantity $(1-g)$ upon surface-to-surface interparticle separation distance for the clusters of seven latex spheres. The dashed line corresponds to the value associated with a single 200-nm latex primary particle.
Figure 52. Dependence of the angle-weighted scattering coefficient $\sigma$ upon surface-to-surface interparticle separation distance for the clusters of seven latex spheres. The dashed line corresponds to the value associated with a single 200-nm latex primary particle.
Chapter 7. Clusters of Titania Particles: A High-Contrast System

Chapters 2 and 5 have emphasized the technological importance of the light scattering properties of high-index white pigment particles. The present chapter describes the effects of near-field interactions between white pigment particles upon scattering efficiency in several different systems. As stated previously, optical interactions between neighboring white pigment particles are known to have profound impact in end-use applications, yet the fundamental aspects of these phenomena have not been directly studied successfully. In Section 7.1, the general scattering properties of the materials system of interest are established. In Section 7.2, the effects of clustering primary pigment particles which are optimized for scattering efficiency is described. In Sections 7.3 and 7.4, the magnitude of near-field interactions between separated particles is investigated for the cases of a seven-sphere cluster and of two morphological rutile particles, respectively.

7.1 Materials Systems of Interest

In Sections 7.2 and 7.4, the results of studies upon the light scattering properties of systems of multiple 200-nm spheres of high-index material are described. The system investigated is that of a high-index material \( n = 2.74 \) embedded in a medium with index of refraction \( n = 1.51 \). The light wavelength studied is 560 nm. This system is representative of rutile titania spheres using the average index approximation. The sphere diameter studied here, as in the case of the latex system in the previous chapter,
is 200 nm. A plot of the scattering coefficient $S$ versus diameter for a single sphere calculated using Mie theory is shown in Figure 53. The sphere diameter producing the maximum $S$ value of 28 $\mu$m$^{-1}$ is 0.3 $\mu$m. A plot of the angle-weighted scattering coefficient $\sigma$ versus diameter for a single sphere calculated using Mie theory is shown in Figure 54. The sphere diameter producing the maximum $\sigma$ value of 12.1 $\mu$m$^{-1}$ is 0.2 $\mu$m. The 200-nm rutile sphere diameter studied here is indicated in each of these two plots with an “x”. The 200-nm diameter studied here is that corresponding to the maximum of the first resonant peak in $S$ in the plot shown in Figure 53. In addition, this sphere diameter produces the maximum $\sigma$ value for this materials system. This particle size may therefore be expected to produce qualitatively different behaviors upon clustering than the 200-nm latex sphere studied in the previous chapter.

The light scattering properties of the single 200-nm rutile sphere under these conditions has been computed using the time-domain finite element method; these results are shown in Figure 10. A comparison of the near-field scattered intensities in Figure 10 with those of the single latex sphere shown in Figure 43 indicates that the main difference between these two systems is the much higher scattered intensities in the vicinity of the titania sphere in Figure 10. Indeed, these near-field scattered intensities are about 50 times higher than in the case of the latex particle. It is the greater optical contrast between the titania particle and its surrounding medium, combined with the resonant diameter of the titania sphere, which produces this stronger scattering interaction.
Figure 53. The scattering coefficient $S$ as a function of sphere diameter for a rutile particle with $n = 2.74$ in a polymer medium with $n = 1.51$ under the average index approximation. The illuminating light wavelength is 560 nm. The 200-nm sphere diameter studied in this chapter is marked with an “x.”

Figure 54. The angle-weighted scattering coefficient $\sigma$ as a function of sphere diameter for a rutile particle with $n = 2.74$ in a polymer medium with $n = 1.51$ under the average index approximation. The illuminating light wavelength is 560 nm. The 200-nm sphere diameter studied in this chapter is marked with an “x.”
7.2 Light Scattering by Titania Sphere Clusters of Increasing Size

As in the case of the latex particles in the previous chapter, a series of computations has been performed using the time-domain finite element method to determine the light scattering properties of particle clusters containing increasing numbers of the 200-nm rutile sphere shown in Figure 10. Cluster sizes investigated consisted of 2, 3, 4, 6, 7, 8, 13, 20, 27 and 64 primary particles. The same geometrical packings used in the case of the latex particles have been used here. In each case, random illumination has been simulated using the Illuminator software, yielding orientation-averaged scattering coefficients along with the individual scattering results for each illumination direction and polarization.

Shown in Figure 55 are geometric views of the cluster containing seven titania particles and the distribution of scattered light in the near field. (Figure 45 shows the analogous case for latex particles). The top two panels show a three dimensional view of the spheres and a cross-sectional slice through the center of the model, while the bottom two panels show the distribution of scattered light at steady state through these two geometric views. The 560-nm light propagates in the +x direction in this case. As in the case of the clustered latex spheres, the results in Figure 55 show that the distribution of scattered light through the seven-sphere cluster is not uniform. Instead the greatest concentration of scattered light is in the forward-scattering hemisphere of the cluster. The incident light intensity for the computation shown in Figure 55 is unity. In the lower two panels of this figure, the maximum scattered intensities observed are therefore about 9 times higher than the incident intensity, indicating that the titania
cluster focuses scattered light in the forward direction. A comparison of near-field scattered intensities observed for the seven-sphere cluster of titania spheres with those observed for the single primary particle (Figure 10) indicate scattered intensities which are about 3 times higher for the cluster.

The effects of titania particle clustering upon the scattering coefficient \( S \) are shown in Figure 56 with \( S \) plotted as a function of the number of spheres contained in a cluster. There is an increase in \( S \) by about 15% as a second sphere is added to the first, and then a dramatic decrease in general as more particles are added to the cluster. The \( S \) value associated with the thirteen-sphere cluster is 50% less than that associated with an isolated primary particle, and the value associated with the sixty-four sphere cluster is about 75% less than that of the isolated primary. In general, clustering of 200-nm titania spheres results in markedly reduced total scattering on a volume-normalized basis compared to the case of the isolated primary.

