Radiative transfer modeling of thermal infrared emissivity spectra: applications to martian regolith observations

Karly Mariah Pitman
Louisiana State University and Agricultural and Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_dissertations

Part of the Physical Sciences and Mathematics Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_dissertations/699

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Doctoral Dissertations by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in
The Department of Physics and Astronomy

by
Karly M. Pitman
A.B., Vassar College, 1999
M.S., Louisiana State University, 2002
December, 2005
Dedication

This manuscript is dedicated to my mother, Laura Pitman, for twenty-five years of unfailing support and investment leading to the production of this manuscript. I also dedicate this work to my father, Vance Pitman, to my fiancé, Damian Crevello, and to everyone in my address book for their encouragement over the years.
Acknowledgments

I would like to thank the members of the Department of Physics and Astronomy and the Department of Geology at Louisiana State University who have served on my doctoral thesis committee: Dr. Dana Browne, Dr. Gary Byerly, Dr. Geoffrey Clayton, Dr. Juhan Frank, and Dr. Joel Tohline. All have provided me with individual consultation far in advance of the writing of this manuscript and have given unique insight into the presentation of this material.

I am indebted to the collaborators and institutions who provided guidance, assistance, and equipment on a strictly pro bono basis, sometimes out of general scientific comradere, more often out of the goodness of their hearts. I recognize in particular members of the Space Science Institute (Dr. Michael Wolff, Dr. Barbara Whitney, and Dr. R. Todd Clancy) in the latter category. I would like to thank members of the Mars Global Surveyor TES and THEMIS instrument teams at Arizona State University’s Mars Space Flight Facility: Dr. Joshua Bandfield (for calibration of laboratory and field spectra), Drs. Steve Ruff and Tim Glotch (for technical assistance with the Nicolet Nexus 670 spectrometer), Deanne Rogers (for providing the inspiration for sample holder prototypes and overseeing the emissivity spectra acquired in my absence), and Trevor Graff (for conversations on compaction and laboratory sample preparation techniques). At Arizona State University’s Department of Geology, I would like to thank Dr. Marsha Presley and her undergraduate assistant, Debbie Kenyon, for donating and preparing quartz and spherical silica samples for my study. Use of the µFT-IR field spectrometer was made possible by ASU, in consortium with USGS Flagstaff and the University of Nevada, Reno. Ryan Taylor (Death Valley National Park) and Janice Davis (Bureau of Land Management) provided assistance with sampling permits, and Alice Baldrige (ASU) provided her field notes on the evaporite sites studied. I am thankful for the helpful comments provided by Dr. Gorden Videen (U.S. Army Research Laboratory; SSI), Dr. Jay Goguen (NASA Jet Propulsion Laboratory), Dr. Ted Roush (NASA Ames), Dr. Phil Christensen (ASU; Mars Space Flight Facility), Dr. Rich Kurtz, Dr. A. Ravi Rau, Mitsuko Murakami, Vayujeet Gokhale (all of LSU’s Dept. of Physics and Astronomy), and Patrick Randerson (Ohio State University).

This research would not have been possible without the following resources. The support staff and fabricators at the LSU Dept. of Physics and Astronomy machine shop, led by Duane Cambre, were instrumental in the creation of the directional emissivity sample holders. Rick Young (LSU Dept. of Geology) assisted in sieve studies of the Death Valley samples. Dr. Patrick Motl (LSU Dept. of Physics and Astronomy) gave excellent training in batch processing and high performance computing; Dr. Michael Wolff (SSI) and Thaddeus Parkinson (formerly of the Advanced Technology Center, Univ. of Missouri-Columbia) provided example code and helpful suggestions to better automate the routines presented here. The postdoctoral
research associates for Dr. Geoffrey Clayton’s interstellar medium research group (Drs. Karl Gordon, Tracy Smith, Wentao Wu, Stefan Cartledge) and recent graduates from the group (Drs. Karl Misselt, Lynne Valencic) all contributed by example to the development of advanced programming and structure in IDL and maintained the machines that ran the radiative transfer codes used in this work.

A special section of acknowledgment is devoted to Drs. Geoffrey Clayton and Michael Wolff, the official and informal primary advisers for my doctoral research, respectively. Geoff has been extremely flexible as an adviser, allowing for and encouraging collaboration with outside institutions. He has been supportive of research that is not in his primary field of expertise; he has been the conduit for most of the work presented here, asking the kinds of questions that a good scientist should consider, focussing on the real world value of this science, and overseeing the quality of publications and presentations related to this project. He is expert at grooming his students to be successful scientists with good prospects for employment while maintaining an atmosphere of relaxation in his research group. As an outside collaborator working out of his home, Mike is not required to mentor anyone. Yet he has been accessible day or night on weekends and holidays and, with his family, has opened his home for weeks at a time to work with me to move this research forward. Mike has supplied codes, books, hardware, and countless ideas on future directions for each aspect of this project. Both of these men have shared what knowledge and resources they have, going above and beyond to help someone starting out in the field. They should know how very much they are professionally respected and personally beloved by many (myself included) and also feel very proud of themselves for successfully completing an unorthodox joint mentorship.

This work has been performed with support from the Louisiana State University Board of Regents and from the National Aeronautics and Space Administration through grants from the Mars Data Analysis Program.
# Table of Contents

Dedication .......................................................... ii
Acknowledgments .................................................. iii
List of Tables ........................................................ vii
List of Figures ...................................................... viii
List of Nomenclature ............................................. xii
Abstract .......................................................... xvii

1. Introduction ....................................................... 1
   1.1 Importance of Thermal Infrared Emissivity Measurements in Planetary Science ............................................. 2
   1.2 Statement of Problem ......................................... 5
   1.3 Goals of the Thesis .......................................... 5

2. Thermal Infrared Directional Emissivity Measurements of Martian Analog Sites ............................................. 7
   2.1 Background .................................................... 7
   2.2 Field Emission Spectroscopy ................................ 12
      2.2.1 Experimental Procedure ................................ 12
      2.2.2 Site Measurements ..................................... 14
   2.3 Laboratory Emissivity Spectroscopy ........................ 18
   2.4 Discussion and Conclusions ................................ 23

3. Application of Modern Radiative Transfer Tools To Model Laboratory Nadir Quartz Emissivity .................................. 26
   3.1 Mie-RT Hybrid Models ...................................... 26
   3.2 Laboratory Thermal IR Emissivity Measurements .......... 32
      3.2.1 Vibrational Spectroscopy ............................ 32
      3.2.2 Laboratory Samples .................................. 32
      3.2.3 Instrumentation, Experimental Conditions and Procedure .......................................................... 33
   3.3 Radiative Transfer Model Description ....................... 34
      3.3.1 Model Inputs and Assumptions ....................... 34
      3.3.2 Numerical Methods .................................. 36
   3.4 Packing Assumptions Revisited ............................ 40
      3.4.1 Diffraction Subtraction ................................ 40
      3.4.2 Static Structure Factor Corrections .................. 41
   3.5 Discussion .................................................... 42
List of Tables

2.1 MGS-TES Emission Phase Function Sequences Exhibiting Directional Emissivity Effects: Moderate to High Albedo Regions ................................................. 9

2.2 MGS-TES Emission Phase Function Sequences Exhibiting Directional Emissivity Effects: Moderate to High Albedo Regions, cont. ............................................. 10

2.3 MGS-TES Emission Phase Function Sequences Exhibiting Directional Emissivity Effects: Low Albedo Regions .......................... 11

3.1 Summary of α-Quartz Model Run Parameters (MC95) ........................................ 27

3.2 RMS Error Values For MC95 α-Quartz Samples (MC95 model) ........................ 31

3.3 \( y = A + Bx \) Fit Parameters (Fig. 3.6) ......................................................... 48

4.1 SiO\(_2\) Laboratory Measured Emissivity Spectra ............................................. 53

4.2 Types of Particle Diameters ................................................................. 56

4.3 Types of Sizing Methods and Coupled Variables ........................................... 57

4.4 Presley (1995) α-Quartz Model Run Parameters .......................................... 62

4.5 Particle Dimensions and Aspect Ratios: \(d < 63 \mu m\) α-Quartz ......................... 69

4.6 Particle Dimensions and Aspect Ratios: \(d = 90-125 \mu m\) α-Quartz .................. 70

4.7 Particle Dimensions and Aspect Ratios: \(d = 500-710 \mu m\) α-Quartz ................ 71
### List of Figures

1.1 Satellite field-of-view observation of planetary regolith .......................... 3
1.2 MGS-TES surface emissivities for Martian high albedo surface .................. 4
2.1 Emissivity variations in MGS-TES EPF sequences for high and low albedo surfaces ......................................................... 8
2.2 Designs & Prototypes\textsuperscript{TM} $\mu$FT-IR portable field spectrometer .... 13
2.3 Multiple emergence angle field emissivity spectra of quartz-feldspar sand particulates at Dumont Dunes ....................................... 15
2.4 Field emissivity spectra of quartz-feldspar sand at Dumont Dunes: MGS-TES EPF sequence observation angles .......................... 16
2.5 High emergence angle field emissivity spectra of undisturbed terrain at Silver Lake Playa ....................................................... 17
2.6 Directional emissivity sample holders .................................................. 18
2.7 Nadir laboratory emissivity spectra of playa surface DEVA-7 and salt surface EVAP-4 ................................................................. 19
2.8 Nadir laboratory emissivity spectra for Silver Lake Playa (\equiv SLP-1b, SLP-2) ................................................................. 20
2.9 Multiple emergence angle emissivity spectra for lab sample SLP-2 ............. 21
2.10 Multiple emergence angle emissivity spectra for lab sample DUNE-6 .......... 22
3.1 Comparing performance of three models to MC95 lab emissivity spectra ........ 28
3.2 Emissivity ratios: $i^{th}$ diameter sample divided by $d = 277$ $\mu$m sample ................................................................. 29
3.3 Emissivity ratios: $i^{th}$ MC95 model spectrum divided by $i^{th}$ MC95 lab spectrum ................................................................. 30
3.4 Model-lab nadir quartz emissivity spectra comparison: two packing corrections (small and large grain sizes) .......... 43
3.5 Mie single scattering albedo and asymmetry parameter for 3 MC95 quartz samples ........................................ 44
3.6 Mie vs. “forced fit” values for single scattering albedo and asymmetry parameter ........................................ 45
3.7 Diffraction subtraction packing corrected single scattering albedo .............................................................. 46
3.8 Static structure factor packing corrected single scattering albedo and asymmetry parameter ..................... 47
3.9 Diffraction subtraction packing corrected asymmetry parameter .............................................................. 49
4.1 $e = 0^\circ$ laboratory emissivity spectra for DRAGONITE™ synthetic silica ..................................................... 54
4.2 $e = 0^\circ$ laboratory emissivity spectra for SIL-CO-SIL 53 synthetic silica ..................................................... 55
4.3 $e = 0^\circ$ laboratory emissivity spectra of $\alpha$-quartz particulates ................................................................. 59
4.4 Laboratory thermal IR emissivity spectra of Presley (1995) small ($d < 63 \mu m$), medium ($d = 90-125 \mu m$), and large ($d = 500-710 \mu m$) sized quartz particulate samples .................. 60
4.5 Frequency abundance profiles as a function of radius for small, medium, and large sized quartz particulate samples .................. 61
4.6 Model-lab nadir quartz emissivity spectra comparison: 3 samples with widely binned particle size distributions .................. 63
4.7 SEM images of representative $\alpha$-quartz grains ($d < 63 \mu m$) ................................................................. 65
4.8 SEM images of representative $\alpha$-quartz grains ($d = 90-125 \mu m$) ............................................................ 66
4.9 SEM images of representative $\alpha$-quartz grains ($d = 500-710 \mu m$) ............................................................ 67
4.10 Electroplated Ni mask used in calculating error bars on field emission SEM (X, Y, D) crosshair measurements .............. 68
A.1 Smooth clay mud, Devil’s Speedway, Death Valley, CA ................................................................. 79
A.2 Field emissivity spectra of Devil’s Speedway smooth mud site ................................................................. 80
A.3 Field conditions and emissivity spectrum for white particulate material on evaporites, Devil’s Speedway, Death Valley, CA ................................................................. 81
D.1 Static structure factor as a function of (particle size) $u = 2\xi r$  105

D.2 Static structure factor packing corrected normalized phase function and asymmetry parameter: small particle radii, different packing fractions . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 108

D.3 Static structure factor packing corrected normalized phase function: large particle radii, different packing fractions . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 109

D.4 Static structure factor corrected asymmetry parameter: large particle radii, different packing fractions . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 110
## List of Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>grain effective radius, $\mu$m</td>
<td>36</td>
</tr>
<tr>
<td>$b$</td>
<td>grain effective variance</td>
<td>36</td>
</tr>
<tr>
<td>$B(f)$</td>
<td>ratio of scattering cross-section of densely packed particles to that of isolated particles</td>
<td>41</td>
</tr>
<tr>
<td>$B_{env}$</td>
<td>environment radiance, i.e., radiance emitted by the chamber isolating the sample in a laboratory spectrometer measurement</td>
<td>33</td>
</tr>
<tr>
<td>$B_{inst}$</td>
<td>instrument radiance, i.e., all radiance reaching the detector that did not originate from the sample</td>
<td>33</td>
</tr>
<tr>
<td>$B_{sam}$</td>
<td>sample radiance</td>
<td>33</td>
</tr>
<tr>
<td>$B_{\lambda}$</td>
<td>Planck function</td>
<td>1</td>
</tr>
<tr>
<td>$c(r)$</td>
<td>short range direct correlation function between nearest neighboring particles</td>
<td>104</td>
</tr>
<tr>
<td>$C_{abs}$</td>
<td>absorption cross-section of one spherical grain, $(\mu$m)$^2$</td>
<td>107</td>
</tr>
<tr>
<td>$\tilde{C}_{abs}$</td>
<td>absorption cross-section of a group of densely packed spherical grains, $(\mu$m)$^2$</td>
<td>107</td>
</tr>
<tr>
<td>$C_{ext}$</td>
<td>extinction cross-section of one spherical grain, $(\mu$m)$^2$</td>
<td>37</td>
</tr>
<tr>
<td>$C_{diff}^{ext}$</td>
<td>diffraction component of the extinction cross-section, $(\mu$m)$^2$</td>
<td>107</td>
</tr>
<tr>
<td>$C_{ray}^{ext}$</td>
<td>ray tracing component of the extinction cross-section, $(\mu$m)$^2$</td>
<td>107</td>
</tr>
<tr>
<td>$\tilde{C}_{ext}$</td>
<td>extinction cross-section of a group of densely packed spherical grains, $(\mu$m)$^2$</td>
<td>106</td>
</tr>
<tr>
<td>$C_{sca}$</td>
<td>scattering cross-section of one spherical grain, $(\mu$m)$^2$</td>
<td>37</td>
</tr>
<tr>
<td>$C_{diff}^{sca}$</td>
<td>diffraction component of the scattering cross-section, $(\mu$m)$^2$</td>
<td>107</td>
</tr>
<tr>
<td>$C_{ray}^{sca}$</td>
<td>ray tracing component of the scattering cross-section, $(\mu$m)$^2$</td>
<td>107</td>
</tr>
<tr>
<td>$\tilde{C}_{sca}$</td>
<td>scattering cross-section of a group of densely packed spherical grains, $(\mu$m)$^2$</td>
<td>106</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>$d$</td>
<td>grain diameter, $\mu$m</td>
<td>2</td>
</tr>
<tr>
<td>$d_A$</td>
<td>sieve diameter, $\mu$m</td>
<td>56</td>
</tr>
<tr>
<td>$d_{Stk}$</td>
<td>Stokes diameter, $\mu$m</td>
<td>56</td>
</tr>
<tr>
<td>$d_v$</td>
<td>equivalent spherical volume diameter, $\mu$m</td>
<td>56</td>
</tr>
<tr>
<td>$D_{ap}$</td>
<td>pinhole aperture in electrical sensing zone analyzer</td>
<td>58</td>
</tr>
<tr>
<td>$e$</td>
<td>angle of emergence, degrees ($^{\circ}$)</td>
<td>3</td>
</tr>
<tr>
<td>$f$</td>
<td>filling factor, i.e., packing fraction</td>
<td>41</td>
</tr>
<tr>
<td>$F$</td>
<td>instrument response function</td>
<td>33</td>
</tr>
<tr>
<td>$g$</td>
<td>asymmetry parameter, i.e., angle-average phase function</td>
<td>38</td>
</tr>
<tr>
<td>$g$</td>
<td>phase angle, radians</td>
<td>38</td>
</tr>
<tr>
<td>$g_c$</td>
<td>acceleration due to gravity = 9.8 m/s$^2$</td>
<td>56</td>
</tr>
<tr>
<td>$g_{diff}$</td>
<td>diffraction subtraction corrected asymmetry parameter</td>
<td>40</td>
</tr>
<tr>
<td>$g_{ff}$</td>
<td>asymmetry parameter that, if supplied to the numerical discrete ordinates RT code, will guarantee a model $\epsilon$ to match the lab $\epsilon$ value</td>
<td>42</td>
</tr>
<tr>
<td>$g_{mie}$</td>
<td>asymmetry parameter result from Mie theory only</td>
<td>40</td>
</tr>
<tr>
<td>$g_{struc}$</td>
<td>$\ddot{g}$, static structure factor corrected asymmetry parameter</td>
<td>41</td>
</tr>
<tr>
<td>$g(r)$</td>
<td>radial distribution function</td>
<td>104</td>
</tr>
<tr>
<td>$G$</td>
<td>geometric cross-section, $(\mu m)^2$</td>
<td>107</td>
</tr>
<tr>
<td>$h(r)$</td>
<td>total correlation function</td>
<td>104</td>
</tr>
<tr>
<td>$H$</td>
<td>$\equiv H(w, \mu)$; Chandrasekhar’s H-function</td>
<td>101</td>
</tr>
<tr>
<td>$i$</td>
<td>angle of light incidence onto a surface, degrees ($^{\circ}$)</td>
<td>3</td>
</tr>
<tr>
<td>$I_D$</td>
<td>scattered radiance measured at a detector, (power per unit area per solid angle)</td>
<td>37</td>
</tr>
<tr>
<td>$J$</td>
<td>incident irradiance</td>
<td>37</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>(k)</td>
<td>imaginary index of refraction</td>
<td></td>
</tr>
<tr>
<td>(K(\xi) \equiv c(\xi))</td>
<td>Fourier transform of the direct correlation function (c(r))</td>
<td></td>
</tr>
<tr>
<td>(l)</td>
<td>expansion coefficient for vector spherical harmonics</td>
<td></td>
</tr>
<tr>
<td>(L)</td>
<td>emitted radiant flux, W m(^{-2})</td>
<td></td>
</tr>
<tr>
<td>(L)</td>
<td>total column length in one radiative transfer layer, m</td>
<td></td>
</tr>
<tr>
<td>(L_\lambda)</td>
<td>measured radiance of an \textit{in situ} surface; satellite radiances given in W cm(^{-2}) sr(^{-1})/cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{bb}\lambda})</td>
<td>spectral radiance from a blackbody at surface temperature (T), W/m(^{2})</td>
<td></td>
</tr>
<tr>
<td>(L_{\text{sky}\lambda})</td>
<td>downwelling atmospheric spectral radiance, W/m(^{2})</td>
<td></td>
</tr>
<tr>
<td>(n)</td>
<td>real index of refraction</td>
<td></td>
</tr>
<tr>
<td>(n(r))</td>
<td>number size distribution</td>
<td></td>
</tr>
<tr>
<td>(n_d)</td>
<td>number density of scattering particles, cm(^{-3})</td>
<td></td>
</tr>
<tr>
<td>(p(\theta))</td>
<td>volume single scattering phase function</td>
<td></td>
</tr>
<tr>
<td>(\tilde{p}(\theta))</td>
<td>static structure factor corrected scattering phase function</td>
<td></td>
</tr>
<tr>
<td>(r)</td>
<td>grain radius, (\mu)m</td>
<td></td>
</tr>
<tr>
<td>(r_{\text{eff}})</td>
<td>particle effective radius, (\mu)m</td>
<td></td>
</tr>
<tr>
<td>(r_f)</td>
<td>resistivity of particle in electrolyte suspension</td>
<td></td>
</tr>
<tr>
<td>(r_{\text{hem}})</td>
<td>directional-hemispherical reflectance</td>
<td></td>
</tr>
<tr>
<td>(r_o)</td>
<td>((1 - \gamma)/(1 + \gamma))</td>
<td></td>
</tr>
<tr>
<td>(\mathcal{R})</td>
<td>(r(i,e,g)); bidirectional reflectance of a surface</td>
<td></td>
</tr>
<tr>
<td>(S(\theta))</td>
<td>static structure factor</td>
<td></td>
</tr>
<tr>
<td>(S_{\alpha,\beta})</td>
<td>((\alpha, \beta)) element of the 2 x 2 amplitude scattering matrix</td>
<td></td>
</tr>
<tr>
<td>(T)</td>
<td>surface temperature of field target, K or (^\circ)C</td>
<td></td>
</tr>
<tr>
<td>(v_{\text{eff}})</td>
<td>effective variance, (\mu)m or dimensionless</td>
<td></td>
</tr>
</tbody>
</table>
\( v_s \)  terminal velocity, m/s² ........................................ 56