The effects of titania particle clustering upon the angle-weighted scattering coefficient \( \sigma \) are shown in Figure 57 with \( \sigma \) plotted as a function of the number of spheres contained in a cluster. These \( \sigma \) results share the same characteristic as the \( S \) data in Figure 56, which is a pronounced decrease with increasing cluster size. Contrary to the \( S \) results, the \( \sigma \) results in Figure 57 do not show an increase as the cluster size is increased from one to two spheres. In addition, the decrease in \( \sigma \) observed for small cluster sizes (<10 spheres) in Figure 57 with increasing cluster size is more pronounced than the decrease in \( S \) in Figure 56 over the same size range. The loss in \( \sigma \) for a four-sphere cluster is about 30% compared to the isolated primary
particle, while a loss in $S$ of only about 10% occurs for this cluster. Similar losses in the
two coefficients $S$ and $\sigma$ occur for clusters larger than 10 spheres. The loss in $\sigma$ for the
thirteen-sphere cluster is 60% compared to the isolated primary, and the loss associated
with the sixty-four sphere cluster is 70%. These results for titania spheres indicate that
the quantity $(1-g)$ decreases rapidly with increasing cluster size for small clusters and
changes more slowly for large clusters.
Figure 55. Finite element model of a cluster of seven 200-nm titania spheres with $n = 2.74$ in a polymer matrix with $n = 1.51$. The 560-nm illuminating light propagates in the $+x$ direction and is polarized in the $z$ direction.
Figure 56. The scattering coefficient $S$ as a function of the number of 200-nm titania spheres composing a particle cluster. These results are for the case of random illumination of each cluster, resulting in orientation-averaged results.

Figure 57. The scattering coefficient $\sigma$ as a function of the number of 200-nm titania spheres composing a particle cluster. These results are for the case of random illumination of each cluster, resulting in orientation-averaged results.
7.3 Near-Field Interactions Between Neighboring Titania Particles

In the previous section, the effects of cluster sizes of 200-nm titania spheres upon scattering efficiency has been studied using the time-domain finite element method. In the present study, the effects of crowding are investigated for the case of the seven-sphere cluster shown in Figure 55 by varying the interparticle separation distance between the center sphere and the six surrounding spheres in the cluster. The surface-to-surface interparticle separation distance is allowed to vary from zero to 0.5 µm. This study is analogous to the study of crowding of latex spheres with this same geometry in Section 6.3.

The dependence of the scattering coefficient $S$ upon interparticle separation distance in these seven-sphere clusters of titania is shown in Figure 58. The horizontal, dashed line in this figure indicates the $S$ value associated with a single, isolated 200-nm titania sphere of which the cluster is composed. The plot in Figure 58 shows that the $S$ values for the seven-sphere clusters is nearly equal to that of the isolated titania sphere (within ~3%) for interparticle separation distances greater than 0.2 µm. The $S$ values for those clusters with interparticle separation distances greater than 0.4 µm in face exceed the value associated with an isolated titania sphere by about 2%; this difference is within the expected error for those computations and may be a result of numerical error. For interparticle separation distances less than 0.2 µm, the scattering coefficient $S$ decreases very sharply with decreasing interparticle separation distance. For the case of touching spheres (zero interparticle separation distance), the value of $S$ is 16% lower than the value associated with an isolated titania sphere. This 16% loss in the total
scattering by the cluster on a volume-normalized basis is the same value indicated in the Figure 56 for the seven-sphere cluster.

The dependence of the angle-weighted scattering coefficient $\sigma$ upon interparticle separation distance in the seven-sphere clusters of titania is shown in Figure 59. The horizontal, dashed line corresponds to the $\sigma$ value associated with an isolated 200-nm titania sphere of which the cluster is composed. The plot in Figure 59 shows that the value of $\sigma$ for the seven-sphere cluster with 0.5-$\mu$m surface-to-surface interparticle separation distance is very nearly equal to that associated with an isolated 200-nm titania sphere. The $\sigma$ value at this separation distance is about 1.5% less than that of the isolated primary particle, which is within the range of expected numerical error for this computation. For interparticle separation distances less than 0.5 $\mu$m, the value of $\sigma$ for these seven-sphere clusters of titania decreases steadily as the separation distance approaches zero. For a surface-to-surface interparticle separation distance of 0.2 $\mu$m, the value of $\sigma$ is 10% less than the value associated with an isolated sphere. For the cluster of seven touching spheres, the value of $\sigma$ is 35% less than the value associated with an isolated sphere, indicating a substantial loss in scattering efficiency a result of particle crowding and agglomeration in this system.
Figure 58. Dependence of the scattering coefficient $S$ upon surface-to-surface interparticle separation distance for the clusters of seven titania spheres. The dashed line corresponds to the value associated with a single 200-nm titania primary particle.

Figure 59. Dependence of the angle-weighted scattering coefficient $\sigma$ upon surface-to-surface interparticle separation distance for the clusters of seven titania spheres. The dashed line corresponds to the value associated with a single 200-nm titania primary particle.
7.4 Near-Field Interactions Between Two Morphological Rutile Particles

Time domain finite element computations have been performed for the case of two morphological rutile titania particles which approach each other in a resin. In this case, two particles with the same geometry and anisotropic optical properties as the particle shown in Figure 40 are positioned within a finite element model with interparticle separations ranging from 0.5 \( \mu \text{m} \) to 0 \( \mu \text{m} \) (touching). Cross-sectional views of the finite element models are shown in upper panels of Figure 60–Figure 62, and the logarithm of scattered intensity through the same cross section are shown in the lower panels. In each of these figures, the illumination direction is perpendicular to the plane of the cross sections shown, and the light polarization is parallel to the long axes of the particles. Asymmetry in the near-field scattered intensities around each of the particles is apparent in each of these figures, indicating that the two particles are interacting at these separations.