\( V \)  particle volume, (\( \mu \)m)³ ........................................ 56

\( V_{bb} \)  voltage measured for a blackbody ......................... 33

\( V_{meas} \)  voltage measured for a sample ......................... 33

\( w \)  \( \equiv w(\tau) \), volume single scattering albedo ............... 37

\( w_{diff} \)  diffraction subtraction corrected single scattering albedo ........ 40

\( w_{ff} \)  single scattering albedo that, if supplied to the numerical discrete ordinates RT code, will guarantee a model \( \epsilon \) to match the lab \( \epsilon \) value ......................... 42

\( w_{mie} \)  single scattering albedo result from Mie theory only ........ 40

\( w^{ray} \)  ray-tracing component of single scattering albedo ........ 41

\( w_{struc} \equiv \tilde{w} \), static structure factor corrected single scattering albedo 41

\( x \)  radius divided by hard sphere diameter .......................... 105

\( X \)  \( = (2\pi r)/\lambda \), size parameter ............................ 36

\( Z \)  phase matrix .................................................... 37

\( \gamma \)  \( = \sqrt{1 - w_{diff}} \) ........................................ 101

\( \Delta R \)  change in resistance ........................................ 58

\( \epsilon(\lambda) \)  emissivity ............................................. 1

\( \epsilon_{diff} \)  diffraction subtraction corrected emissivity .......... 43

\( \epsilon_{struc} \)  static structure factor corrected emissivity ........... 43

\( \eta_f \)  viscosity of settling fluid ................................ 56

\( \theta \)  scattering angle, radians .................................. 37

\( \lambda \)  incident light wavelength, \( \mu \)m ................................ 1

\( \mu_d \)  mean effective diameter, \( \mu \)m ................................ 36

\( \xi \)  wavenumber, cm\(^{-1}\) ........................................ 1
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>average density of an isotropic, homogeneous fluid at any radius, cm$^{-3}$</td>
<td>104</td>
</tr>
<tr>
<td>$\rho(r)$</td>
<td>surplus of density, cm$^{-3}$</td>
<td>104</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>density of settling fluid, cm$^{-3}$</td>
<td>56</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>density of a single particle, cm$^{-3}$</td>
<td>56</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>single scattering cross-section for one spherical grain, $\mu$m$^2$</td>
<td>35</td>
</tr>
<tr>
<td>$\sigma_d$</td>
<td>standard deviation for $\mu_d$, $\mu$m</td>
<td>36</td>
</tr>
<tr>
<td>$\sigma_{SB}$</td>
<td>Stefan-Boltzmann constant $= 5.67 \times 10^{-8} \text{ W m}^{-2} \text{K}^{-4}$</td>
<td>1</td>
</tr>
<tr>
<td>$\tau$</td>
<td>optical depth of a medium</td>
<td>37</td>
</tr>
<tr>
<td>$\phi$</td>
<td>azimuthal angle, radians</td>
<td>101</td>
</tr>
<tr>
<td>$\phi_d$</td>
<td>$= -\log^2 d$; particle diameter unit</td>
<td>36</td>
</tr>
<tr>
<td>$\omega$</td>
<td>spectrometer field of view; $d\omega = \sin \theta d\theta d\phi$</td>
<td>101</td>
</tr>
</tbody>
</table>
Abstract

Satellite and rover remote sensing of planetary regolith surfaces, in the form of thermal infrared emissivity spectra taken at nadir and off-nadir angles of emergence from the surface, requires use of theoretical models for interpretation of constituent grain physical properties. However, such models have remained in stasis in recent years, with nearly a ten-year gap in significant advances. To date, no radiative transfer model (semiempirical, exact, or hybrid solution) has been able to adequately predict the nadir emissivity behavior of simple mineral assemblages. Few measurements have been attempted in the laboratory or field regarding directional emissivity effects of planetary regoliths; such measurements are necessary for modeling and interpreting directional emissivity effects that are clearly present in the Mars Global Surveyor Thermal Emission Spectrometer (MGS-TES) and Mars Exploration Rover mini-TES datasets. The research goals of this dissertation directly involve the extraction of information on two major dust microphysical properties: particle size and packing fraction. Results of a theoretical model are compared to laboratory-measured thermal infrared (wavenumber \( = 2000-200 \text{ cm}^{-1} \)) emissivities for micron-sized quartz particles. This work shows that Mie theory, a widely used but poor approximation to irregular grain shape, fails to produce the single scattering properties needed to arrive at the desired laboratory emissivity values and also illustrates shortcomings of popular dense packing correction methods. Through numerical experiments, I provide evidence that, assuming RT methods work given sufficiently well-quantified inputs, assumptions about the scatterer itself constitute the most crucial aspect of modeling nadir emissivity values. Also included in the dissertation are detailed laboratory investigations used to obtain realistic and quantifiable input parameters to the theoretical model, i.e., particle size distribution and particle shape. Nadir and directional emissivity comparison datasets obtained in the laboratory and in the field at Mars terrestrial analog sites are presented to set the stage for modeling directional emissivity. Future directions (e.g., how to incorporate nonspherical particle shapes into the model) are briefly discussed.
1. Introduction

The primary physical property of interest in this work is emissivity, a quantity of great relevance in interpreting Mars regolith\(^1\) grain properties from past, recent, and future Mars mission observations. By definition, emissivity is the ratio of the power radiated by a material at a certain temperature to the power radiated by a blackbody\(^2\) at that same temperature. If an object were to emit energy per unit area according to the Stefan-Boltzmann Law\(^3\),

\[
L = \sigma_{SB} T^4,
\]

it would be considered a blackbody. This law states that the emitted radiant flux (i.e., the rate of flow of electromagnetic radiation) is proportional to the temperature of the object. However, if an object is not a perfect blackbody, then the expression for radiant flux per unit wavelength interval must be modified by a correction factor: the emissivity. Emissivity, denoted by \(\epsilon(\lambda)\), is effectively the ratio of spectral radiance\(^4\) (i.e., specific intensity) divided by the Planck function,

\[
\epsilon(\lambda) = \frac{L_\lambda}{B_\lambda}.
\]

By definition, \(\epsilon\) ranges from 0.0 to 1.0. Snow and water have emissivity values on the order of 0.99, whereas for rocks and dust, the value of \(\epsilon\) changes more strongly as a function of wavelength \(\lambda\). The wavelength regime where most Mars regolith particulates radiate is the thermal infrared. In addition to wavelength, this seemingly innocent dimensionless quantity carries a variety of dependences, the exploration of which constitutes the science focus of this investigation.

---

\(^1\)Regolith is a geologic layer composed of unconsolidated rock fragments and inorganic soil which lies above and is not necessarily compositionally or texturally related to the bedrock layer of a planetary surface. Meteoritic impacts and surface weathering processes generate fragments with sizes on orders of submicrons and greater in the Martian regolith, dominated by dust with estimated particle diameters \(\lesssim 5 \mu m\) (Mustard & Hays, 1997 and references therein); here we concentrate on particle diameters from 0-1000 \(\mu m\).

\(^2\)A blackbody is an idealized perfect radiator and absorber of energy at all electromagnetic wavelengths. The term comes from the fact that a cold blackbody appears visually black.

\(^3\)\(\sigma_{SB}\) is the Stefan-Boltzmann constant, \(5.67 \times 10^{-8}\) \(\frac{W}{m^2 K^4}\), radiant flux, \(L\), is in \(\frac{W}{m^2}\), and temperature, \(T\), is in Kelvin.

\(^4\)The satellite observations presented in Chapter 2 are spectral radiances, in units of power per unit area per unit solid angle per wavelength interval (\(W\) cm\(^{-2}\) sr\(^{-1}\) / cm\(^{-1}\)). The expression for the Planck function in these units is \(B_\lambda(T) = (\alpha_1 \xi^3)/[10^7(\exp(\alpha_2 \xi/T) - 1)]\), where \(\xi = 10^4/\lambda \equiv\) wavenumber in cm\(^{-1}\), \(\alpha_1 = 1.191066 \times 10^{-5}\) J m\(^2\) s\(^{-3}\), and \(\alpha_2 = 1.438833\) K cm.
1.1 Importance of Thermal Infrared Emissivity Measurements in Planetary Science

There is a need for theoretical tools to model planetary regolith emissivity developed via intermediate comparisons between both field-laboratory and laboratory-model explorations. In the absence of samples returned from the Martian surface, the set of remote sensing measurements obtained from satellite orbiters remains an important source of information about Martian surface mineralogy (Christensen et al., 2001; Christensen et al., 2000a, 2000b; Bandfield, 2002; Hamilton et al., 2001). While physical properties of the Martian surface (i.e., grain size, grain shape, degree of packing) traditionally have been inferred from surface temperature measurements, thermal infrared emissivity spectra also contain unique sensitivities to surface physical properties when decoupled from atmospheric contributions. Mars surface spectral shapes and lack of significant absorption at wavenumbers $< 1300 \text{ cm}^{-1}$ clearly indicate the presence of fine particulates in high albedo regions and sand-sized particulates in low albedo regions (Bandfield et al., 2000; Christensen et al., 2001; Bandfield & Smith, 2003; Ruff & Christensen, 2002). To date, little has been explored beyond these first order characterizations regarding Mars surface emissivity and its relation to physical properties of the surface. To infer Mars regolith grain physical properties from spacecraft infrared observations, one may compare these data to laboratory emissivity measurements, to terrestrial field emissivity measurements, or to emissivities obtained by a theoretical model. Mars terrain analogs on Earth may serve as important comparisons to Martian emissivity data, but there will inevitably be important differences in grain size distributions, shapes, and compositions. Theoretical emissivity models utilizing semi-empirical or exact radiative transfer solutions (e.g., Hapke 1993a, 1993b, 1996, 2002; Mishchenko et al., 1999) have not yet been extensively tested against both laboratory and field emissivity spectra.

In modeling laboratory emissivity spectra ($\equiv \epsilon(\lambda)$), there exist problematic yet intriguing theoretical considerations. When grains are in close proximity, they no longer scatter light like single particles. Properly treating multiple scattering events remains a challenge for radiative transfer (RT) models of the photometric properties of dense media surfaces such as the Martian regolith. In addition to proximity, assumptions about the maximal grain dimension (i.e., diameter $d$ for spheres) and incident light wavelength $\lambda$ must be treated carefully when modeling emissivity for grains with $d \sim \lambda$. This condition is not uncommon in the thermal infrared (IR) data from instruments such as the Mars Global Surveyor Thermal Emission Spectrometer (MGS-TES), the Mars Odyssey Thermal Emission Imaging System (THEMIS), and the Mars Exploration Rover (MER) mini-TES. Despite recent advances in computing and numerical techniques, RT models have difficulty in reproducing laboratory reflectance measurements at nadir, calling into question model assumptions about the fundamental scatterer (Piatek et al., 2004); similar problems are expected to be encountered in emissivity models. To address these concerns from an empirical standpoint, one must first examine the
Figure 1.1: Satellite field-of-view observation of planetary regolith. The field-of-view in the broadband solar channel is maintained on a single location on Mars as the spacecraft passes overhead. The primary photometric variable is the emission angle $e$, the angle between the observer and the normal to the surface. Only the angle between the Sun and the surface normal (angle of incidence $i$) is fixed during an emission phase function sequence observation. Adapted with author permission from Clancy & Lee (1991) (V. Gokhale).

algorithms and underlying assumptions used to calculate theoretical nadir emissivity values in previous works and determine what worked and what did not.

Directional effects observed in emissivity spectra of particulate media also pose a challenge for theoretical radiative transfer models of planetary regolith. While a spacecraft orbits a planet, the spectrometer hanging below the craft samples the sunlight reflected, scattered, and reemitted off of the surface at different angles of emergence, denoted by $e$ (Fig. 1.1). In this work, I refer to the terms angle of emergence and emission angle interchangeably. MGS-TES has returned thousands of multiple emission angle
observations, collected over a variety of sites, which allow one to determine phase function values for the Martian surface. These emission phase function (EPF) and nadir (i.e., zero surface emission angle) sequences display a clear dependence of surface emissivity on emission angle within moderate to high albedo regions (Fig. 1.2). Instruments aboard the 2003-04 Spirit and Opportunity Mars Exploration Rovers (MER) and the 2009 Mars Science Laboratory will also be returning emissivities of the Martian surface taken at nadir and off-nadir geometries. Because the majority of previous and future global studies of the Martian surface have involved and will depend upon orbiter and rover remote sensing emissivity measurements, it is critical to establish the emissivities of Mars-relevant materials. Though the effects of particle microphysical properties clearly influence surface emissivity measurements, these effects are not well documented or understood beyond empirical determinations of particle size fraction spectra of geologic materials from nadir or near-nadir geometries (Salisbury & Walter, 1989; Moersch & Christensen, 1995; Salisbury et al., 1997).
1.2 Statement of Problem

Theoretical models of planetary emissivity spectra taken at nadir have remained in stasis in recent years, with nearly a ten year gap in significant model advances. Radiative transfer and scattering models developed by the physics and astronomy community can be used to augment the initial nadir emissivity modeling attempts. Little has been done in the laboratory or the field regarding directional emissivity effects with application to planetary regoliths. These measurements are necessary to develop models and establish a dataset for interpreting directional emissivity effects that are clearly present in the MGS-TES dataset and are likely to be apparent in MER mini-TES data. To invert Mars orbiter emissivity measurements to obtain grain physical properties, most planetary science groups directly compare orbiter emissivity measurements to laboratory emissivity measurements, to terrestrial field emissivity measurements, or to emissivities obtained via a theoretical model. However, an integrated approach is needed to account for the limitations of each individual level of comparison (e.g., laboratory and in situ field emissivity spectra may fundamentally differ depending on the sample preparation methods; Johnson et al., 1998).