Random illumination conditions have been simulated for each of the interparticle separations investigated using the Illuminator software. The presence of three mutually perpendicular mirror planes in the geometry of the finite element models limited the number of illumination directions to twenty-five in one octant of the finite element model. The scattering parameter \( S \) has been computed for this two-particle system as a function of surface-to-surface interparticle separation distance. This result is shown in Figure 63; the horizontal line indicates the value of the scattering coefficient for a single morphological rutile particle (Figure 40) for comparison with the two-particle results. The scattering coefficient \( S \) decreases with decreasing separation.
between the two particles. For an interparticle separation of 0.5 µm, the scattering coefficient is very nearly equal to that associated with the isolated particle. For the case of zero interparticle separation, the value of the scattering coefficient $S$ is 8% lower than that associated with a single, isolated particle. That is, the two-particle aggregate scatters 8% less total light than the isolated particle.

Results for the angle-weighted scattering coefficient $\sigma$ for the two-particle system are shown in Figure 64 as a function of the interparticle separation distance. The horizontal line in the figure indicates the $\sigma$ value associated with a single morphological rutile particle (Figure 40). The results Figure 64 show that the value of the angle-weighted scattering coefficient $\sigma$ for the interparticle separation of 0.5 µm is nearly equal to that associated with the isolated particle. For the case of the two particles touching, the value is 20% lower, indicating that the two-particle aggregate is significantly less effective in the limit of multiple scattering than the isolated particle.

As in the case of the isolated rutile particle, it is possible to determine the diameters of spheres with equivalent far-field scattering properties for the case of two interacting rutile particles described above. This case is especially interesting since the total volume of scattering material remains constant as the two rutile particles approach each other, yet the far-field scattering properties of the system change markedly as the interparticle distance changes. These results are presented in Table 9, with the sphere diameters producing the same values of the scattering coefficients $S$ and $\sigma$ as the two-particle system for each of the interparticle separation distances considered. As in the
case of the single rutile particle, multiple values of $S$ and $\sigma$ occur for each of the interparticle separation distances.
Figure 60. Finite element model cross section and near field scattering results for two anisotropic morphological rutile particles in $n = 1.51$ resin for light incident normal to the cross section shown and with a wavelength of 560 nm. The interparticle spacing is 0.5 $\mu$m.
Figure 61. Finite element model cross section and near field scattering results for two anisotropic morphological rutile particles in $n = 1.51$ resin for light incident normal to the cross section shown and with a wavelength of 560 nm. The interparticle spacing is 0.3 μm.
Figure 62. Finite element model cross section and near field scattering results for two anisotropic morphological rutile particles in $n = 1.51$ resin for light incident normal to the cross section shown and with a wavelength of 560 nm. The interparticle spacing is 0 µm.
Figure 63. Scattering coefficient $S$ for two morphological rutile particles as a function of interparticle separation. The horizontal line shows the results for one of the morphological rutile particles.

Figure 64. Angle-weighted scattering coefficient $\sigma$ for two morphological rutile particles as a function of interparticle separation. The horizontal line shows the results for one of the morphological rutile particles.
Table 9. Diameters of spheres exhibiting the same far-field scattering coefficients as the system of two rutile particles for each interparticle separation distance considered, using both the average index and weighted sum approximations.

<table>
<thead>
<tr>
<th>Interparticle Separation (µm)</th>
<th>$S$ Basis</th>
<th>$\sigma$ Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.186</td>
<td>0.183</td>
</tr>
<tr>
<td></td>
<td>0.211</td>
<td>0.278</td>
</tr>
<tr>
<td></td>
<td>0.254</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.292</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
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<td>0.183</td>
</tr>
<tr>
<td></td>
<td>0.212</td>
<td>0.279</td>
</tr>
<tr>
<td></td>
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Chapter 8. Discussion: Light Scattering by Complex Microstructures in the Resonant Regime

The light scattering properties of several previously unknown systems have been determined computationally in this dissertation research. The results of these studies, presented in Chapters 4–7, provide a basis for the elaboration of new insights about the light scattering properties of complex microstructures. This chapter contains a discussion of these learnings on a general footing.

8.1 Accuracy of the Time-Domain Finite Element Method

Studies have been presented in Chapter 4 upon the accuracy of the time-domain finite element method with different finite element model configurations and far-field extrapolation conditions. The methodology used in this work has been to systematically vary computational conditions in the finite element method and compare the numerical results to known, analytical results from Mie theory. The materials systems investigated using Mie theory were as closely related to the more complex systems of interest in subsequent research as possible. In each of the variations in computational conditions studied, wide variations in the accuracy of the finite element method were observed. It is significant that those computations which were grossly in error showed no outward signs of any problem, such as crashes or error messages. Without the foundations of understanding developed in the error analysis work, it would be impossible to apply the time-domain finite element method to unknown cases with confidence.
The explosion in computational power which has occurred in the late 1990’s has created an unprecedented environment for successful application of computational modeling to complex physical phenomena. This opening has been accompanied by the development of diverse numerical methods in a given field, putting at one’s disposal numerous approaches to the modeling of a given system. Each approach has its unique advantages and disadvantages for the solution of a particular problem. In the field of computational modeling and simulation (and in experimental work, for that matter), there is an unfortunate tendency for researchers to vaunt the particular numerical methods they develop or apply, at the expense of alternative approaches, and to avoid discussion of their shortcomings. Careful and detailed studies of the accuracy of any numerical method under the full range of computational conditions is critical, for it is only through a sound understanding of the limitations of a numerical method that its strengths can be appreciated.