1.3 Goals of the Thesis

The research goals of this thesis directly involve the extraction of information from nadir emissivity spectral measurements and models on three major dust microphysical properties: particle size, particle shape, and packing fraction\(^5\). In this work, I create a theoretical model that can self-consistently predict laboratory-measured emissivities of geologic particulates in the 0-1000 micron diameter size range at nadir. Surface directional emissivity effects prominently seen in remote sensing orbiter data for Mars have not been extensively studied either in the laboratory or field for Martian terrestrial analog sites, nor have they been successfully modeled; directional emissivity is addressed in Chapter 2. In Chapter 3, I concentrate on the connection between laboratory and model development and construct a proof to illustrate that packing and shape assumptions must be upgraded to result in successful model-lab emissivity spectral fits. I describe ways to quantify the radiative transfer model inputs to better match realistic laboratory samples in Chapter 4. Portions of Chapters 1, 3, and 4 have been accepted for publication (Pitman et al., 2005\(^6\)).

The most time-intensive part of the project is the construction of a numerical solution to the equation of radiative transfer that inputs realistic and quantifiable particle properties (i.e., radius \(r\), incident wavelength \(\lambda\), material composition given by indices of refraction \(n\) and \(k\), and size distribution of particles \(n(r)\)) and outputs emissivity for dust grains mantling a planetary body.

\(^5\)“Packing fraction” as used here is the volume of a collection of spherical particles divided by the volume of the smallest cube that can enclose them (Sec. 3.4.2).

\(^6\)Reproduced by permission of American Geophysical Union (Appendix E).
regolith. The assembly and development of this model demonstrates mastery of fundamental physics disciplines and formalisms, as evidenced by electromagnetic scattering calculations, statistical mechanics derivations, and astrophysical radiative transfer algorithms presented in text. As the comparison dataset for the radiative transfer model, I also present thermal IR (7-13 µm wavelength regime) field emissivity measurements for Mars terrain analogs and thermal IR (200-2000 cm⁻¹ wavenumber regime) laboratory emissivity spectra for well characterized natural and synthetic SiO₂ particulates, acquired by myself in collaboration with the Mars Space Flight Facility, Arizona State University. While the investigative approach (i.e., measurement followed by iterative numerical calculation to obtain best spectral fit) is direct, the development of this theoretical model and the characterization of its input parameters represents at least one of the most computationally intense and detailed efforts to date in attempting to understand the remote sensing of planetary surfaces in the thermal IR.
2. Thermal Infrared Directional Emissivity Measurements of Martian Analog Sites

Before embarking on a campaign to isolate competing effects from true directional emissivity spectral signatures, it is essential to investigate whether or not this phenomenon truly exists. Thermal infrared emissivity data returned from the Mars Global Surveyor satellite indicate that the angle at which a single Martian surface site is observed modifies the emissivity spectral profile (Fig. 2.1; Tables 2.1, 2.2, and 2.3); similar effects are likely to be apparent in the datasets returned from the Mars Exploration Rovers. Directional emissivity effects have been observed terrestrially in the field and may provide insight into surface structures, thermal inertias, and non-isotropic corrections to thermal emission measurements on Mars (Jakosky et al., 1990). To date, little has been done in the field or in the laboratory to determine if these directional emissivity effects are also observed in Mars terrain analog sites on Earth. In this chapter, I present a set of field emissivity data in the thermal infrared wavelength region ($\lambda \sim 7$-$13$ $\mu$m) for three undisturbed Mars terrain analog sites (playa and evaporite surfaces in Death Valley National Park and Baker, CA; Howard, 2001) and analyze them for the presence or absence of directional emissivity effects. This field dataset and corresponding laboratory emissivity spectral analyses support the conclusion that variations in emissivity values of Mars terrestrial analog field sites are truly a function of observation angle, as they appear to be from satellite observations of the Martian surface. Thus, the theoretical investigations in the remainder of the thesis are warranted.

2.1 Background

The Emission Phase Function (EPF) sequences collected by the Mars Global Surveyor Thermal Emission Spectrometer (MGS-TES) constitute a substantial thermal IR remote sensing radiance dataset\(^1\) at angles that are both on and off-nadir (i.e., observed from top down and at $\sim 30^\circ$, $50^\circ$, and $70^\circ$ angles from the vertical). Within moderate to high albedo (bright) regions, the EPF sequences display a clear and vital dependence on emission angle $\theta$ (i.e., angle of observation) (Table 2.1, 2.2, upper panel, Fig. 2.1); similar trends are also observed in a smaller number of EPF sequences acquired over low albedo regions (Table 2.3, lower panel, Fig. 2.1). These observations suggest that the angle at which a single site is observed modifies the emissivity spectral profile ($\equiv \theta$); directional emissivity effects are also likely to be

---

\(^1\)As of July 2005, nadir and off-nadir measurements for over 25,000 orbits have been acquired by MGS-TES (c.f., http://tes.asu.edu/data_archive/).
Figure 2.1: Emissivity variations as a function of emergence angle $e$ are observed in representative MGS-TES EPF sequences measured for a moderate to high albedo surface (upper panel) and for a low albedo surface (lower panel). For many of the OCK/ICK pairs listed in Tables 2.1, 2.2, and 2.3, the change in emissivity with increasing $e$ value is less strongly pronounced.
Table 2.1: MGS-TES Emission Phase Function Sequences Exhibiting Directional Emissivity Effects: Moderate to High Albedo Regions

<table>
<thead>
<tr>
<th>OCK</th>
<th>ICK</th>
<th>Longitude (°)</th>
<th>Latitude (°)</th>
<th>$T_{surf}$ (K)</th>
<th>$\varepsilon$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2684</td>
<td>1897</td>
<td>67.0</td>
<td>15.3</td>
<td>276.9</td>
<td>18,38,39,43,45,46,49,51,52,55,56,58,59,62,63,65,66</td>
</tr>
<tr>
<td>2719</td>
<td>1803</td>
<td>347.7</td>
<td>5.7</td>
<td>275.2</td>
<td>18,38,39,43,45,46,49,51,52,55,56,58,59,62,63,65,66</td>
</tr>
<tr>
<td>2720</td>
<td>1897</td>
<td>17.6</td>
<td>15.2</td>
<td>276.6</td>
<td>18,38,39,43,45,46,49,51,52,55,56,58,59,62,63,65,66</td>
</tr>
<tr>
<td>2792</td>
<td>1897</td>
<td>279.0</td>
<td>15.3</td>
<td>276.3</td>
<td>18,38,39,43,45,46,49,51,52,55,56,58,59,62,63,65,66</td>
</tr>
<tr>
<td>2827</td>
<td>1803</td>
<td>199.8</td>
<td>5.6</td>
<td>276.2</td>
<td>18,38,43,45,49,51,52,55,56,58,62,63,65,66</td>
</tr>
<tr>
<td>2828</td>
<td>1897</td>
<td>229.6</td>
<td>15.0</td>
<td>276.8</td>
<td>18,38,43,45,46,49,51,52,55,56,58,59,62,63,66</td>
</tr>
<tr>
<td>2995</td>
<td>1742</td>
<td>327.9</td>
<td>-0.4</td>
<td>280.5</td>
<td>0,51</td>
</tr>
<tr>
<td>3020</td>
<td>1897</td>
<td>325.6</td>
<td>15.4</td>
<td>282.5</td>
<td>18,38,39,43,45,46,49,51,52,55,56,58,59,62,63,65,66</td>
</tr>
<tr>
<td>3128</td>
<td>1897</td>
<td>177.0</td>
<td>15.3</td>
<td>282.1</td>
<td>18,38,39,43,45,46,49,51,52,55,56,58,59,62,63,65,66</td>
</tr>
<tr>
<td>3355</td>
<td>1803</td>
<td>193.3</td>
<td>5.7</td>
<td>282.0</td>
<td>18,38,39,43,45,46,49,51,52,55,56,58,59,62,63,65,66</td>
</tr>
</tbody>
</table>

$^a$ OCK ("Orbit Counter Keeper") and its subinterval ICK ("Incremental Counter Keeper") refer to the MGS-TES instrument team’s orbit numbering system.

$^b$ Italicized values indicate forward- and aft-viewing measurements available for the specified $\varepsilon$ angle.
Table 2.2: MGS-TES Emission Phase Function Sequences\(^a\) Exhibiting Directional Emissivity Effects: Moderate to High Albedo Regions, cont.

<table>
<thead>
<tr>
<th>OCK</th>
<th>ICK</th>
<th>Longitude (°)</th>
<th>Latitude (°)</th>
<th>( T_{surf} ) (K)</th>
<th>( e ) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3379</td>
<td>1803</td>
<td>160.2</td>
<td>5.7</td>
<td>283.9</td>
<td>18,38,39,43,45,46, 49,51,52,55,56,58, 59,62,63,65,66</td>
</tr>
<tr>
<td>3488</td>
<td>1897</td>
<td>41.4</td>
<td>15.2</td>
<td>275.6</td>
<td>18,38,39,43,45,46, 49,51,52,55,56,58, 59,62,63,65,66</td>
</tr>
<tr>
<td>3894</td>
<td>1595</td>
<td>139.0</td>
<td>-15.0</td>
<td>286.6</td>
<td>0,51,52</td>
</tr>
<tr>
<td>4146</td>
<td>1595</td>
<td>153.0</td>
<td>-15.0</td>
<td>290.4</td>
<td>0,51,52</td>
</tr>
<tr>
<td>4303</td>
<td>1742</td>
<td>329.0</td>
<td>0.0</td>
<td>289.9</td>
<td>0,51,52</td>
</tr>
<tr>
<td>4422</td>
<td>1595</td>
<td>134.0</td>
<td>-15.0</td>
<td>293.3</td>
<td>0,51,52</td>
</tr>
<tr>
<td>4735</td>
<td>1742</td>
<td>95.0</td>
<td>0.0</td>
<td>285.7</td>
<td>0,51,52</td>
</tr>
<tr>
<td>4950</td>
<td>1599</td>
<td>128.0</td>
<td>-15.0</td>
<td>295.3</td>
<td>0,29,54,64,65</td>
</tr>
<tr>
<td>5011</td>
<td>1746</td>
<td>76.0</td>
<td>0.0</td>
<td>288.5</td>
<td>0,29,54,64,65</td>
</tr>
<tr>
<td>5214</td>
<td>1452</td>
<td>123.0</td>
<td>-30.0</td>
<td>302.0</td>
<td>0,29,54,64,65</td>
</tr>
<tr>
<td>5239</td>
<td>1452</td>
<td>119.0</td>
<td>-29.0</td>
<td>301.4</td>
<td>0,29,54,64,65</td>
</tr>
<tr>
<td>5252</td>
<td>1599</td>
<td>133.0</td>
<td>-13.0</td>
<td>297.5</td>
<td>0,29,54,64,65</td>
</tr>
<tr>
<td>5384</td>
<td>1893</td>
<td>315.0</td>
<td>15.0</td>
<td>278.3</td>
<td>0,29,54,55,65</td>
</tr>
<tr>
<td>5608</td>
<td>1329</td>
<td>239.0</td>
<td>-43.0</td>
<td>300.0</td>
<td>18,38,43,45,49,51, 55,58,62,65</td>
</tr>
<tr>
<td>5707</td>
<td>1746</td>
<td>199.0</td>
<td>-3.0</td>
<td>290.7</td>
<td>0,30,53,55,64,65</td>
</tr>
<tr>
<td>5718</td>
<td>1599</td>
<td>151.0</td>
<td>-18.0</td>
<td>295.4</td>
<td>0,29,30,53,55,64,65</td>
</tr>
<tr>
<td>5875</td>
<td>1746</td>
<td>328.0</td>
<td>0.0</td>
<td>295.4</td>
<td>0,29,54,64,65</td>
</tr>
<tr>
<td>5888</td>
<td>1893</td>
<td>342.0</td>
<td>15.0</td>
<td>279.8</td>
<td>0,29,30,54,55,65</td>
</tr>
<tr>
<td>6044</td>
<td>1893</td>
<td>127.0</td>
<td>15.0</td>
<td>284.8</td>
<td>0,29,30,54,55,65</td>
</tr>
<tr>
<td>6068</td>
<td>1893</td>
<td>94.0</td>
<td>15.0</td>
<td>281.4</td>
<td>0,29,30,54,55,65</td>
</tr>
<tr>
<td>6116</td>
<td>1893</td>
<td>335.0</td>
<td>15.0</td>
<td>284.2</td>
<td>0,30,55,66</td>
</tr>
<tr>
<td>6428</td>
<td>1893</td>
<td>319.0</td>
<td>15.0</td>
<td>287.5</td>
<td>0,29,54,65</td>
</tr>
<tr>
<td>6510</td>
<td>1599</td>
<td>142.0</td>
<td>-14.0</td>
<td>294.2</td>
<td>0,29,54,64,65</td>
</tr>
<tr>
<td>6932</td>
<td>1894</td>
<td>345.0</td>
<td>15.0</td>
<td>286.5</td>
<td>0,29,54,55</td>
</tr>
</tbody>
</table>

\(^a\) All calibrated, atmospherically corrected surface radiance spectra provided courtesy of J. Bandfield and the MGS-TES team, Mars Space Flight Facility, ASU.
Table 2.3: MGS-TES Emission Phase Function Sequences<sup>a</sup> Exhibiting Directional Emissivity Effects: Low Albedo Regions

<table>
<thead>
<tr>
<th>OCK</th>
<th>ICK</th>
<th>Longitude (°)</th>
<th>Latitude (°)</th>
<th>( T_{surf} ) (K)</th>
<th>( \epsilon ) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5071</td>
<td>1746</td>
<td>354.0</td>
<td>0.0</td>
<td>292.1</td>
<td>0,29,54,64,65</td>
</tr>
<tr>
<td>6605</td>
<td>1452</td>
<td>339.0</td>
<td>-30.0</td>
<td>295.1</td>
<td>0,29,30,53,54</td>
</tr>
<tr>
<td>6881</td>
<td>1452</td>
<td>319.0</td>
<td>-30.0</td>
<td>287.1</td>
<td>0,29,54,64</td>
</tr>
</tbody>
</table>

<sup>a</sup> All calibrated, atmospherically corrected surface radiance spectra provided courtesy of J. Bandfield and the MGS-TES team, Mars Space Flight Facility, ASU.

apparent in the datasets returned from the Mars Exploration Rovers. To date, directional emissivity has not received much attention in the literature, due in part to a paucity of published experimental studies on planetary terrain analogs. The goal of this study is to determine whether or not variations in emissivity values observed by instruments aboard Mars-orbiting satellites are truly a function of observation angle by attempting to confirm that directional effects occur in Mars terrain analog sites.

For naturally occurring Earth materials, it has been confirmed via past theoretical modeling, laboratory measurements, and field experiments that emissivity monotonically decreases as the angle of emergence \( \epsilon \) increases. Early Mie theory + doubling method numerical calculations indicated a pronounced effect in theoretical \( \epsilon \) spectra generated for quartz and Saharan dust dielectric functions at \( \lambda = 11 \ \mu m \) for \( \epsilon < 60^\circ \) (Takashima & Masuda, 1987, 1988). Past studies which have experimentally measured emissivity at varying viewing angles have focused on general classes of geologic materials like sand, soils, and gravel (Nerry et al., 1990a; Labed & Stoll, 1991; Snyder et al., 1997; Sobrino & Cuenca, 1999; Cuenca & Sobrino, 2004); additional works have demonstrated the angular dependence of emissivity in the IR for water and ice (Masuda et al., 1988; Rees & James, 1992), as well as for vegetative coverings (e.g., rice paddies, Matsushima & Kondo, 1997). Of the general classes of terrestrial materials, laboratory-measured emissivity spectra of clay present the least variation with change in \( \epsilon \), with changes in emissivity between approximately 10° and 50° reported at less than 1% (Snyder et al., 1997). As also seen in laboratory directional emissivity measurements of quartz size fractions (Wald & Salisbury, 1995), sand observed in the field is more profoundly affected by changes in \( \epsilon \), being strongly depressed in the main restrahlen<sup>2</sup> band (8.0-9.0 \( \mu m \)).

<sup>2</sup>Restrahlen features (broad minima in an emissivity spectrum) are generated when light cannot propagate in the medium and must reflect back.
These previous emissivity angular dependence measurement studies were conducted primarily in laboratory or in controlled outdoor settings, not in situ at specific planetary terrestrial analog sites. The only planetary terrestrial analog site which has been explored for directional emissivity effects is the Lunar Crater Volcanic Field, near Tonopah, Nevada. Using hand-held instruments, members of the Geological Remote Sensing Field Experiment (GRSFE) measured emissivity for terrestrial smooth playa, sand, aa lava flows, and constructed sites, at emission angles of 0°, 30°, and 60° (with every 45° of azimuth for 30° and 60° measurements); the results returned from the field were in agreement with predicted theory (Jakosky et al., 1990). For the sand and playa surfaces in that study, a decrease in emissivity with increasing $e$ was also observed.

In this chapter, I present evidence that directional emissivity effects do occur in Mars terrain analog sites, specifically in sand and playa surfaces located in Death Valley National Park and offroad near Baker, California. Section 2.2 describes the field emissivity measurements acquired by Dr. Joshua Bandfield and myself, taken at nadir and at angles corresponding to the MGS-TES EPF sequences. Details on my directional emissivity laboratory measurements of samples from the Mars terrain analog sites are presented in Section 2.3. Spectral analyses and implications for interpreting MGS-TES EPF sequences are discussed in Section 2.4.

### 2.2 Field Emission Spectroscopy

#### 2.2.1 Experimental Procedure

Field emissivity measurements were collected with the Designs & Prototypes™ µFT-IR portable field spectrometer (Hook & Kahle, 1996; Korb et al., 1996), available through the Mars Space Flight Facility at Arizona State University in consortium with USGS Flagstaff and the University of Nevada, Reno. The instrument consists of a tripod-mounted cooler, interferometer with periscope and telescope attachments, laptop computer to acquire and store interferograms and emissivity spectra, electronics suitcase to regulate temperature, and a blackbody attachment (Fig. 2.2). Peripherals include a reflective gold plate to sample downwelling, background radiation, a black plate for atmospheric radiation, a handheld radiometer gun, external batteries, and 1-2 nitrogen canisters for coolant. This particular instrument was not designed for the utility of measuring directional emissivity in the field. Measured direct sky radiation and projected surface areas can vary strongly when pointing significantly off-nadir as a result of this instrument’s fore-optic design. Also, use of a broadband rather than narrow-band channel can cause a large error in brightness temperature of quartz sand soils (Taylor, 1979). The 8.2-9.2 µm channel in particular may be the most sensitive to changing angle of emergence (Cuenca & Sobrino, 2004). However, nadir emissivity measurements obtained via this instrument are considered reliable and, with care, directional emissivity measurements may be acquired. After
assembly, approximately 1 hour is required for the system to cool before acquiring measurements. The estimated time of operation, including time to assemble and disassemble the instrument, was approximately 8 hours per day. To obtain absolute focus, the baseline from the tripod-mounted interferometer to the ground target must be 1 m at minimum. The manufacturer lists the ground target area as 7.6 cm; in practice, the infrared imaged area has been measured to be twice as large (Korb et al., 1996). Defining a pair of blackbody temperatures $\sim 5^\circ\text{C}$ above and below the surface temperature $T$, spectral radiances of cool and hot blackbodies ($\equiv L_{\text{bb}\lambda}(T)$) are acquired first, followed by measurements of sky radiance incident upon the surface ($\equiv L_{\text{sky}\lambda}$) and target radiance ($\equiv L_{\lambda}$); surface emissivity $\epsilon_{\lambda}$ is obtained via Eq. 2.1 (Hook & Kahle, 1996),

$$
\epsilon_{\lambda} = \frac{L_{\lambda} - L_{\text{sky}\lambda}}{L_{\text{bb}\lambda} - L_{\text{sky}\lambda}}.
$$

(2.1)
It is generally assumed that performing field emission spectroscopy under clear-sky conditions is optimal for minimizing error in hemispheric downwelling radiances (Rees & James, 1992; Sobrino & Cuenca, 1999). However, a clear sky itself has significant directional variation which should be measured. In practice, variation in background radiation is typically ignored and treated as “diffuse,” so that one may exchange hemispherical-directional reflectance for directional-hemispherical reflectance to satisfy Kirchhoff’s law. The assumption of diffuse atmospheric background radiation introduces significant systematic error into surface emissivity measurements and may in fact only be validly applied for field measurements acquired during overcast sky conditions (Kribus et al., 2003). Our directional emissivity field measurements for the sand and playa sites were acquired under partly cloudy to overcast conditions. We have not directly measured the directional dependence of the atmospheric background radiation with the field spectrometer because the measured contribution would have been confined to ~5° around the zenith (Hook & Kahle, 1996) and instead account for sky radiance $L_{\text{sky},\lambda}$ averaged for all angles by means of a gold target.

### 2.2.2 Site Measurements

In December 2003, we acquired a set of field emissivity data in the thermal infrared ($\lambda \sim 7-13 \ \mu m$) with the Designs & Prototypes™ µFT-IR portable field spectrometer for three undisturbed Mars terrain analog sites (Badwater Basin and Devil’s Golf Course, Death Valley National Park; Silver Lake Playa, near Baker, CA) and analyzed them for the presence or absence of directional emissivity effects. The carbonates, sulfates, and halite deposits found in the typical basinward sequence along the western margin of Badwater Basin are of interest for both the intrinsic spectral properties of these mineral types and the link to Mars mineralogy established by previous investigation (Baldridge et al., 2004). Emissivity spectra for these types of mineral assemblages can exhibit significant interband (transparency) features or, in the case of halite, be nonabsorbing and featureless (Lane & Christensen, 1998); directional emissivity effects have not previously been explored for spectra of this nature. Playas (i.e., dry lakes) and evaporite deposits on Earth may be analogous to putative palaeolake basins on Mars. MGS-TES EPF sequence analyses suggest that carbonates may be present on Martian dust-coated surfaces (Bandfield et al., 2003). Silver Lake Playa, located north of Baker, California and east of the Soda Mtns., was vital to our study because it was selected as the test site for the field prototype of the 2003/2005

---

3Following the convention of Hapke (1993a), the first adjective preceding the word “reflectance” describes the degree of collimation of the source and the second adjective describes the degree of collimation of the detector. For bidirectional reflectance (Sec. 3.3.2), the degree of collimation for the source and the detector are both equally high. For directional-hemispherical reflectance, the source is more highly collimated than the detector, and vice versa for hemispherical-directional reflectance. The models presented in Sec. 3.3.2 calculate directional-hemispherical reflectance $r_{\text{hem}}$. 
Figure 2.3: Field emissivity spectra of quartz-feldspar sand at Dumont Dunes, at angles corresponding to MGS-TES EPF sequence observation angles: $\epsilon = 0^\circ, 30^\circ, 50^\circ$, and $70^\circ$. Emissivity is shown to decrease with a monotonic increase in $\epsilon$, in agreement with the trend expected from past laboratory, field, and modeling studies (c.f., Section 2.1).

Mars rover FIDO (Field Integrated Data & Operations); its surface is fine-grained, mudcracked silt and clay (Petroy & Arvidson, 1990).

Directional emissivity spectra (emission angle $\epsilon = 0^\circ, 45^\circ, 55^\circ, 85^\circ$) were obtained for approximately 15 targets (salt flats, smooth clay mud, sulfates) at Devil’s Golf Course and Badwater Basin; 15 additional targets ($\epsilon = 0^\circ$-80°, in increments of 10°) were measured at Silver Lake Playa and Dumont Dunes near Baker, CA. Sample sites were photographed to document surface condition and morphology. All field $\epsilon$ spectra measurements were acquired at ambient temperatures of $\sim 10$-$15^\circ$ C, with sample temperatures ranging from 12° C for the Devil’s Golf Course and Badwater Basin sites to 20° C for Silver Lake Playa and Dumont Dunes. For Silver Lake Playa, two sites were observed and sampled: (1) a pristine, smooth playa surface with few mudcracks and (2) a disrupted, overturned playa surface. At Dumont Dunes, the quartz-feldspar sands measured were first planed with a straight edge in two directions before changing $\epsilon$. Field $\epsilon$ spectra and site photographs are presented in Appendix A and Figs. 2.3, 2.4, and 2.5.
Figure 2.4: Multiple emergence angle field emissivity spectra of quartz-feldspar sand particulates at Dumont Dunes: $e = 0^\circ$, $10^\circ$, and $20^\circ$ (upper panel) and $e = 0^\circ$, $60^\circ$, $70^\circ$, and $75^\circ$. While the difference between $10^\circ$, and $20^\circ$ gives little indication of a trend, a decrease in $\epsilon$ with increasing $e$ is observed in the high angle field spectra.
Figure 2.5: High emergence angle emissivity spectra of natural, undisturbed terrain at Silver Lake Playa: $e = 70^\circ$, $78^\circ$, $85^\circ$, and $87^\circ$. Collectively, the spectra presented here and in Figs. 2.3 and 2.4 support the idea that directional emissivity effects can be seen in Mars terrain analog sites in situ.
Figure 2.6: Directional emissivity sample holders manufactured at LSU in use at the Mars Space Flight Facility, ASU. Angle of emergence $e$ for the holders increases from $e = 10^\circ$ to $70^\circ$ in increments of $10^\circ$ from left to right. Photo credit: K. Pitman.

2.3 Laboratory Emissivity Spectroscopy

The radiative properties of laboratory samples may be sufficiently different from the same material in a field or “remote sensing” environment as to produce mutually exclusive, or at least quite distinct, mineralogical interpretations. Differences in emissivity spectra taken under field and laboratory conditions may be due to moisture content, porosity, and surface roughness variations (Nerry et al., 1990b). Thus, in addition to acquiring field $\epsilon$ spectra, we obtained 2.5” square, 1” deep hand samples from each site in order to measure laboratory $\epsilon$ spectra for exactly the same material. In July 2004, I acquired laboratory $\epsilon$ spectra with the Nicolet Nexus 670 transmission spectrometer, located at the Mars Space Flight Facility, ASU. This spectrometer is the same instrument used to calibrate the thermal emission spectrometers TES and THEMIS aboard Mars Global Surveyor and Mars Odyssey, respectively. The wavelength range acquired in the lab is $\sim 5-50 \mu m$, at 4 cm$^{-1}$ resolution. Laboratory $\epsilon$ measurements acquired at nadir and off-nadir angles using the sample mounts illustrated in Fig. 2.6 are plotted in Appendix A and Figs. 2.7, 2.8, 2.9, and 2.10.
Figure 2.7: Upper panel: Nadir laboratory emissivity spectra of a playa surface (\(\equiv\) DEVA-7) (upper panel) and of a rough salt surface (\(\equiv\) EVAP-4) sample (lower panel), Devil’s Speedway, Death Valley, CA, 2003/12/02. The upper panel \(\epsilon\) spectra illustrate the typical level of variability in profiles for \(\epsilon\) spectra acquired at \(\epsilon = 0^\circ\). In the lower panel, moving the target sample slightly underneath the beam results in measurement of different compositions.
Figure 2.8: Nadir laboratory emissivity spectra for hand samples obtained from the south end (≡ SLP-1b, upper panel) and from a plains region of Silver Lake Playa (≡ SLP-2, lower panel), Baker, CA, 2003/12/03. In the upper panel, all three $e = 0^\circ$ spectra were averaged to yield the nadir $\epsilon$ spectrum in Fig. A.14. The blue spectrum was excluded from the averaged $e = 0^\circ$ spectrum in Fig. 2.9.
Figure 2.9: Multiple emergence angle emissivity spectra for lab sample SLP-2: $e = 0^\circ$ (solid black line), $10^\circ$ (red), $30^\circ$ (purple), and $40^\circ$ (blue). Emissivity decreases as angle of emergence increases for the $e = 10^\circ$, $30^\circ$, and $40^\circ$ spectra at wavenumber $> 1400$ cm$^{-1}$ ($\lambda < 7.5$ $\mu$m).
Figure 2.10: Multiple emergence angle emissivity spectra for lab sample DUNE-6: $e = 0^\circ$ (solid black line), $10^\circ$ (red), $20^\circ$ (purple), $30^\circ$ (blue), and $40^\circ$ (magenta). The $e = 20^\circ$-$40^\circ$ sequence does follow the monotonically decreasing $e$ with increasing $e$ trend.
To acquire emissivity spectra of the hand samples at angles corresponding to those observed in the field (i.e., $\varepsilon = 10^\circ$-$70^\circ$, in increments of $10^\circ$), directional emissivity sample holders manufactured at Louisiana State University were used (Fig. 2.6). Each directional emissivity sample holder consists of a removable 1.5” diameter hollow copper pipe base fitted to a 1.5” diameter solid copper rod which has been routered out to accommodate a circular copper sample cup. Total height of base and cup holder is approximately 3.25”. Modular copper sample cups (1” inner diameter, 1 mm deep) are equipped with a 0.5” lip that extends halfway across the base of the cup to prevent hand and particulate samples from falling out at angles greater than the angle of repose$^4$ of the sample material. A thin coating of molybdenum disulfide powder was placed on the bottom of the cup to prevent galling between copper components and to permit easy transfer and removal of the sample cup without disturbing sample integrity.

Because of the spectral profile variability that can occur when there are slight changes in blackbody calibration temperatures and resistances (upper panel, Fig. 2.7), proper selection of the $\varepsilon = 0^\circ$ spectrum is critical when comparing to $\varepsilon$ spectra for multiple angles of emergence. Two methods were tested to achieve the best $\varepsilon = 0^\circ$ measurement: (1) measuring multiple nadir spectra calibrated with slightly different blackbody references and averaging those spectra (e.g., upper panel, Fig. 2.8), and (2) selecting the nadir spectrum with the blackbody references closest to those of the other $\varepsilon > 0^\circ$ spectra acquired (e.g., lower panel, Fig. 2.8). Overall the second method seemed to work best. The $\varepsilon = 0^\circ$ spectra which were too noisy or seemed not to have the shape of the $\varepsilon > 0^\circ$ profiles were excluded from averaging and comparison. For compositional reasons, the beam must strike the same spot on each sample. Even slight excursions created a noticeable difference in terms of $\varepsilon$ spectral feature depth. For the evaporite samples, if the beam strikes the underlying material instead of the salt crust, the spectral profile is profoundly different (c.f., lower panel, Fig. 2.7).

### 2.4 Discussion and Conclusions

Of the Martian terrain analogs observed in this field study, the sand and playa samples showed the most promising evidence of directional emissivity effects in the 7-13 $\mu$m wavelength regime. The field sites that were anticipated to be poor candidates for measuring directional emissivity effects at these wavelengths (smooth mud, sulfates, and salt flats) were proven to be so (Appendix A). For the salt flats in particular, we found that the nadir spectra were essentially flat (i.e., without emissivity features in the IR). While the smooth mud functioned more as a “control group” for the field experiment, it was important to attempt measurements of directional emissivity effects

$^4$The angle of repose is defined as the maximum angle or slope at which granular, cohesionless particulates will not slide downward. The angle of repose is a function of particle size, shape, roughness, and surface charge; for Mars, atmospheric conditions may also influence angle of repose.
in the salt flats and sulfates for two reasons: (1) because prior to our field study, no attempts to observe directional emissivity effects in these types of surfaces had been made, and (2) had directional effects been observed in the salt flats' field emissivity spectra, those results would have unequivocally supported the case for directional emissivity effects occurring on Mars. Of the field emissivity spectra acquired, the natural, undisturbed sites at Silver Lake Playa appeared to show evidence of directional emissivity effects at high angles of emergence (Fig. 2.5). The field $\epsilon$ spectra of the quartz-feldspar sands at Dumont Dunes displayed the clearest evidence of directional emissivity effects (Figs. 2.3, 2.4). For sand, one can clearly see a distinct monotonically decreasing trend in $\epsilon$ with increasing $e$ at MGS-TES EPF sequence $e$ values (Fig. 2.3). Our findings in the sand and playa samples support the results of Jakosky et al. (1990), who also found that sand and playa surfaces in the Lunar Crater Volcanic Field, NV, exhibit noticeable directional effects; we improved upon their experimental methods by using a tripod-mounted FT-IR rather than a handheld radiometer and also acquired our field emissivity spectra at smaller emergence angle intervals (i.e., every $10^\circ$ as opposed to $30^\circ$).

In the laboratory, thermal IR emissivity spectra for the sand sample corroborated the trend observed in our field emissivity spectra results. The lab sample of the quartz-feldspar sands from Dumont Dunes does exhibit the monotonically decreasing $\epsilon$ with increasing $e$ trend at angles $e = 20-40^\circ$ (Fig. 2.10). This finding is in agreement with the laboratory studies of directional emissivity listed in Section 2.1. Lab results for the playa sample did not unequivocally support the field emissivity spectra. Of the laboratory spectra for the Silver Lake Playa sites, emissivity decreases as angle of emergence increases for $e = 10^\circ$, $30^\circ$, and $40^\circ$ spectra at wavenumber $> 1400$ cm$^{-1}$ ($\lambda < 7.5$ $\mu$m) (Fig. 2.9). Lab results from two additional sites at Silver Lake Playa do not support the same conclusion. At the time of the laboratory measurements, the playa samples were very fragile and presented less uniform surfaces, so the laboratory spectra do not necessarily negate the effects observed in the field experiment. Based on combined field and lab data, we conclude that directional emissivity effects can definitely be seen for quartz-feldspar sands at Dumont Dunes and are considered probable for Silver Lake Playa. This constitutes a recent and satisfactory confirmation that directional emissivity spectral effects are occurring in natural, in situ Mars terrain analog surfaces.