8.2 Light Scattering by Complex, Resonant Particles

The light scattering properties of core-shell pigment particles illustrate important principles about the design of complex particle architectures in the resonant regime. It is well-known that the scattering of light arises from dielectric discontinuities between different materials. It could therefore be argued that increased light scattering could be produced by creating a large number of interfaces in an engineered composite particle. One could imagine a complex particle consisting of a series of alternating, concentric shell layers of high- and low-index materials; each interface in the particle would create a source of light scattering, resulting in a particle with light scattering properties which
are superior to either of the constituent materials alone. In the case of the core-shell particles studied in Chapter 5, which consist of a high-index titania shell surrounding lower-index core materials, it has been demonstrated that this sort of approach is not a viable means of producing pigment particles with superior light scattering properties in the resonant regime. Instead, the core-shell architecture produces the same trends in behavior as reducing the effective refractive index of the composite particle. Core-shell particles with optimized diameter exhibit substantially lower scattering coefficients than particles of the high-index material with optimized diameter. An explanation for these observations lies in the relationship between the core-shell particle size and the wavelength of the illuminating light. Since the core-shell particle diameters producing optimal light scattering are on the order of the light wavelength in size, the potential for increased light scattering by a multi-layer particle architecture is limited by the resolution of the illuminating light. In simple terms, the light does not “see” the internal particle interfaces so much as it “sees” a particle with reduced effective refractive index. The strategy for producing white pigment particles with maximum light scattering power is to produce optimally sized, solid particles of the highest refractive index, non-absorbing material available.

The effects of optical anisotropy upon light scattering in the resonant regime have been investigated for the first time in the study presented in Chapter 5. The results of that study revealed the expected phenomena of orientation- and polarization-dependent light scattering properties in the anisotropic spheres studied. Changes in the scattering coefficients \( S \) by as much as 50% were demonstrated for different
illumination directions and light polarizations in the case of the highly resonant 0.2-µm sphere. This orientation and polarization dependence is an essential difference between the anisotropic spheres and the isotropic spheres considered in Mie theory. Calculation of the scattering parameters $S$ and $\sigma$ on an orientation-averaged basis, on the other hand, revealed that the scattering properties of anisotropic spheres can be approximated reasonably, within 10%, by isotropic scattering models. The approximate formulations do not describe the orientation-averaged scattering behavior of the anisotropic spheres rigorously, but the errors were not dramatic. These results suggest that dilute ensembles of optically anisotropic particles which are truly randomly oriented may be well approximated using isotropic models which can be far less complex to analyze. They also highlight the fact that there are potential opportunities to improve the scattering properties of ensembles of anisotropic particles forcing the particles to adopt preferred orientations during processing. For example, it is possible to deliberately align particles with high aspect ratios during processing, which may be advantageous for light scattering performance in certain systems.

Finite element computations on the light scattering properties of a single, morphological rutile titania particle demonstrate the ready applicability of the method to even the most complex particle shapes. This resonant particle is faceted and exhibits anisotropic optical properties. The absence of cylindrical symmetry in the rutile particle makes its scattering properties especially difficult to model using techniques like the T-matrix method which are not based upon piece-wise solution of Maxwell’s equations through a large system of volume elements. The computed light scattering properties of
the rutile particle have been compared to those of the equivalent-volume sphere using two approximations based upon scattering by an isotropic sphere. As in the case of anisotropic spheres, the isotropic scattering models were in reasonable statistical agreement with the computed scattering coefficients of the rutile particle, with errors less than 10% in all cases. It can be concluded that equivalent-volume, isotropic spheres approximate reasonably the light scattering coefficients of complex single particles in the resonant regime, but rigorous agreement is not achieved.

The computed coefficients $S$ and $\sigma$ of the morphological rutile particle were also used to identify those isotropic sphere diameters producing the same scattering coefficients. In this case, there were multiple sphere diameters in each case which exhibited the same scattering coefficients. This study highlights the ambiguity of assigning equivalent spherical diameters to particles with complex shapes and therefore more degrees of freedom in their geometry than a simple sphere. Particle sizing methods based upon light scattering and the assignment of equivalent spherical diameters should be regarded as effective engineering control tools rather than absolute measures of true particle size.

### 8.3 Light Scattering by Densely Packed Particle Aggregates

The light scattering coefficients of multiple-sphere clusters containing different numbers of primary particles have been determined using the time-domain finite element approach in two different materials systems. The first system, representing clusters of 200-nm latex spheres in water (Chapter 6), is a low-contrast system in which
the refractive index ratio of the two materials is 1.13. The second system, representing clusters of 200-nm titania spheres in a polymeric resin (Chapter 7), is a high-contrast system in which the refractive index ratio of the two materials is 1.81. It is interesting to note that, while 488-nm light was used in the case of the latex-water system and 560-nm was used in the titania-resin system, the effective light wavelengths in the two systems were nearly identical due to the different refractive indices of the water and the resin. In the case of the latex-water system, the effective light wavelength is 488-nm/1.33 = 367 nm. In the case of the titania-resin system, the effective light wavelength is 560-nm/1.51 = 371 nm. The large difference in contrast ratio between these two systems result in very different far-field scattering coefficients for the isolated 200-nm primary particle used to build the clusters in both cases (compare Figure 41-Figure 42 with Figure 53-Figure 54.)