The fact that sand, a low albedo material, exhibited strong directional emissivity effects in our field and lab study and in past lab, field, and modeling studies done by others is seemingly in contrast to the current inventory of MGS-TES EPF sequences which indicates that moderate to high albedo (dust covered) Martian surfaces exhibit directional emissivity effects. Within the EPF sequences presented in Tables 2.1-2.3, there are preferentially more moderate to high albedo regions represented because the low albedo surfaces tend not to be uniform. Of the moderate to high albedo surface EPF sequences presented in Tables 2.1-2.2, the relative differences between emissivity spectra acquired at different $e$ angles are typically less pronounced than the "high amplitude" directional emissivity effects seen in Fig. 2.1.
Barring compositional differences between the terrestrial low to moderate albedo Mars analog sites studied here and what is expected for Mars high albedo surfaces\(^5\), the fact that we see emissivity changing with angle of emergence for Mars terrain analog sites and that the magnitude of the relative decrease in \(\epsilon\) may change with the type of geologic material allows us to conclude that the spectral changes observed in the low albedo surface EPF sequences and the more subtle effects observed in the high albedo surface EPF sequences are in fact real directional effects (not artifacts of improper calibration). Analysis of the MGS-TES EPF observations is ongoing and will be presented in a future Geophysical Research Letter.

\(^5\)The Mars high albedo surfaces are covered by micron-scale silicate dust thought to be composed of plagioclase, zeolite, and/or palagonite (Wyatt et al., 2004 and references therein). Mars low albedo surfaces are basaltic or basaltic/andesitic compositions (Bandfield, 2002).
3. Application of Modern Radiative Transfer Tools To Model Laboratory Nadir Quartz Emissivity

Planetary remote sensing of regolith surfaces requires use of theoretical models for interpretation of constituent grain physical properties. In this chapter, we review and critically evaluate past efforts to strengthen numerical radiative transfer (RT) models with comparison to a trusted set of nadir incidence laboratory quartz emissivity spectra (Pitman et al., 2005, in press\(^1\)). By first establishing a baseline statistical metric to rate successful model-lab emissivity spectral fits, we assess the efficacy of hybrid computational solutions (Mie theory + numerically exact RT algorithm) to calculate theoretical emissivity values for micron-sized \(\alpha\)-quartz particles in the thermal infrared (2000-200 cm\(^{-1}\)) wavenumber range. We show that Mie theory, a widely used but poor approximation to irregular grain shape, fails to produce the single scattering albedo and asymmetry parameter needed to arrive at the desired laboratory emissivity values. Through simple numerical experiments, we show that corrections to single scattering albedo and asymmetry parameter values generated via Mie theory become more necessary with increasing grain size. We directly compare the performance of diffraction subtraction and static structure factor corrections to the single scattering albedo, asymmetry parameter, and emissivity for dense packing of grains. Through these sensitivity studies, we provide evidence that, assuming RT methods work well given sufficiently well-quantified inputs, assumptions about the scatterer itself constitute the most crucial aspect of modeling emissivity values.

3.1 Mie-RT Hybrid Models

Moersch & Christensen (1995), hereafter MC95, reviewed several general categories of (non-numerical) theoretical models available at the time to calculate emissivity: Hapke’s 2-stream analytical approach, Mie single scattering theory + multiple scattering via Conel (1969), and Mie theory + multiple scattering via Hapke (1993b). The first model, Hapke’s 2-stream analytical approach (Hapke, 1981, 1993a, 1993b), was designed for closely packed particles with \(d >> \lambda\); it is a geometrical optics model that explicitly neglects diffraction effects. Mie single scattering theory coupled with a multiple scattering method of solution to the equation of radiative transfer, though formally appropriate for well-separated, spherical particles, has produced reasonable results for packed media under certain conditions (Conel, 1969; Goguen, 1993). In the second and third models, the Mie/Conel (1969)

\(^1\)Reproduced by permission of American Geophysical Union.
Table 3.1: Summary of α-Quartz Model Run Parameters (MC95)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Predicted Diameter Range (μm)</th>
<th>μd (μm)</th>
<th>σd (μm)</th>
<th>r_eff (μm)</th>
<th>v_eff (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>210-250</td>
<td>277</td>
<td>49</td>
<td>147.17</td>
<td>0.03</td>
</tr>
<tr>
<td>D</td>
<td>125-149</td>
<td>185</td>
<td>29</td>
<td>97.05</td>
<td>0.02</td>
</tr>
<tr>
<td>G</td>
<td>74-90</td>
<td>102</td>
<td>20</td>
<td>54.92</td>
<td>0.04</td>
</tr>
<tr>
<td>I</td>
<td>53-63</td>
<td>61</td>
<td>12</td>
<td>32.86</td>
<td>0.04</td>
</tr>
<tr>
<td>L</td>
<td>30-37</td>
<td>43</td>
<td>8</td>
<td>22.99</td>
<td>0.03</td>
</tr>
<tr>
<td>M</td>
<td>20-30</td>
<td>28</td>
<td>6</td>
<td>15.29</td>
<td>0.04</td>
</tr>
<tr>
<td>N</td>
<td>11-20</td>
<td>15</td>
<td>3</td>
<td>8.10</td>
<td>0.04</td>
</tr>
</tbody>
</table>

and Mie/Hapke (1993b) hybrid methods, different analytical expressions for a 2-stream approximation to the RT equation were used; resulting expressions for ε depended solely on the single scattering albedo and the asymmetry parameter, or on the single scattering albedo and Chandrasekhar’s H-functions, respectively (Chandrasekhar, 1960). Most of the models examined in MC95 did not calculate the scattering phase function in full; an isotropic phase function was assumed. To examine the models’ performance, MC95 measured laboratory emissivity spectra of quartz powder samples, with mean particle diameters ranging from 15 to 277 μm in narrow, well-characterized grain size distributions (Table 3.1). Upon comparison between theoretical and laboratory emissivity spectra, they determined that the most promising model for predicting emissivity was the Mie/Hapke (1993b) hybrid. This model qualitatively reproduced trends in ε(λ) with grain size, the emission maximum in quartz spectra, and the overall patterns of class 1 (imaginary optical constant k > 2), class 2 (0.5 < k < 1), and class 3 (k < 0.1, real optical constant n ~ 2) emissivity spectral regions; it worked well for small and moderate values of k but not for large k.

Since MC95, Mie + RT algorithm hybrid solutions have continued to be used in modeling densely packed powders. To model laboratory directional hemispherical reflectance spectra of powdered quartz, Wald & Salisbury (1995) approximated the scattering phase function with the Henyey-Greenstein (HG) function (Henyey & Greenstein, 1941). Their RT model was a 100-stream doubling calculation that used particle size distributions (rather than single particle sizes) as inputs and treated close packing of large spheres (d > 75 μm) by subtracting out the diffraction contribution to the Mie scattering cross-sections. The angular emissivity models of quartz sand grains in the thermal IR (8-12 μm region, corresponding to field radiometer studies) of McAtee et al. (2003) were based on a Mie/delta-Eddington approximation hybrid model originally developed for the spectral albedo of
Figure 3.1: Comparing performance of new Mie + reconstructed Hapke (1993b) analytical RT emissivity model (diamonds) vs. MC95 Mie + Hapke (1993b) analytical RT emissivity model (dashed line), as compared to MC95 laboratory emissivity spectra (solid line). Emissivity spectra are displayed in terms of wavenumber in cm\(^{-1}\) (lower x-axis) and wavelength in \(\mu\text{m}\) (upper x-axis), offset in units of 0.5 in emissivity; conversions between wavenumber and wavelength were made assuming that the index of refraction of air is equal to unity. Both models were integrated over the (circular) spectrometer field of view (= 42°; see Appendix C). The new Mie algorithm implementation can be expected to deliver single scattering properties comparable to the values used to generate MC95 models. Wavenumber bands for MC95 class 1 (\(k > 2\)), class 2 (\(0.5 < k < 1; n \sim 2\)), class 3 (\(k < 0.1; n \sim 2\)), and class 4 (\(k < 0.1; n \sim 1\)), subdivided as per restrictions on optical constants \(n, k\) and Fig. 6a, MC95 (see left hand column, Table 3.2 for wavenumber values), are plotted along the abscissa.
Figure 3.2: Emissivity ratios (ith diameter sample divided by \( d = 277 \) \( \mu m \) sample) illustrate the wavenumber regions in which the MC95 model-lab fit was poorest. y-axis offsets are in units of 0.5. Solid line \( \equiv \) ratio of lab \( \epsilon \) spectra measured; dashed line \( \equiv \) Mie + Hapke (1993b) analytical RT emissivity model (both from MC95). Certain wavenumber regions (classes k1-k6, summarized in Table 3.2) appear sensitive to model-lab mismatch.

snow (Warren & Wiscombe, 1980). Another snowpack bidirectional reflectance model which reproduces the scattering phase function to arbitrary precision bypasses the calculation of the internal radiation field by iteratively solving Ambartsumian’s nonlinear integral equation, resulting in improved numerical accuracy over most complete RT solutions (Mishchenko et al., 1999).

Given the wide use of the Mie + RT hybrid model and the wide range of analytical and numerical RT algorithms, the hybrid model paradigm would seem like the perfect starting point for developing subsequent emissivity models. However, after superimposing laboratory measured and model predicted \( \epsilon(\lambda) \) values from MC95, the Mie + RT hybrid model spectra noticeably differ from the observed laboratory spectra (Fig. 3.1). In the wavenumber region 1250-1000 \( \text{cm}^{-1} \), the MC95 Mie/Hapke (1993b) model \( \epsilon \) differs from the laboratory \( \epsilon \) values on the order of 0.1-0.15 for the \( d = 15 \) \( \mu m \) sample. For
Figure 3.3: Emissivity ratios (ith MC95 model spectrum divided by ith MC95 lab spectrum) identify specific wavenumber regions not necessarily associated with deep $\epsilon$ features where MC95 model-lab fit could be improved. y-axis offsets are in units of 0.5.

$d = 61 \mu m$ and $277 \mu m$, the models overestimate laboratory $\epsilon$ values by approximately 0.1 and 0.1-0.2, respectively. Measuring the systematic changes in emissivity from model to model (Fig. 3.2) and defining a metric to quantitatively determine what constitutes a satisfactory RT model fit to thermal IR laboratory emissivity spectra of regolith proxies can help us to identify and improve poor model-lab fits. Because there are no published goodness-of-fit statistics for the MC95 model spectra, we cannot use the established $\chi^2$ metric to determine how successfully or poorly their models fit their laboratory $\epsilon$ spectra. As an alternative goodness-of-fit statistic, we calculated root-mean-square error values (Table 3.2) for the MC95 model fits of the 7 laboratory quartz samples over 15 selected wavenumber regions, including the MC95 classes 1, 2, 3, and 4 corresponding to resonance and continuum regions of the quartz dielectric function (Fig. 3.1) and also to wavenumber intervals defined by emissivity ratios where the MC95 model-lab fits are poor (Fig. 3.3). Based on these values and noting that a change in emissivity of 0.1-0.15 amounts to nearly the depth of the main $\epsilon$ feature for fine particulate
Table 3.2: RMS Error Values For MC95 α-Quartz Samples (MC95 model)

<table>
<thead>
<tr>
<th>Class</th>
<th>Wavenumber Range (cm⁻¹)</th>
<th>Mean Effective Diameter (µm)</th>
<th>15</th>
<th>28</th>
<th>43</th>
<th>61</th>
<th>102</th>
<th>185</th>
<th>277</th>
</tr>
</thead>
<tbody>
<tr>
<td>k1</td>
<td>1399.06–1352.08</td>
<td>0.019</td>
<td>0.490⁴</td>
<td>0.091</td>
<td>0.362</td>
<td>0.410</td>
<td>0.410</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>1390.06–1309.09</td>
<td>0.042</td>
<td>0.069</td>
<td>0.073</td>
<td>0.055</td>
<td>0.036</td>
<td>0.024</td>
<td>0.018</td>
<td></td>
</tr>
<tr>
<td>k2</td>
<td>1248.46–1206.24</td>
<td>0.072</td>
<td>0.031</td>
<td>0.040</td>
<td>0.036</td>
<td>0.063</td>
<td>0.062</td>
<td>0.067</td>
<td></td>
</tr>
<tr>
<td>k3</td>
<td>1199.27–1150.20</td>
<td>0.070</td>
<td>0.071</td>
<td>0.069</td>
<td>0.071</td>
<td>0.113</td>
<td>0.126</td>
<td>0.130</td>
<td></td>
</tr>
<tr>
<td>k4</td>
<td>1148.25–1103.53</td>
<td>0.080</td>
<td>0.032</td>
<td>0.033</td>
<td>0.058</td>
<td>0.093</td>
<td>0.086</td>
<td>0.078</td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>1123.50–1077.38</td>
<td>0.078</td>
<td>0.087</td>
<td>0.082</td>
<td>0.125</td>
<td>0.182</td>
<td>0.181</td>
<td>0.176</td>
<td></td>
</tr>
<tr>
<td>k5</td>
<td>1096.52–1051.63</td>
<td>0.080</td>
<td>0.149</td>
<td>0.141</td>
<td>0.166</td>
<td>0.208</td>
<td>0.223</td>
<td>0.229</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>979.28–835.14</td>
<td>0.046</td>
<td>0.033</td>
<td>0.026</td>
<td>0.017</td>
<td>0.018</td>
<td>0.025</td>
<td>0.028</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>802.30–795.31</td>
<td>0.034</td>
<td>0.041</td>
<td>0.025</td>
<td>0.033</td>
<td>0.043</td>
<td>0.039</td>
<td>0.041</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>754.24–709.17</td>
<td>0.062</td>
<td>0.032</td>
<td>0.025</td>
<td>0.015</td>
<td>0.017</td>
<td>0.023</td>
<td>0.029</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>702.17–699.16</td>
<td>0.042</td>
<td>0.013</td>
<td>0.006</td>
<td>0.006</td>
<td>0.010</td>
<td>0.014</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>k6</td>
<td>699.16–600.14</td>
<td>0.209</td>
<td>0.105</td>
<td>0.077</td>
<td>0.065</td>
<td>0.031</td>
<td>0.013</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>683.19–638.16</td>
<td>0.229</td>
<td>0.096</td>
<td>0.083</td>
<td>0.072</td>
<td>0.032</td>
<td>0.012</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>520.34–496.24</td>
<td>0.080</td>
<td>0.059</td>
<td>0.054</td>
<td>0.039</td>
<td>0.049</td>
<td>0.063</td>
<td>0.070</td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>474.17–448.76</td>
<td>0.038</td>
<td>0.044</td>
<td>0.056</td>
<td>0.097</td>
<td>0.127</td>
<td>0.154</td>
<td>0.180</td>
<td></td>
</tr>
</tbody>
</table>

*Italicized value indicates unacceptable fit between original MC95 model and lab data.

quartz, we consider RMS error values greater than 0.1 in emissivity to be a poor fit for this material.

In this chapter, we describe our attempts to determine specifically what parts of the Mie + RT hybrid model are responsible for causing the RMS mismatches between model and laboratory emissivity values. Mismatches between Mie + RT hybrid model and lab emissivity spectra in MC95 are anticipated to be due in part to the model input assumptions. For example, Mie single scattering theory assumes that particles are isolated and spherical; in reality, the sample quartz grains are neither. The possibility that the packing assumption used in MC95 masks the poor approximation to grain shape must be explored in parallel. In MC95, the Mie single scattering phase function was represented by a Legendre polynomial, truncated after the second term. Other methods to calculate the phase function (e.g., via use of the asymmetry-parameter-equivalent Henyey-Greenstein phase function, or full Legendre expansion of the phase function) may result in a better fit. We
will compare thermal IR laboratory emissivity spectra from MC95 and new laboratory emissivity spectra obtained for this study to theoretical emissivity values we calculate via a Mie theory + rigorous numerical RT algorithm hybrid solution (Stamnes et al., 1988; Mishchenko et al., 1999). In Sec. 3.2, we describe the laboratory samples and procedures used; in Sec. 3.3, we outline our numerical methods and model assumptions. In the remainder of this work, we reevaluate the validity of grain packing assumptions used in a Mie + RT hybrid model paradigm, specifically comparing the performance of diffraction subtraction and static structure factor corrections to single scattering properties.

3.2 Laboratory Thermal IR Emissivity Measurements

3.2.1 Vibrational Spectroscopy

Laboratory thermal IR emissivity measurements are based on the principle that mineral crystal lattices vibrate at certain fundamental frequencies which depend on the crystal’s structure and elemental composition. For most geologic materials, the wavelengths corresponding to these fundamental frequencies typically occur at $5 \mu m < \lambda < 100 \mu m$ ($2000 \text{ cm}^{-1} > \xi > 100 \text{ cm}^{-1}$) (Christensen et al., 2001). Within different anion groups, fundamental vibrations produce distinct spectral bands, allowing mineral families (e.g., carbonates, sulfates, phosphates, silicates, oxides, and hydroxides for anion groups CO$_3$, SO$_4$, PO$_4$, and SiO$_4$, respectively) to be readily identified. Taking a simplistic view of a polyatomic molecule as a quasi-harmonic oscillator in which different bonded components vibrate independently, stretching vibrations due to alternate stretching and compression motions and deformation vibrations (including bending for linear and nonlinear molecules) may occur in the bonded components containing major cations. Atomic and electron displacement from equilibrium resulting from these vibrations cause the formation of an oscillating dipole; the emitted phonon in a dense, optically thick medium is reabsorbed, producing characteristic infrared absorption features (valleys) in the emissivity spectrum. For quartz, the main absorption features in the emissivity spectra are the restrahlen bands which are due to stretching and bending in the Si-O bonds.

3.2.2 Laboratory Samples

We modeled the laboratory emissivity spectra of high-purity quartz grains given in Fig. 5a of MC95 (solid line, Fig. 3.1). Size sorting via sieving and Stokes settling separation yielded a predicted range of diameters for grains in each sample; measuring the long and short axes of $\sim 60$ grains for each sample, statistics on effective diameters were calculated. Mean effective diameters and standard deviations for the MC95 laboratory samples ranged...
from 15 μm to 277 μm (Table 3.1). For the MC95 samples separated by sieving, the mean effective diameter was on the order of 20% higher than the upper limit on the mesh size, presumably due to larger acicular particles passing through the mesh lengthwise. The particle size distributions for the well-separated quartz particulates of MC95 were Gaussian volume size distributions.

### 3.2.3 Instrumentation, Experimental Conditions and Procedure

The laboratory emissivity spectra of MC95 were obtained with a Mattson Cygnus 100 Fourier transform infrared spectrometer adapted for emission spectroscopy, in operation at Arizona State University until replaced by the Nicolet Nexus 670 instrument in mid-1999. The Nicolet Nexus 670, used to acquire laboratory emissivity spectra presented in Chapter 4, operates with the same 4 cm\(^{-1}\) resolution (2 cm\(^{-1}\) sampling) as the Mattson Cygnus 100 and a similar spectral range: 2000-200 cm\(^{-1}\) (≈ 5-50 μm), versus Mattson Cygnus’ 2000-400 cm\(^{-1}\) (5-25 μm). The experimental procedure used in MC95, method 1 of Christensen & Harrison (1993), is similar to that used to acquire the laboratory emissivity spectra in Chapter 4 (Eq. 3.1, Ruff et al., 1997) in that both assume \(\varepsilon = 1.0\) when solving for instrument and environment Planck radiances \((B_{\text{inst}} \text{ and } B_{\text{env}})\),

\[
\varepsilon = \frac{V_{\text{meas}} - B_{\text{env}} + B_{\text{inst}}}{B_{\text{sam}} - B_{\text{env}}}.
\]  

In Eq. 3.1, \(V_{\text{meas}}\) is the measured voltage, \(B_{\text{sam}}\) is the sample Planck radiance, and \(F = V_{bb}(T_1) - V_{bb}(T_2)/(B_{bb}(T_1) - B_{bb}(T_2))\) is the instrument response function, determined by the difference of two blackbody voltages over the difference of two blackbody radiances. Before emissivity measurements were acquired, quartz particulates were poured into Krylon black painted copper sample cups 3 cm in diameter, 1-3 mm deep. To increase the measured signal and to remove any adsorbed water from the quartz grains, samples were heated to 80-90°C in a laboratory oven for approximately 1 day before spectral acquisition. Emissivity spectra were first measured and resistances and temperatures recorded for warm (≈ 70°C) and hot (100°C) blackbody targets to define the instrument response function and the initial instrument energy. The target (i.e., the copper sample cup) was then inserted into a Plexiglas\(^{TM}\) glove box adjacent to the external port of the spectrometer, mounted in a copper holder supported by a quartz block, and raised into the sample chamber by means of a crank-shaft platform. Spectral acquisition consisting of interferogram scans was achieved in ≈ 3 minutes. Warm and hot blackbody measurements are typically repeated at least once midway through measurement of all samples to check the stability of the instrument energy. To minimize the presence of CO\(_2\) and water vapor spectral features in emissivity spectra acquired with the new Nicolet Nexus 670 instrument,
the relative humidity inside the Plexiglas\textsuperscript{TM} glove box was maintained to \( \sim 0\% \) via continuous purge. Each emissivity spectrum is measured for a single target (spot size on the particulate sample \( \sim 1 \text{ cm} \)), with 180 interferograms co-added per measured spectrum to improve signal-to-noise performance. With the experimental calibration used in MC95, the laboratory \( \epsilon \) spectra of MC95 are assumed to be accurate within \( \sim 2\-3\% \).

### 3.3 Radiative Transfer Model Description

#### 3.3.1 Model Inputs and Assumptions

**Composition**

Emissivity spectra are highly sensitive to particle mineralogical composition, defined in the theoretical models by the dielectric function. The source of Mars surface components are generally taken to be (1) dust that settled from the atmosphere, (2) sand transported across the surface by wind, impact, and possibly water, and (3) materials developed in place by inferred weathering processes, forming duricrust and clods. A number of mineralogical components have been proposed to be present in Martian soils and dust, including phyllosilicates, plagioclase, zeolites, sulfates, carbonates, and iron oxides (Bell, 1996). The thermal infrared spectral response of the dust is dominated by silicates, however (e.g. Toon et al., 1977) and can be roughly approximated with a few materials such as palagonite or basalt. Given the dominance of silicates and the current mismatches between model and laboratory \( \epsilon \) spectra, we believe model development and validation techniques are best served by considering examples of a few representative mineral classes. Basalt, while a more realistic match to Mars surface compositions, is not the best choice for constraining composition in model parameter space due to the variety of possible basalt chemical compositions. As pointed out in MC95, the best material with which to test a model is natural quartz. Quartz has a simple emissivity profile (i.e., one dominant characteristic feature at \( \lambda \sim 9 \mu\text{m} \)), and the optical constants for bulk quartz are well characterized over a broad wavelength range (Philipp, 1985). MC95 modeled the quartz dielectric function of Spitzer & Kleinman (1961); we model the Spitzer & Kleinman (1961) and Wenrich & Christensen (1996) thermal IR quartz dielectric functions, which return comparable emissivity values in the wavenumber range 1400-400 cm\(^{-1}\) for Mie + RT hybrid solutions (both analytical and numerical). The advantage to using the Wenrich & Christensen (1996) optical constants is the extended wavenumber coverage (2000-200 cm\(^{-1}\)), useful for comparing to recently acquired laboratory \( \epsilon \) spectra. We note that in the thermal IR, the O-ray and E-ray optical constants are significantly different in the 400-800 cm\(^{-1}\) and 1000-1300 cm\(^{-1}\) regions; to represent the dichroic behavior of the material as best as possible, we use the traditional (1/3-2/3) weighting approximation (Eq. 3.2), in which the single scattering cross section \( \sigma \) is a single value with 1/3 of the contribution to \( \sigma \) coming from the
E-ray (parallel) and 2/3 from the O-ray (perpendicular) components (Draine & Malhotra, 1993, and references therein),

\[ \sigma = \frac{\sigma_{||} + 2\sigma_{\perp}}{3}. \]  

(3.2)

Differences between modeled and measured emissivities in the 450-500 cm\(^{-1}\) and 1050-2000 cm\(^{-1}\) wavenumber regions may be caused in part by the (1/3-2/3) weighting approximation. The Spitzer & Kleinman (1961) and Wenrich & Christensen (1996) quartz dielectric functions were determined for polished, single-crystal disks of quartz. When \(d < \lambda\), use of IR optical constants for a bulk rather than particulate sample of any composition may cause a mismatch between theoretical and laboratory spectra (Jurewicz et. al, 2003, and references therein); mismatches between \(n\) and \(k\) magnitudes have been noted in comparisons of bulk and powdered quartz IR optical constants (Arnold et al., 1996). Despite this caveat, the quartz dielectric functions of Wenrich & Christensen (1996) appear to be the best optical constants currently available for modeling recently acquired laboratory \(\epsilon(\lambda)\) spectra.

**Particle Shape**

To calculate scattering properties of a single particle, previous modeling attempts have invoked Mie algorithms. Mie theory strictly applies to the case of isolated spherical particles. Fine particulates in a planetary regolith are not isolated, nor does crushing a conchoidally fractured mineral yield spherical particles. However, the settling and particle sizing methods used to calculate the mean effective diameter and standard deviation values provided by MC95, which we use as model input parameters, assume that the grains are volume-equivalent spheres. To model close packing conditions with a more realistic alternative than a Mie algorithm (a code that can approximate axially symmetric yet nonspherically shaped particles) also poses a serious problem because the assumption of spherical grain geometry is built into the packing equations. We do not advocate the use of Mie theory as the ultimate method for calculating single scattering properties in planetary regoliths. We use Mie theory here for continuity with the MC95 Mie + analytical RT hybrid model, to remain strictly consistent with the shape assumptions inherited from laboratory sample preparation and present in packing assumptions, and because a single algorithm does not currently exist for a more sophisticated treatment of particle shape (e.g., T-matrix, finite element methods) over the entire wavenumber region of interest.

**Wavelength (Wavenumber)**

We restrict our study to the thermal IR wavenumber regime (2000-200 cm\(^{-1}\), or \(\lambda = 5-50 \mu m\)), matching the wavenumber range and sampling corresponding to the specifications of TES, THEMIS, and mini-TES instruments. Given that grain sizes in our models must be on the order of 10-1000
μm in diameter to extend from Martian regolith fine fraction out to ASU TES spectral library sample sizes, working in the thermal IR regime requires the investigation of nonspherical grain shapes at a later date. Current T-matrix codes, including the quad precision implementation of Mishchenko et al. (1999), will not routinely converge for large size parameters, i.e., $X > 50$, which still falls short of the geometric optics regime.

### Particle Size Distribution

For each laboratory $\epsilon$ spectrum of quartz particulates, we specify the model size distribution by supplying values from laboratory-measured particle size distributions (PSDs). Our model inputs for the size distributions are normalized probability density functions of each sample, i.e., in terms of frequency, not in terms of weight or volume such as in sedimentology -log $\phi_d$ plots. Thus, the Gaussian (volume) PSDs of the MC95 samples are supplied as gamma size distribution (frequency) PSDs to our model. The functional form for the gamma size distribution is given by Mishchenko et al. (2002),

$$n(r) = (\text{constant})r^{(1-a)b} \exp \left( -\frac{r}{ab} \right), \quad b \in (0, 0.5),$$  \hspace{1cm} (3.3)

where $r \equiv$ grain radius, $a \equiv$ effective radius, and $b \equiv$ effective variance. To successfully import mean effective diameter $\mu_d$ and standard deviation $\sigma_d$ values into the model, one must first calculate effective radius $a = (2\sigma_d^2/\mu_d + \mu_d$ and effective variance $b = \sigma_d^2/(\mu_d^2 + 2\sigma_d^2)$. Defining the size and size distribution in this manner is advantageous because $a$ and $b$ are easily portable into many mathematical expressions for size distribution. Eq. 3.3 was used to model the quartz particulates of MC95; effective radius and variance values for the MC95 samples are presented in Table 3.1.

### 3.3.2 Numerical Methods

We are using the Mie theory + RT solution model paradigm advocated by MC95 but attempt to improve their fit to lab data by first investigating whether or not it is advantageous to include a higher number of terms in the phase function; we also use a numerically exact rather than analytical approximation to the RT equation to avoid the use of empirical representations and approximations and to simplify the number of parameters.

### Calculating Emissivity

By definition, $\epsilon(\lambda)$ is related to directional-hemispherical reflectance,

$$\epsilon = 1 - r_{\text{hem}},$$  \hspace{1cm} (3.4)

where $r_{\text{hem}}$ is the ratio of (total power scattered into the upper hemisphere by a unit area of surface) to (collimated power incident on a unit area of surface). The most important task of the theoretical model, then, is to calculate $r_{\text{hem}}$. 
In the following, assume that, for a column of total length $L$ and optical depth $\tau$, number density per unit volume is given by $n_d$, and $C_{sca}$ and $C_{ext}$ are the total scattering and extinction cross sections, respectively:

$$C_{sca} = 2\pi \int_{\theta=0}^{\pi} (Z11) \sin \theta d\theta,$$

$$C_{ext} = \frac{\tau}{n_d L}.$$  \hspace{1cm} (3.5) \hspace{1cm} (3.6)

The radiance measured at a detector (given in units of power per unit area per unit solid angle) is an integral of the source function, i.e.,

$$I_D \propto \int_0^\infty w(\tau) p(\tau, g) e^{-\alpha \tau} d\tau.$$  \hspace{1cm} (3.7)

$g = \pi - \text{(scattering angle } \theta \text{)}$ is the phase angle, $w(\tau)$ is the volume single scattering albedo,

$$w(\tau) = \frac{C_{sca}}{C_{ext}},$$  \hspace{1cm} (3.8)

and $p(\tau, g)$ is the volume single scattering phase function (Appendix B). $p(\tau, g) \equiv p(\theta)$ describes the angular redistribution of light of wavenumber $\xi$ after it has been scattered by a dust grain,

$$p(\theta) = \frac{S11}{|\xi|^2 * C_{sca}}.$$  \hspace{1cm} (3.9)

The bidirectional reflectance of a surface (denoted by $R(i, e, g)$)$^4$ is the ratio of scattered radiance at the detector to the incident irradiance,

$$R \equiv R(i, e, g) = \frac{I_D}{I}.$$  \hspace{1cm} (3.10)

One may then divide the bidirectional reflectance by $\mu_0 (= \cos i)$ to get the ratio of the radiance scattered by the surface into a given direction to the collimated power incident on the unit surface area$^5$. The integration of this quantity over scattering and azimuthal angles is $r_{hem}$,

$$r_{hem}(i) = \frac{1}{\mu_0} \int_{2\pi} R(i, e, g) \mu \sin e d\phi.$$  \hspace{1cm} (3.11)

$^2$Z11 is the (1,1) element of the phase matrix: $Z11 = \frac{1}{4}(|S11|^2 + |S12|^2 + |S21|^2 + |S22|^2)$, where $S_{\alpha\beta}$ denotes the $(\alpha, \beta)$ element of the 2 x 2 amplitude scattering matrix. (Multiplying $S_{\alpha\beta}$ by the incident electric field vector results in the scattered electric field vector.)

$^3$This is the scattering angle between incident and scattered beams, i.e., $\theta = \cos^{-1}(\hat{r} \cdot \hat{n}_{\text{inc}})$. $^4i$ is the angle of incidence of light from the sun on the surface; $e$ is the angle of emergence of scattered light from the surface.

$^5$Similarly, $\mu = \cos e$. $\alpha$ in Eq. 3.7 carries dependence on both $\mu_0$ and $\mu$. 


Thus, to characterize emissivity values in any radiative transfer model, there are only three major quantities that one can vary: optical depth of the medium $\tau$ (which is stipulated in the RT solution and held fixed), single scattering albedo $w$ (allowed to vary as a function of wavelength $\lambda$), and the single particle phase function $p(\theta)$ (a function of the scattering angle $\theta$).

**Single Scattering Phase Function**

The single scattering phase function quantifies how much light is scattered into all directions from an optically thin, infinitessimal volume. One may empirically obtain the phase function through experimentation or, more usually, one may mathematically represent the phase function with exact (e.g., Mie theory) or analytical (e.g., HG approximation) forms. Mie theory describes interference and diffraction of a plane wave incident light source for homogeneous, independently scattering target particles regardless of size; in this representation, the phase function is expressed in terms of vector spherical harmonics, weighted by expansion coefficients (where the $l = 1$ expansion coefficient is the asymmetry parameter $g$). The HG phase function has a simple, rapidly converging expansion for typical asymmetry parameters. In this chapter, we have used Mie theory to explicitly calculate the single scattering properties (e.g., $w, C_{\text{sc}}, C_{\text{ext}}$). In Section 3.4, we use both Mie theory and the HG phase function in the most common way: calculate $g$ via Mie theory, then insert it into the HG approximation to quickly generate the scattering phase function. The number of terms in the expansion for the phase function is the key variable to control; additionally, there are instances in which one mathematical representation (Mie theory or HG approximation) offers an advantage over the other. Many formulations use two terms of the HG phase function (Hapke, 1996; Hartman & Domingue, 1998). To account for the slow monotonic decrease in the expansion coefficients, the number of terms required to adequately represent a single particle phase function may be much higher (on the order of $\geq 10^2$ or, for grain effective radii $= 1000 \mu m, 10^3$ terms). Using Mie theory, we are guaranteed to generate enough terms in the phase function expansion initially. Additionally, by using an exact expression, we are avoiding the unrealistic phase functions that can be generated by simple analytic approximations at small near-forward or large near-backward scattering angles.

**Specifying the Number of Streams**

One might intuitively reason that increasing the number of streams as a means of improving the angular resolution of the scattering phase function will result in a more accurate determination of emissivity. The radiating wave is modeled as streams of photons propagating in one direction (i.e., $N$ upwelling and $N$ downwelling hemispheric diffusive flux densities). The number of streams ($\equiv 2N$) dictates how many terms in the phase function expansion are retained. 2 or 4 streams are considered adequate approximations for flux and mean intensity calculations, while 16 or greater streams
are recommended for accurate determinations of intensities (Stamnes et al., 2000\textsuperscript{6}). A preference for 2 or 4 streams versus 16 or greater streams also depends on whether the application is to dense media (e.g., planetary surfaces, vegetative canopies) or to diffuse media (e.g., atmospheres, oceans, interstellar medium). The higher the number of streams, the more CPU intensive the program becomes; for example, using the discrete ordinates RT code of Stamnes et al. (1988), the computation time goes roughly as the number of streams cubed. Ideally, one wishes to use the least number of streams necessary to solve the problem at hand while retaining enough terms to adequately specify the phase function. Because high numerical accuracy has been shown to be unnecessary for reflectance measurements of particulates that could make up a planetary regolith (Hapke, 1999), we conducted a test confirming that high numerical accuracy is unnecessary for nadir emissivity measurements of particulates. By varying the number of streams in our modified discrete ordinates RT routine (from the minimum allowed by the program \(\equiv 4\) to higher orders: 16, 32, 64, 128) for model runs of different sizes and packing fractions (normalized phase functions and asymmetry parameters for these runs depicted in Appendix D: Fig. D.2, D.3, and D.4), we found that variations in the resulting emissivity values were much less than 1%. Thus, for the remainder of this work, the number of streams is 4.