The results of computing the scattering coefficients of the packed particle clusters studied in these two systems illustrate the fact that the multiple-particle clusters exhibit very different scattering properties than the isolated primaries composing them. In addition, the trends in the scattering coefficients $S$ and $\sigma$ as a function of the number of 200-nm primaries in a cluster were in some cases opposite in these two materials systems. That is, there exists no simple function which can be used to predict how the scattering coefficients will change for clustering of arbitrarily sized primary particles in an arbitrary materials system.

For the formation of multiple-particle clusters from a given primary particle size and optical constants, an important consideration is the relationship between the
scattering coefficient $S$ or $\sigma$ of the isolated primary particle compared to the diameter associated with the optimal value of that scattering coefficient. In other words, a critical question is where the primary particle diameter is positioned on the computed scattering coefficient curve from Mie theory. This knowledge provides the ability to predict in a semi-quantitative way how the scattering coefficient of clusters of the primary particle will trend with increasing cluster size. For example, for a primary particle diameter which is much smaller than the diameter producing the maximum value of the angle-weighted scattering coefficient $\sigma$ in a given materials system, the formation of multiple-particle clusters of increasing size will result in increased $\sigma$ values. These increased $\sigma$ values, however, will not attain the value of the solid particle which is of optimal size in the system. Likewise, for a primary particle diameter which is equal to that producing the maximum $\sigma$ value in a system, the formation of clusters of increasing size from that primary particle will result in decreased $\sigma$ values. It appears that this sort of comparison is the only reliable means of predicting trends in scattering coefficients as a function of the degree of particle clustering.

Comparisons are made here between the scattering properties of clusters composed of arbitrary numbers of primary particles and the results of Mie theory computations for single, equivalent-mass spheres. Shown in Figure 65 is a comparison between values of the scattering coefficient $S$ in the latex-water system as a function of the number of spheres in a cluster (from Figure 46) and the results of Mie theory computations for equivalent-mass spherical particles (dashed curve). The Mie theory computations correctly predict the upward trend in $S$ with increasing cluster size. In a
quantitative sense, however, the agreement between the two sets of data is statistically poor for the largest cluster sizes investigated. For the cluster consisting of sixty-four 200-nm latex spheres, for example, the predicted value of $S$ is 45% greater for the equivalent-mass sphere than the value computed for the actual cluster. Differences between the two sets of data arise from the different microstructures of the solid sphere and the more complex, porous cluster of primary particles. Shown in Figure 66 is an analogous comparison between values of the angle-weighted scattering coefficient $\sigma$ in the latex-water system (from Figure 48) and the results of Mie theory computations for equivalent-mass spherical particles (dashed curve). In this case, the agreement between the two sets of data is much better than in the case of the $S$ data in Figure 65. The two exhibit the same trend with increasing cluster size. For the case of the sixty-four sphere cluster, the predicted value of $\sigma$ is 20% less for the equivalent-mass sphere than the value computed for the actual cluster.

For the titania-resin system, the comparison between $S$ values for the multiple-particle clusters (from Figure 56) and equivalent-mass spheres (dashed curve) is shown in Figure 67. As in the case of the latex-water system, the equivalent-mass Mie theory computations correctly predict the trend in $S$ as a function of the number of spheres in a cluster. The statistical agreement between the two sets of data is poor for the larger cluster sizes investigated. For cluster sizes greater than eight spheres, the equivalent-mass results underestimate the value of $S$ by as much as a factor of 2.5. Shown in Figure 68 is the analogous comparison between values of the angle-weighted scattering coefficient $\sigma$ in the titania-resin system (from Figure 57) and the results of Mie theory
computations for equivalent-mass spherical particles (dashed curve). As in the case of the latex-water system, agreement between the two sets of data is much better than in the case of the scattering coefficient $S$. For the largest clusters investigated (twenty-seven and sixty-four spheres), deviations between the two sets of data are the greatest, with the results for clusters greater than the predicted values from Mie theory by 50% and ~100%, respectively.

It is concluded that semi-quantitative trends in the effects of particle clustering upon the light scattering coefficients $S$ and $\sigma$ can be predicted using Mie theory calculations for equivalent-mass spheres. For a particular materials system, these trends are determined by the relationship between the size of the primary particle composing the clusters and the particle size corresponding to the maximum value of the scattering coefficient. For example, increasing cluster sizes containing particles of sub-optimal diameter primary particles result in increased scattering coefficient, while increasing cluster sizes containing optimal diameter primary particles result in decreased scattering coefficient. Far better statistical agreement between the scattering properties of multiple-particle clusters and Mie theory calculations for equivalent-mass spheres has been found in the angle-weighted scattering coefficient $\sigma$ than in $S$. The reasons for this difference are not understood. This result suggests that opposite trends exist, with increasing cluster size, in the scattering coefficient $S$ and the factor $(1-g)$, where $g$ is the asymmetry parameter.
Figure 65. The scattering coefficient $S$ as a function of the number of 200-nm latex particles composing a particle cluster (solid curve). For comparison, the results of Mie theory computations on single, equivalent-mass spheres are shown (dashed curve).

Figure 66. The scattering coefficient $\sigma$ as a function of the number of 200-nm latex particles composing a particle cluster (solid curve). For comparison, the results of Mie theory computations on single, equivalent-volume spheres are shown (dashed curve).
Figure 67. The scattering coefficient $S$ as a function of the number of 200-nm titania particles composing a particle cluster (solid curve). For comparison, the results of Mie theory computations on single, equivalent-mass spheres are shown (dashed curve).