Numerical Implementation

The numerical (plane-parallel) multiple-scattering radiative transfer tools used in this parameter exploration rely on well-tested and validated public-domain subroutines, specifically two FORTRAN codes: the DMiLay Mie algorithm (to calculate single scattering properties) and the DISORT subroutine library (Stamnes et al., 1988) (to calculate emissivity). The use of the discrete ordinates code for calculating multiple scattering terms offers potential for computational efficiency if one can demonstrate that fewer numbers of streams are necessary. This approach has been validated against integral routines (e.g., Mishchenko et al., 1999) at selected wavelengths. Using the single scattering albedo, wavelength, and scattering matrix elements from the Mie DMiLay algorithm-based code, our DISORT-based implementation calculates plane albedo (a.k.a., hemispherical reflectance) over a range of emission angles corresponding to the width of the laboratory spectrometer beam. Hemispherical reflectance is then converted via Kirchhoff’s Law to emissivity (c.f. Hapke, 2002). The far-field approximation requires that particles be separated by at least 3 particle radii (van de Hulst, 1957); for a system of two identical spheres, calculations of the phase function and linear polarization indicate that the independent scatterer assumption may become valid at separations of 4 radii between particle centers (Mishchenko et al., 1995). To bring particles into close contact (as would be necessary for

modeling planetary regolith fines), we test two packing correction methods: diffraction subtraction (Wald, 1994) and the monodisperse static structure factor (Mishchenko, 1994).

### 3.4 Packing Assumptions Revisited

Before they are supplied to the RT solution, both \( w \) and \( p(\theta) \) must be modified to account for close packing conditions. So that we may directly compare the two packing methods described here, instead of varying \( p(\theta) \) directly, we specify \( p(\theta) \) to be the HG phase function and vary the normalized, cosine-weighted angle-averaged phase function \( \equiv g \), hereafter the asymmetry parameter.

There are two methods, one grounded in geometric optics and the other based on statistical mechanics, that treat the case of close packing. Both of these methods (diffraction subtraction and static structure factor correction) approximate dense packing in essentially the same way, with one difference. When using the static structure factor correction, in addition to subtracting out the diffraction component, one can quantify and control the level of packing of spheres in a representative cubic volume. To that end, the equations in Section 3.4.2 offer some advantage over those in Section 3.4.1 in that one can moderate the degree to which the Mie single scattering albedo and asymmetry parameter \( (\equiv w_{\text{mie}} \text{ and } g_{\text{mie}}) \) are modified. Being able to change filling factor values to model a range of loosely to densely packed regolith would be most desirable when comparing model to field, orbiter, or rover data.

#### 3.4.1 Diffraction Subtraction

The first packing correction method, diffraction subtraction, eliminates the forward scattering contribution to \( w_{\text{mie}} \) and \( g_{\text{mie}} \) on the grounds that forward scattered light cannot be distinguished from unscattered light (Wald, 1994; Wald & Salisbury, 1995). The resulting diffraction subtracted albedo \( (\equiv w_{\text{diff}}) \) and diffraction subtracted asymmetry parameter \( (\equiv g_{\text{diff}}) \) are the quantities supplied to the RT codes,

\[
\begin{align*}
  w_{\text{diff}} &= 2w_{\text{mie}} - 1, \\
  g_{\text{diff}} &= \frac{2g_{\text{mie}}w_{\text{mie}} - 1}{2w_{\text{mie}} - 1}.
\end{align*}
\]

These expressions strictly apply to spherical particles with diameters that are very large in comparison to the incident wavelength (van de Hulst, 1957). Particles with diameters on order of 100 \( \mu \text{m} \) or greater would satisfy this criterion for thermal IR wavelengths. For transparent (on the order of \( d \leq 5 \mu \text{m} \)) particles there is no need to modify \( w \) and \( g \) (Goguen, unpublished data, 1995; Wald & Salisbury, 1995).
3.4.2 Static Structure Factor Corrections

The second packing correction method, derived from statistical mechanics, is a modification of single scattering properties via the monodisperse static structure factor, $S(\theta)$ (Mishchenko, 1994; Mishchenko & Macke, 1997). Using $S(\theta)$ amounts to assuming that a planetary regolith is a “fluid” medium in which grains are treated as localized densities, with the range in grain sizes narrow as compared to the mean grain size. $S(\theta)$ is related to the isothermal compressibility of a medium; by definition, $S(\theta)$ is the Fourier transform of the probability that two hard, impenetrable spherical grains of fixed radius $r$ are located at two distinct coordinates,

$$S(\theta) = \frac{1}{1 - n_d K(\xi)}.$$  \hspace{1cm} (3.14)

In Eq. 3.14, $n_d$ is the number density of scattering particles and $\xi$ represents wavenumber. $K(\xi)$ is the Fourier transform of the direct correlation function, the quantity that dictates how other particles can be arranged about a fixed particle without overlapping. $K(\xi)$ is a sum which carries internal dependencies on $n_d$, $r$, and the filling factor $f \equiv (4\pi n_d r^3)/3$, i.e., the ratio of a volume of spheres to the volume of the smallest cube that can enclose them. When $f \geq 0.05$, then a cluster of particles is considered “dense” (Lumme et al., 1997).

Single scattering properties (albedo and asymmetry parameter as well as scattering and extinction cross-sections and the phase function) are modified via $S(\theta)$. The expressions for close-packed albedo and asymmetry parameter, $w_{\text{struc}}$ and $g_{\text{struc}}$, are presented in Eqs. 3.15, 3.16; expressions for the remaining scattering properties and internal variables are given in Appendix D. The expression for $w_{\text{struc}}$ is in terms of the ray-tracing component of the single scattering albedo and $B(f)$, i.e., the ratio of the scattering cross section of densely packed particles to that of isolated particles,

$$w_{\text{struc}}(f) = \frac{(1 + w^{\text{ray}})B(f)}{(1 + w^{\text{ray}})B(f) - w^{\text{ray}} + 1}. \hspace{1cm} (3.15)$$

$$g_{\text{struc}} = \frac{\int_{1}^{f} [p(\theta)S(\theta)]d\cos\theta}{\int_{1}^{f} [p(\theta)S(\theta)]d\cos\theta}. \hspace{1cm} (3.16)$$

When filling factor $f = 0$, the packed albedo $w_{\text{struc}}$ = the unpacked albedo $w_{\text{mic}}$; as $f$ increases, the single scattering albedo $w_{\text{struc}}$ decreases. Given that we desire an increase in $\epsilon$ in the resonance regions (spectral valleys), the lower values of $f$ are expected to yield the best model-lab fits.
3.5 Discussion

3.5.1 How Emissivity Spectra Behave Under Packing Assumptions

Emissivity is expected to increase with increased packing because reflectivity decreases when diffraction disks of the nearest neighboring particles overlap, a phenomenon discussed by Hapke (1981, 1993) and Wald (1994). As porosity increases, photon traps, which serve to increase the number of reflections and the probability of photon absorption, may form in quartz particulates (Salisbury & Eastes, 1985). To verify these expectations and to gauge the effects of the two packing correction methods on emissivity spectra, we modeled $\epsilon$ values at 25 representative wavelength points for three quartz grain sizes (mean diameter = 15, 61, and 277 $\mu$m) corresponding to the laboratory $\epsilon$ spectra of MC95 (solid line in Fig. 3.4). With the exception of the $\sim$ 700-650 cm$^{-1}$ region, the static structure factor packing correction provides a better overall model-lab fit for the $d = 15$ $\mu$m case; applying the diffraction subtraction correction in this case doubles the calculated RMS error. In general, applying either packing correction moves the emissivity value higher, so that for increasing grain diameter (deepening $\epsilon$ valleys), correcting for packing actually worsens the model-lab fit. For example, in each wavenumber subclass of the $d = 277$ $\mu$m case, applying diffraction subtraction or the static structure factor packing correction tends to increase the RMS error on the order of 0.01 or 0.005, respectively, as compared to Mie theory alone.

3.5.2 The Effect of Packing on the Single Scattering Albedo

To isolate which factors might be contributing to this worsening RMS error, we examined the effect of packing on $w$ and $g$. We first reconstructed $w_{\text{mie}}$ and $g_{\text{mie}}$ values with our new Mie implementation to approximate the values obtained by MC95 in generating their model $\epsilon$ (Fig. 3.5). Iterating on $w_{\text{mie}}$ or $g_{\text{mie}}$ within the discrete ordinates RT model to fit the MC95 laboratory $\epsilon$ spectra as closely as possible (to yield the “forced fit” $w_{\text{ff}}$ and $g_{\text{ff}}$, y-axis, Fig. 3.6), we looked for trends in $w$ and $g$ as a function of size in the case of no packing (x-axis) and attempted linear fits on all three size populations (fit parameters given in Table 3.3). In Fig. 3.6 (upper panel), we note that for the smallest size population, $w$ values cluster reasonably close (within 3$\sigma$ in y-intercept) to the solid line, i.e., to the desired condition that $w_{\text{mie}}$ matches $w_{\text{ff}}$. Before a correction for packing is even applied, the $w$ values returned by Mie theory are not much different than the $w$ needed to arrive at laboratory $\epsilon$ values. For intermediate particles, $w$ values clearly fall above the $w_{\text{mie}} = w_{\text{ff}}$ (solid) line, and the best linear fit to $w$ values for the largest grain size is even farther above that, with a slope well above 3$\sigma$ as compared to the $w_{\text{mie}} = w_{\text{ff}}$ line. This indicates that a correction in the
Figure 3.4: Model-lab nadir quartz emissivity spectra comparison for two packing corrections (small and large grain sizes). MC95 laboratory measured emissivity (solid line) is plotted with modeled emissivity spectra for the $d = 15 \mu m$ (upper panel) and $277 \mu m$ (lower panel) quartz samples (optical constants of Spitzer & Kleinman, 1961). Short dashed lines ≡ unpacked grains (Mie theory only), long dashed lines ≡ packed grains (Mie theory + diffraction subtraction correction), and dotted lines ≡ packed grains (Mie theory + static structure factor correction with filling factor $f = 0.2$; n.b., when $f$ increases to 0.4 or 0.6, static structure factor corrected $\epsilon$ values approach diffraction subtraction corrected $\epsilon$ values). With the exception of the $\sim 700$-$650$ cm$^{-1}$ region, the static structure factor packing correction provides a better overall model-lab fit in the $15 \mu m$ sample; however, at most wavenumbers, applying either packing correction does not significantly improve the model-lab fit. As grain size (and depth of emissivity features) increases, neither the diffraction subtraction nor the static structure factor packing corrections perform to improve model-lab fit.
Figure 3.5: Mie theory calculated single scattering albedo (top panel) and asymmetry parameter (bottom panel) versus wavenumber for 3 MC95 quartz samples (small = $15 \mu m$, medium = $61 \mu m$, large = $277 \mu m$ diameter). Composition is O-E ray $\alpha$-quartz (Spitzer & Kleinman, 1961). By virtue of Fig. 1, we can reasonably assume that these $w_{\text{mie}}$ and $g_{\text{mie}}$ values correspond to MC95 model $\epsilon$ values.

Single scattering albedo, presumably for packing, becomes more necessary with increasing particle size.

In Fig. 3.7, we show the effect of diffraction subtraction on $w$ for all three selected sizes. While diffraction subtraction (strictly valid for particle diameters $> 100 \mu m$ in the thermal IR) was expected to be successful for the $d = 277 \mu m$ sample, in all cases, we observe no systematic improvements to the model-lab fit when we make the diffraction subtraction correction. For $d = 15 \mu m$, the unmodified Mie albedo values are significantly closer to the forced fit albedos than are the diffraction subtraction corrected albedos. As is shown in column 1, Fig. 3.8, modifying the single scattering albedo with the static structure factor packing correction ($w_{\text{struc}}$) will return a much lower value than the desired $w_{ff}$. As grain size increases, the disparity between $w_{\text{struc}}$ and $w_{ff}$ increases dramatically. Albedo values with filling factor values closer to 0 provide the best, albeit unsatisfactory, fits to $w_{ff}$.
Figure 3.6: Mie vs. “forced fit” values for single scattering albedo and asymmetry parameter. Mie theory calculated single scattering albedo ($\bar{w}_\text{mie}$) vs. single scattering albedo required by RT algorithm ($\bar{w}_{ff}$) (upper panel) and Mie theory calculated single particle asymmetry parameter ($\bar{g}_\text{mie}$) vs. asymmetry parameter required by RT algorithm ($\bar{g}_{ff}$) (lower panel) to produce MC95's laboratory measured emissivity spectra for 3 sizes of quartz (diamonds: 15 $\mu$m, asterisks: 61 $\mu$m, crosses: 277 $\mu$m diameter). Solid lines indicate where $\bar{w}_{ff} = \bar{w}_\text{mie}$ and $\bar{g}_{ff} = \bar{g}_\text{mie}$. For the smallest size (diamonds, best fit parameters in Table 3.3), $w$ and $g$ values cluster most tightly around the solid line; single scattering theory in the absence of packing corrections yields $w$ and $g$ reasonably close to what is needed to arrive at lab $\bar{\epsilon}$ values. For intermediate sized particles (asterisks, fit by dashed lines), $w$ values are clearly falling above and $g$ values are falling below the solid lines. For the largest sized particles (crosses, fit by dotted lines), there are apparent linear trends in $g$ and $w$, well removed from the $x = y$ solid lines. Collectively, these results imply that as size increases toward the geometric optics regime, a correction to $w_{\text{mie}}$ and $g_{\text{mie}}$ becomes more necessary in order for models to achieve lab $\bar{\epsilon}$ values.
Figure 3.7: Diffraction subtraction packing corrected single scattering albedo $w$ for diameter = 15, 61, 277 $\mu$m. For all diameters, diffraction subtraction fails to bring $w_{\text{mie}}$ and $w_{\text{ff}}$ into agreement.
Figure 3.8: Static structure factor packing corrected single scattering albedo $w$ (column 1) and asymmetry parameter $g$ (column 2) for particles with diameter = 15, 61, 277 $\mu$m. Diamonds denote $w_{\text{mie}}$ and $g_{\text{mie}}$ (no packing), crosses represent $w_{\text{ff}}$ and $g_{\text{ff}}$ (values required to match lab $\epsilon$). Asterisks, triangles, and squares stand for static structure factor corrected $w_{\text{struc}}$ and $g_{\text{struc}}$ with filling factors of $f = 0.2$, 0.4, 0.6, respectively. Composition is O-E ray $\alpha$-quartz (Spitzer & Kleinman, 1961). Packing via static structure factor correction does not bring $w$ or $g$ into agreement with what would be required to reproduce lab $\epsilon$ spectra and typically performs worse as grain size increases.
Table 3.3: \( y = A + Bx \) Fit Parameters (Fig. 3.6)

<table>
<thead>
<tr>
<th>Property</th>
<th>( \mu_d ) (( \mu m ))</th>
<th>A</th>
<th>B</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( w )</td>
<td>15</td>
<td>0.360±0.086</td>
<td>0.518±0.110</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>0.279±0.121</td>
<td>0.689±0.169</td>
<td>0.065</td>
</tr>
<tr>
<td></td>
<td>277</td>
<td>0.261±0.105</td>
<td>0.806±0.159</td>
<td>0.092</td>
</tr>
<tr>
<td>( g )</td>
<td>15</td>
<td>0.235±0.170</td>
<td>0.675±0.254</td>
<td>0.407</td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>-1.003±0.270</td>
<td>2.052±0.343</td>
<td>0.467</td>
</tr>
<tr>
<td></td>
<td>277</td>
<td>-1.295±0.218</td>
<td>2.216±0.261</td>
<td>0.313</td>
</tr>
</tbody>
</table>

3.5.3 The Effect of Packing on the Asymmetry Parameter

For the asymmetry parameter (lower panel, Fig. 3.6), we note that for the smallest grain population, \( g \) values cluster most tightly around the \( g_{\text{mie}} = g_{\text{ff}} \) (solid) line, with a best linear fit to the model data points within 1.5\( \sigma \) as compared to the \( g_{\text{mie}} = g_{\text{ff}} \) line. \( g \) values for intermediate sized grains tend to fall below the \( g_{\text{mie}} = g_{\text{ff}} \) line. As grain size increases, the slopes in the apparent linear trends also increase; \( g \) values generated via Mie theory definitely require correction to bring them into agreement with what is demanded by the RT solution to yield lab equivalent \( \varepsilon \).