Figure 68. The scattering coefficient $\sigma$ as a function of the number of 200-nm titania particles composing a particle cluster (solid curve). For comparison, the results of Mie theory computations on single, equivalent-mass spheres are shown (dashed curve).
8.4 Near-Field Optical Interactions Between Particles

8.4.1 Titania and Latex Systems

Changes in the number of primary particles composing densely packed clusters of spheres produce dramatic changes in the far-field scattering properties of both the latex-water and titania-resin systems compared to the isolated primary particles. Near-field optical interaction between the neighboring particles in these clusters is the cause of these deviations in scattering properties. Of interest is the length scale over which these near-field interactions are important, a question which has not been addressed comprehensively in the literature.

Computations using the time-domain finite element approach for the case of multiple particle approaching each other have been performed for three different systems in this thesis: seven-sphere clusters of both latex particles in water (Section 6.3) and titania particles in resin (Section 7.3), and two morphological rutile particles in resin (Section 7.4). Those results were presented in the form of the scattering coefficients $S$ and $\sigma$ as functions of the distance (in microns) between neighboring particles. In order to place these diverse systems on a common basis, these same results are presented here as a function of the number of effective light wavelengths between the centers of neighboring particles. The center-to-center spacing is adopted here for the sake of general applicability to different particles sizes. In the case of the latex-water system, the light wavelength studied was 488 nm, corresponding to an effective light wavelength of $488\text{ nm}/1.33 = 367$ nm. In both the titania-resin systems, the light...
wavelength studied was 560 nm, corresponding to an effective light wavelength of 560-nm/1.51 = 371 nm. In addition, the values of \( S \) and \( \sigma \) are expressed here as a percentage of the values associated with the isolated primary particle in each system; this normalization scheme makes it convenient to plot the latex-water and titania resin systems, which exhibited very different magnitudes of \( S \) and \( \sigma \), on the same axis.

The results for the percent-normalized scattering coefficient \( S \) are plotted as a function of the center-to-center interparticle separation distance (in effective light wavelengths) in Figure 69. The upper curve (solid triangles) corresponds to the seven-sphere latex-water system, while the lower curves correspond to the seven-sphere titania system (solid circles) and the two morphological rutile system (hollow squares). The \( S \) values in the two titania-resin systems converge more rapidly to the value associated with the isolated primary particle with increasing particle separation than the latex-water system. The \( S \) values in both the titania systems is within 10% of the value associated with the isolated primary particles in ~0.8 light wavelengths, while the latex system converges to within 10% of the isolated primary particle value in ~1.6 light wavelengths. Even for the center-to-center interparticle separation of 2.2 light wavelengths, the latex system deviates from the value of the isolated primary by several percent. While this value is on the order of the expected error level in the finite element method for that finite element mesh density, there is no evidence of numerical noise in the smoothly decaying curve.

The corresponding plot of the percent-normalized scattering coefficient \( \sigma \) as a function of the center-to-center interparticle separation distance (in effective light
wavelengths) is shown in Figure 70. In this case, a comparison of the interparticle separation distances for which there is a 10% deviation in each system from the $\sigma$ values associated with the isolated primary particles indicates similar length scales determined for $\sigma$ in Figure 69. While the latex system does not deviate by this much for any of the separation distances studied, there are deviations of 10% relative to the isolated primary particles for the seven-sphere titania and the two morphological rutile systems at 1.4 and 0.8 wavelengths, respectively. All three systems converge to within 3% of the $\sigma$ values associated with the isolated primary particles for an interparticle separation distance of 2.0 light wavelengths.

Examining the data in Figure 69 and Figure 70 collectively, it can be concluded that appreciable near-field optical interactions between neighboring particles with sizes in the resonant regime occur over approximately two light wavelengths. Beyond this separation, these optical interactions are very weak compared to those which occur between neighboring particles which are nearly in contact. In this context, it is interesting to consider additionally the data presented in Section 4.3.3 on the effects of the far-field sphere radius upon error in the extrapolation of near-field scattering results to far field. In that case, it was determined that placement of the far-field sphere surface $>10$ $\mu$m from the scattering particle was sufficient to ensure that evanescent components of the scattered light not effect the accuracy of extrapolation. For extrapolation surfaces placed 2 and 5 $\mu$m from the spherical titania particle, deviations of just 0.02% and 0.09%, respectively, were observed in the computed scattering cross section, (see Figure 19). For the 560 nm light studied in those cases, these distances
expressed in light wavelengths are 3.6 and 8.9 wavelengths, respectively. These vanishingly small errors confirm that near-field optical interactions operating in these resonant systems are extremely weak at separation distances greater than 3 light wavelengths.

The intensity of the evanescent electric field components which exist in the vicinity of a scattering particle decay exponentially with increasing distance from the particle. Based upon this physical argument, the three curves shown in Figure 69 and Figure 70 have been fit using a parametric, exponential curve of the following form:

\[
\begin{align*}
\text{Equation 81} & \quad S(\%) = 100 + a \exp\left(\frac{(x - b)}{c}\right) \\
\end{align*}
\]

where the left-hand argument can be either \( S \) or \( \sigma \), and \( x \) is the separation distance between the centers of neighboring particles expressed in units of light wavelength in the medium. The second term on the right-hand side of Equation 81 is the deviation with separation distance in the scattering efficiency of a multiple-particle cluster relative to an isolated primary particle. The parameter \( b \) is equal to the center-to-center spacing of touching particles expressed in units of light wavelength, equal to 0.47 for both the 200-nm titania and latex spheres and 0.47 for the two morphological rutile particles. The parameters \( a \) and \( c \) are variable fitting parameters. The parameter \( a \) is approximately equal to the percent deviation in the left-hand argument for touching particles, relative to the 100\% value associated with an isolated primary particle. The parameter \( c \) is a decay constant equal to the distance, expressed in light wavelengths,
over which the left-hand argument in Equation 81 decreases by the factor $e$ (2.718282…).

The results of these curve fits are presented in Table 10, which shows the values of the fitting parameters $a$ and $c$ for each case and the value of the quality of fit parameter $R^2$. This quantity is equal to unity for perfect curve fits and less than one for curve fits which do not intersect all of the points in a data set. Wide variations in the value of the fitting parameter $a$ are observed in Table 10 for the six different cases studied, ranging from $-34.2$ to $74.3$; these are consistent with the variations observed in the scattering coefficients $S$ and $\sigma$ for touching particles compared to an isolated primary particle. The value of the fitting parameter $c$ varies in the range 0.24-0.46. The variation in the parameter $c$ reflects differences in the percent change in scattering efficiency relative to an isolated primary particle in the different systems studied. Larger $c$ values indicate slower convergence of the scattering coefficients to the value 100% with increasing interparticle separation distance. The $R^2$ values in Table 10 are greater than or equal to 0.93 in all but one case, indicating that the exponential curve defined in Equation 81 is a sound basis for describing the changes in the scattering coefficients observed in Figure 69 and Figure 70. In the case of the scattering coefficient $\sigma$ for the seven latex spheres, the $R^2$ value of 0.66 indicates a poor fit. This result is not surprising considering the erratic behavior of $\sigma$ in this case.
Table 10. Results of parametric fits of the six curves shown in Figure 69 and Figure 70 using the expression in Equation 81.

<table>
<thead>
<tr>
<th>Case</th>
<th>$a$</th>
<th>$c$</th>
<th>$R^2$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$, Seven TiO$_2$</td>
<td>-15.9</td>
<td>0.26</td>
<td>0.93</td>
</tr>
<tr>
<td>$S$, Seven Latex</td>
<td>74.3</td>
<td>0.40</td>
<td>0.97</td>
</tr>
<tr>
<td>$S$, Two Morph. Rutiles</td>
<td>-8.29</td>
<td>0.37</td>
<td>0.97</td>
</tr>
<tr>
<td>$\sigma$, Seven TiO$_2$</td>
<td>-34.2</td>
<td>0.46</td>
<td>0.99</td>
</tr>
<tr>
<td>$\sigma$, Seven Latex</td>
<td>-6.09</td>
<td>0.24</td>
<td>0.66</td>
</tr>
<tr>
<td>$\sigma$, Two Morph. Rutiles</td>
<td>-19.2</td>
<td>0.43</td>
<td>0.99</td>
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</tbody>
</table>

Figure 69. Scattering coefficient $S$ (%) for the three different multiple-particle systems as a function of the center-to-center interparticle spacing expressed in wavelengths. The value 100% corresponds to the $S$ value for an isolated primary particle in each case.
Figure 70. Angle-weighted scattering coefficient $\sigma$ (%) for the three multiple-particle systems as a function of the center-to-center interparticle spacing expressed in wavelengths. The value 100% corresponds to the $\sigma$ value for an isolated primary particle in each case.

8.4.2 Extension to Other Materials Systems

The combined use of equivalent-mass, single spheres to approximate the light scattering properties of particle agglomerates and the curve-fitting methodology for particle clusters described in Section 8.4.1 suggests a means of approximating the light scattering properties of systems other than titania and latex. As described in Section 8.3, it is possible to estimate the scattering properties of particle agglomerates through Mie theory calculations on equivalent-mass spheres. In addition, the results described in Section 8.4.1 indicate that the scattering coefficient for a particle cluster as a function of interparticle separation varies between the values associated with the agglomerate (touching particles) to that of an isolated primary particle (with very large separation distances). The exponential curve defined in Equation 81 can be used to compute...
approximately the dependence of $S$ or $\sigma$ on interparticle separation distance by setting the parameter $a$ equal to the percent change in scattering coefficient for the agglomerate (estimated from Mie theory) and setting the parameter $c$ equal to a value in the range 0.25-0.45.

The difficulties associated with this generalization to unknown materials systems lie in the inaccuracy of using Mie theory to estimate the scattering properties of agglomerated primary particles and the range of possible values in the exponential decay length $c$ in Equation 81. The two systems studied, titania in resin and latex in water, represent two extreme cases in optical contrast, which is useful in defining bounds on the value of the parameter $c$. On the other hand, the 200-nm titania primary particle is the optimal size for scattering efficiency while the 200-nm latex sphere is smaller than optimal. It would be interesting to determine the scattering properties of sphere clusters for sub-optimal titania particles and optimal latex particles to complete the space of primary particle sizes investigated. It should also be pointed out that the simple exponential form of the expressing in Equation 81 may not be an adequate description of more complex cases, such as a case where the scattering coefficient $S$ or $\sigma$ associated with agglomerates of primary particles passes through a maximum with changing interparticle separation distance.
Chapter 9. Conclusions

In the present study, a computational optics approach using a time-domain finite element technique has been applied to determine the light scattering properties of complex microstructures in the resonant regime. The scattering behavior such systems have been largely unknown due to the difficulties associated with performing the large-scale computations required for numerical solutions to Maxwell’s equations. Especially difficult in this respect are individual scattering features with highly asymmetric geometries and ensembles containing many scattering features with near-field optical interactions occurring between them. In this chapter, general conclusions are drawn from the details of the work presented in earlier chapters.

In the application of any numerical code to simulate physical phenomena, it is critical that the accuracy of the code be tested against case with a known, analytical solution. The analytical test case should be as closely related as possible to the physical phenomena being simulated. The results of numerical methods always contain some degree of error, and systematic quantification of this error under various simulation conditions provides an important basis for applying the numerical method with appropriate confidence in cases having no known solution. In the present work on light scattering by three-dimensional objects, the analytical results of Mie theory are very well suited for comparison with the time-domain finite element approach. It is clear from the accuracy testing in the present study that the construction of the finite element models bears great influence upon the accuracy of the numerical method.
It has been demonstrated in the computation of the light scattering properties of core-shell pigment particles that the light scattering efficiency of composite particles containing high- and low-index materials is limited by the content of the lower refractive index material. In the case of particles whose sizes are on the order of the illuminating light wavelength, the presence of a lower refractive index material creates a particle having a reduced overall refractive index, which in turn shifts the optimal diameter for scattering to larger sizes and reduced the maximum scattering efficiency possible. While it may appear attractive to create a scattering particle containing multiple interfaces between two index mismatched materials, these interfaces do not produce the desired additional refraction and reflection in the particle since these inhomogeneities are small compared to the light wavelength and effectively invisible.

In the case of light scattering by anisotropic spheres, it has been demonstrated that, while the effects of optical anisotropy are pronounced when particular angles of light incidence and polarizations are considered, these effects are effectively washed out under conditions of random illumination. Reasonable agreement was found between the results of random illumination of anisotropic spheres using the time-domain finite element approach and two approximate models based upon scattering by isotropic spheres. This implies that ensembles of randomly oriented particles which are optically anisotropic or irregularly shaped may be modeled accurately using optically isotropic materials. This will certainly not be true in cases involving particles with high aspect ratios under processing conditions which cause the particles to adopt preferred orientations.
Computation of the light scattering properties of a morphological rutile titania particle highlighted the inherent difficulty in fitting scattering data by complex particle shapes to equivalent spherical diameters. As in the case of the anisotropic spheres, approximating the shaped, optically anisotropic rutile particle as an equivalent volume, optically isotropic sphere predicted reasonably well the orientation-averaged scattering properties of the particle. The inverse problem of fitting a spherical particle size based upon the scattering properties of the complex shaped particle, however, presents the difficulty of representing particles which require multiple geometrical parameters in their description as spherical particles with just geometrical parameter. Indeed, strictly speaking, equivalent spherical diameters computed in the inverse problem are not meaningful. In the case of irregularly shaped particles, particle sizing by light scattering methods may provide a sound measure of engineering control, but the results of such particle sizing should not be taken in an absolute sense.

The light scattering properties of clusters of multiple spheres of both high and low refractive index have been studied systematically using the time-domain finite element approach. These computations demonstrated that the near-field optical interactions which act between neighboring particles in wavelength-sized, hard contact clusters produce light scattering properties which deviate substantially from those of the individual primary particles composing the cluster. The effects of particle clustering upon scattering efficiency depends upon the relationship of the size of the primary particles in the cluster compared to the optimal particle size for scattering in that materials system. In the case of primary particles which are smaller in size than the
optimal size, clustering will produce improved light scattering efficiency compared to the primary particles. This improvement will be less dramatic than producing fully dense, single particles of the same mass since the illuminating light samples both the particles in the cluster and the interstitial material. In the case of primary particles which are nearly optimal in size for light scattering efficiency, clustering causes a reduction in scattering efficiency which can be dramatic. In the case of rutile titania particles, for example, losses in volume-normalized scattering efficiency of 70% occur for the largest agglomerates studied. This reduction is more pronounced in high-contrast systems, which exhibit strong resonances with the illuminating light at particular sizes and produce very high scattering efficiencies.

For separated clusters of either latex or titania particles, near-field optical interactions between neighboring particles diminish rapidly with increasing particle separation, with appreciable near-field interactions not extending beyond separations of 2-3 light wavelengths. In most cases, changes in scattering efficiency with interparticle separation distance could be well fit using an exponential decay. The decay constant of these spatial variations varies in the range 0.25-0.45 light wavelengths for these systems, with appreciable optical interactions not extending beyond 2-3 light wavelengths.
Appendix. Typical EMFlex Input Deck

grid 111 83 83

geom

  xcrd -0.15e-6 0.25e-6
  ycrd -0.15e-6 0.15e-6
  zcrd -0.15e-6 0.15e-6

end

matr

  prop poly 20.30e-12 0.0 1.2566e-6 /* m = 1.51 + 0.0i
  prop rutl 66.47e-12 0.0 1.2566e-6 /* m = 2.74 + 0.0i

end

topo

  regn poly

  sphr rutl 0.0.0.0.1e-6 /* 0.2-um diameter sphere centered at (0,0,0)

end

ilum

  symb c0 = 2.998e8
  symb wavl = 0.560e-6
  symb freq = $c0 / $wavl

/* vertically propagating, z-polarized plane wave:

  pwav wavl $freq 1.0.1.0.0.1.

ffld 1 1
boun /* illumination boundary conditions on all six sides

side 1 ilum
side 2 ilum
side 3 ilum
side 4 ilum
side 5 ilum
side 6 ilum
calc

wndo 1 * 1 * 1 * /* calculate amp & phase over entire model
esst scat /* calculate scattered quantities
intn /* calculate intensity
pout rate 1

hist ez 20 60 20 60 20 60 20 60 20 60 20 20 60 20 60 20 20 60 20 20 60 20 /*Collect time histories in the model
rest no
prcs
data out modl
exec cycl 15 /* execute to steady-state
calc on /* calculate amplitude & phase
end
exec cycl /* execute 1 cycle
kirc /* Kirchoff box definition
ref cntr 0. 0. 0.
defn srf1 cntr in

node 5 5 5 77 5 77
node 105 105 5 77 5 77
node 5 105 5 5 5 77
node 5 105 77 77 5 77
node 5 105 77 77 5 5
node 5 105 5 77 77 77
writ srf1

data /* export data for plotting with Review

   out insc

stop
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