To illustrate the effect of diffraction subtraction on \( g \), we turn to Fig. 3.9. Diffraction subtraction meets with some success around wavenumber \( \sim 1250\text{-}1000 \text{ cm}^{-1} \) and provides closer \( g \) values at wavenumber \( \sim 500 \) and 435 cm\(^{-1} \) for the \( d = 277 \mu m \) quartz sample; however, for both \( d = 277 \) and 61 \( \mu m \), it is clear that diffraction subtraction removes too much from the \( g \) values overall. For diameter \( = 15 \mu m \), the diffraction subtraction packing correction seems to offer no advantage. Using the static structure factor packing correction (column 2, Fig. 3.8), \( g_{\text{struc}} \) appears to approach \( g_{\text{ff}} \) only in the \( d = 15 \mu m \) quartz sample. Results for the \( d = 277 \mu m \) quartz sample seem counterintuitive. To decrease \( \varepsilon \), we would need to also decrease \( g \); therefore, in the resonance regions, we expect to see better fits to the RT desired \( g_{\text{ff}} \) for higher \( f \). For the continuum regions, lower \( f \) (not \( f \) on the order of 0.4 or greater, as in the \( d = 277 \mu m \) case) should yield better fits.

3.5.4 Coherent Effects

In a closely packed medium, the diffraction contribution to the scattering cross-section as well as to the volume single scattering phase function must
Figure 3.9: Diffraction subtraction packing corrected asymmetry parameter $g$ for particles with diameter = 15, 61, 277 $\mu$m. With the exception of the 277 $\mu$m mean effective diameter quartz grain sample at 1200-1020 cm$^{-1}$, diffraction subtraction performs poorly for these samples.

be taken away (Hapke, 1999). We have demonstrated that altering $w_{\text{mie}}$ or $g_{\text{mie}}$ via diffraction subtraction or static structure factor packing corrections, while satisfying that requirement, may in fact worsen the model-lab fit. Application of the mathematical expressions for packing have the opposite effect in the main restrahlen bands as compared to what seems to occur in lab data.

What is clearly missing within these packing assumptions is an adequate treatment of coherent effects. While a description on how coherent effects influence the single scattering albedo is not currently available in the literature, coherent effects are known to simultaneously raise and lower asymmetry parameter values in dense media. In their study on the effect of particle separation distance on $g$, Videen et al. (1998) discuss the competing effects of interaction and interference. The first proximity effect, interaction, involves mode mixing. If an observer at some remote vantage point watches an incoming beam of light encounter 1 of 2 target particles (where the particles are not overlapping or touching and have no inclusions), light will be scattered from particle 1 to the observer, then from particle 1 to particle 2; in the space
between the particles, constructive interference occurs. Backscattered intensity increases, resulting in a decreased value for the asymmetry parameter \( g \). The other proximity effect, interference, superimposes a high frequency structure on the scattering phase function (as separation distance increases, the spatial frequency of this structure also increases). This causes light to preferentially scatter in the forward direction, resulting in an increased value for \( g \). The particles modeled by Videen et al. (1998) ranged in size from radius between \( 10^{-2} \) and \( 10^1 \) in units of \( \lambda \); for smaller size parameters, the polarizabilities of the particles will also interact.

### 3.6 Conclusions

Emissivity models as applied to nadir incidence laboratory measurements of proxy planetary regolith samples are in need of improvement. In this work, we have developed ways to quantitatively assess whether or not a model-lab emissivity spectral fit is successful, identified modifications that can be immediately implemented in existing Mie + RT hybrid models to improve the quality of model-lab fits, and targeted the assumptions which require further development to be properly incorporated into future hybrid models.

1. MC95 presented the Mie/analytical RT model, with a qualitative ranking of different RT models as compared to laboratory emissivity data; they did not overlay the best model and lab data to quantitatively show how good or poor this “best fit” was. In the literature to date, a quantitative metric for determining goodness-of-fit for emissivity models has not been defined. To fill this need, we adopt the root-mean-squared error as our goodness-of-fit statistic and reject model-lab fits with RMS error \( > 0.1 \) for quartz. For materials with emissivity feature depths that are different from those of quartz, a different numeric value should be assigned for the acceptable RMS error. For example, model-lab emissivity spectral fits for basalt are anticipated to be acceptable for an order of magnitude smaller RMS error value given a surface with emissivity feature depths on order of 0.05.

2. We have investigated the utility of a Mie + 4-stream discrete-ordinates radiative transfer solution. With regard to model inputs, Mars regolith fine fraction grain sizes and Mars orbiter and rover spectrometer relevant wavenumbers can be supplied successfully to this type of model. Although not studied here, this model is expected to also easily support Mars surface relevant (e.g., basalt) mineral compositions. Minimizing the uncertainty in model inputs and using the full phase function expansion does improve model-lab fits. We feel that this improvement is a step forward but, as is evident from the degree of correction to single scattering properties implied by Fig. 3.6, it is not entirely sufficient to solve the problems encountered in modeling emissivity spectra. What remains lacking in this type of model is a realistic treatment of particle shape (not even a first order correction for irregular shapes, such as...
removing 10% of the asymmetry parameter, has been made here or in the MC95 study).

3. A good method for closely packing grains is also lacking. The diffraction subtraction correction decreases $w$ and $g$ more than is needed to arrive at agreement with laboratory emissivity values at all wavenumbers and may work better for the asymmetry parameter (in larger grain sizes only) than the single scattering albedo. Unlike diffraction subtraction, by varying the filling factor in the static structure factor packing correction, one can moderate the degree of the cut in $w$ and $g$. The static structure factor correction also modifies other single scattering properties and is therefore at least in principle superior to the diffraction subtraction correction. However, neither method fully addresses the interplay between interference and interaction effects.
4. Improvements Upon Quantifying Radiative Transfer Model Inputs

From the previous chapter, it is obvious that laboratory sample preparation methods can introduce “hidden” assumptions into the model inputs. These assumptions are often inadequately communicated to the theoretical modeler and effectively limit the number of options a modeler has in selecting appropriate algorithms, e.g., choosing a realistic shape for the single scatterer. In this chapter, I explore methods to decouple and eliminate interdependences in the model input variables, namely particle composition, particle size distribution, and particle shape. I also present laboratory emissivity spectra of angular quartz particles in narrow size bins, to build upon the existing set of laboratory sample emissivity spectra that can be modeled.

4.1 Particle Composition

As compared to a more realistic Mars surface proxy mineral, natural quartz has an easier composition but a harder shape to model. A potential solution to restrict shape dependence to spherical or spheroidal geometry (and obviate the need for developing more intensive theoretical methods for calculating single scattering properties) is to obtain laboratory emissivity spectra of spherically shaped single scatterers with a similar composition to that of quartz. I investigated the utility of solid glass beads as uniform size, spherical proxies for the natural, angular quartz grains (Table 4.1). Solid glass beads, or “grinding media,” are often used in industrial applications, e.g., to polish optics and to mill paints and pigments. Manufacturers specify these glass beads to be high density, resistant to abrasion and corrosion, and crack-free. Lead-free DRAGONITE™ glass beads manufactured by Jaygo, Inc. (specific gravity = 2.55, average weight percent composition: 67% SiO₂, 10% Na₂O, 7% K₂O, 6% BaO, 5% CaO, 2% B₂O₃, 1% Al₂O₃, 1% MgO) have been previously studied in comparison to micron-sized quartz grains, in size fractions from < 11 μm up to 710-900 μm, for particle shape effects on thermal conductivity properties under simulated Martian atmospheric conditions (Presley, 1995). I obtained those samples, as well as a 2 pound sample of SIL-CO-SIL 53 fine ground silica product manufactured by U. S. Silica Company (sieve diameters for 98% of grains < 53 μm, composition: 99.7% SiO₂ and trace oxides, parent source: Mill Creek, OK). The DRAGONITE™ glass beads failed to produce laboratory emissivity spectra with discernable quartz features and are therefore unsuitable proxies (Fig. 4.1). The SIL-CO-SIL 53 samples produced laboratory emissivity spectral profiles similar to d < 15.6 μm quartz in the λ = 8-10 μm region but dissimilar in terms of feature depth elsewhere (Fig. 4.2). Thus, for the purposes of modeling emissivity measurements, laboratory samples composed of natural quartz grains are preferred to these alternative “spherical” SiO₂ proxies.
Table 4.1: SiO$_2$ Laboratory Measured Emissivity Spectra

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameter Range (μm)</th>
<th>$e$ ($\degree$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Quartz</td>
<td>&lt; 15.6</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>20-30</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>&lt; 25</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>25-30</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>30-40</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>30-63</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>50-63</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>63-70</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>70-75</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>160-180</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>180-250</td>
<td>0</td>
</tr>
<tr>
<td>SIL-CO-SIL$_{TM}$</td>
<td>&lt; 53</td>
<td>0, 10, 20, 30, 40</td>
</tr>
<tr>
<td>DRAGONITE$_{TM}$</td>
<td>30-48</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>55-70</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>100-125</td>
<td>0</td>
</tr>
</tbody>
</table>

4.2 Particle Size Distribution

Addressing the issue of particle size in a theoretical model is a matter of running the codes with different target particle effective radii, effective variances, and other coefficients specific to the desired particle size distribution. However, to properly input a laboratory measured (i.e., realistic) particle size distribution into a model, one should be aware that the sizing technique used to measure particle diameter (see Table 4.2) and particle characteristics other than size can impact the values for mean and modal sizes as well as the entire particle size distribution. One should also ensure that upper and lower boundaries on bin size (first approximated by the minimum and maximum diameters for the size fraction) are appropriate for the assumptions of monodispersion made later in the packing corrections.
Figure 4.1: $e = 0^\circ$ laboratory emissivity spectra for DRAGONITE™ synthetic silica (grinding media manufactured by Jaygo, Inc.) for three different sizes. Diameters are reported in $d_{Stk}$ (ref. Table 4.2). The flat spectrum is characterized as a generic "glass," i.e., compositions other than SiO$_2$ in the material contribute significantly to the spectral character.

4.2.1 Selecting the Appropriate Sizing Technique

Common techniques available to laboratory geologists to quantify particle size distribution for a given sample are compared in Table 4.3: sieving, sedimentation, imaging (e.g., microscopy), electrical sensing zone (i.e., resistance pulse) particle counting, and light scattering. Detailed descriptions of and comparisons between these and additional sizing methods are available in the literature (Singer et al., 1988; McCave & Syvitski, 1991). The most expedient and inexpensive methods are sieving and Stokes’ law sedimentation. In the former method, crushed rock particles are passed through a series of up to seven 8” diameter brass sieves, each with a specified square aperture mesh size on the order of tens of microns up to millimeters in diameter. The sieves are shaken for > 5 minutes by machine to ensure that all particles have been well sorted. The size bins for sieved samples are typically broad by light scattering model standards (e.g., < 63 µm, 90-125 µm, 710-1000 µm). Stokes’ law sedimentation (i.e., water column settling) is used to
Figure 4.2: $e = 0^{\circ}$ laboratory emissivity spectra for SIL-CO-SIL 53 synthetic silica (manufactured by U.S. Silica Co.). While wavenumber positions of $e$ features are consistent with similar sized $\alpha$-quartz spectra, feature depths are not.

Further subdivide the sieved sample particles into narrow size bins approaching monodispersion (e.g., 20-30 $\mu$m, 70-75 $\mu$m). Unfortunately, the sieving technique provides information on sieve diameters; if oriented preferentially, a single, nonspherical particle may pass through a sieve mesh which is smaller than its equivalent spherical volume diameter. When the mean effective diameter (i.e., the diameter of a sphere having the same volume as an ellipsoid with long and short axes matching measurements taken from images of individual grains) is calculated for particles whose long and short axis dimensions have been measured via imaging, the equivalent spherical volume diameter for the sample can be on the order of 20% higher than the upper sieve screen size (MC95). Equivalent spherical volume diameter is in fact the quantity of interest for light scattering models; out of the numerous types of diameters that can be measured for a given nonspherical particle (volume diameter, surface volume diameter, drag diameter, free-falling diameter, Stokes’ diameter, projected area diameter, perimeter diameter, sieve diameter; Allen, 1981), only the volume diameter remains constant when different.
Table 4.2: Types of Particle Diameters$^a,b$

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Formula</th>
<th>Diameter Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_A$</td>
<td>—</td>
<td>Sieve diameter</td>
<td>Diameter width of 1 aperture element in a mesh screen</td>
</tr>
<tr>
<td>$d_{stk}$</td>
<td>$v_s = \frac{(\rho_p - \rho_f)g_c(d)^2}{18\eta_f}$</td>
<td>Stokes diameter</td>
<td>Free-fall diameter of a spherical particle in suspension</td>
</tr>
<tr>
<td>$d_v$</td>
<td>$d_v = \left(\frac{6V}{\pi}\right)^{1/3}$</td>
<td>Equivalent spherical diameter</td>
<td>Diameter for a sphere with volume $V$</td>
</tr>
</tbody>
</table>

$^a$ Adapted from Table 4.1, Definitions of particle size, Allen (1981).  
$^b$ $g_c \equiv 9.8 \text{ m/s}^2$.

orientations and possible projected cross-sections are considered. To obtain particle size distributions accurately with sedimentation methods, it is assumed that a laboratory sample is composed of materials with the same density. When using light scattering (e.g., diffraction, Fraunhofer approximation) techniques, optical properties of the particulates (e.g., refractive indices) are assumed to be identical. The mineralogical composition of a representative “sand” or “sediment” sample is likely to be of varying densities and refractive indices. Both sedimentation and light scattering methods are sensitive to particle shapes that deviate from spherical geometry. Electrical sensing zone particle counting, while not suitable for porous particles, is insensitive to varying refractive indices, densities, and particle shapes and is thus the method of choice for sizing particulate samples with total mass $\geq 2$ grams. (For particles with $d > 500 \mu m$, an imaging method, the OptiSizer 5400, may be comparable. With the OptiSizer 5400, a CCD camera images particles as they fall off a vibrating ultrasonic feeder. The 2-D area of a particle is computed from the size and number of pixels needed to cover 1 particle; the 3-D volume is calculated assuming either cubic or spherical geometry.) The Elzone Analyzer, a specific electrical sensing zone particle counting instrument, counts particles within the diameter range 0.4 to 1200 $\mu m$ at rates of up to 2000 per second. A small concentration of particles is suspended in an electrolyte solution of resistivity $\eta_f$ in a sample vessel.
Table 4.3: Types of Sizing Methods and Coupled Variables

<table>
<thead>
<tr>
<th>Sizing Method</th>
<th>Quantity Measured</th>
<th>“Size”</th>
<th>Coupled Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieving</td>
<td>Cross-sectional area</td>
<td>$d_A$</td>
<td>Shape; orientation</td>
</tr>
<tr>
<td></td>
<td>or perimeter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sedimentation</td>
<td>Settling velocity</td>
<td>$d_{Stk}$</td>
<td>Shape;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>of particles, fluid; Reynolds number</td>
</tr>
<tr>
<td>Microscopy</td>
<td>Linear dimensions</td>
<td>$\frac{\sum d}{# \text{particles}}$</td>
<td>Shape;</td>
</tr>
<tr>
<td></td>
<td>of particle</td>
<td></td>
<td>orientation</td>
</tr>
<tr>
<td>Electrical sensing</td>
<td>Displacement volume</td>
<td>$\frac{\sum d^3}{# \text{particles}}$</td>
<td>Porosity;</td>
</tr>
<tr>
<td>zone</td>
<td></td>
<td></td>
<td>wettability</td>
</tr>
<tr>
<td>Light scattering</td>
<td>Volume (mass moment)</td>
<td>$\frac{\sum d^4}{\sum d^3}$</td>
<td>$n, k$ of particle, medium; shape;</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td></td>
<td>orientation;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>surface roughness;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>incident $\lambda$;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>polarity</td>
</tr>
</tbody>
</table>

* Adapted from “Interpretation of Particle Size Reported by Different Analytical Techniques” by Paul Webb (http://www.micromeritics.com/products/article_interpretation.aspx) and “Basic Principles of Particle Size Analysis” by Alan Rawle (http://www.malverninstruments.org).
containing an electrode. A steady electric current travels from the primary electrode to a secondary electrode via a tube with a pinhole of aperture \( D_{ap} \) at one end through which particles may pass. The electrolyte solution is drawn through the tube by a partial vacuum. When a particle encounters the end of the tube, it obstructs part of the pinhole, thereby displacing the electrolyte solution. Assuming that the particle’s resistivity is not equal to \( r_f \), a change in voltage will occur; the size of the resulting pulse is proportional to the volume of the grain. The change in resistance \( \Delta R \) is related to particle equivalent spherical diameter via Eq. 4.1 (McCave & Syvitski, 1991),

\[
\Delta R = \left[ \frac{8r_fd}{3\pi D_{ap}^4} \right] \left[ 1 + \frac{4}{5} \left( \frac{d}{D_{ap}} \right)^2 + \frac{24}{35} \left( \frac{d}{D_{ap}} \right)^4 + ... \right].
\]  

(4.1)

An advantage to using this particular sizing method is that one obtains both frequency and volume size distributions for a given particulate sample; typically, information on the frequency size distribution (i.e., the normalized probability density function) is not obtained using alternate methods.

4.2.2 Determining the Appropriate Bin Size

I have acquired nadir incidence thermal IR laboratory emissivity spectra of \( \alpha \)-quartz particulates in a variety of bin sizes, reported in sieve diameters and Stokes diameters (Fig. 4.3). Well-separated samples with bin sizes on the order of 5 \( \mu \)m in width for small diameter particles are ideal for theoretical modeling; however, laboratory proxy samples for entries in the ASU TES spectral library and real Martian regolith particles have larger diameters and possess wide PSDs which current models cannot readily support as inputs. To investigate just how sensitive different diameter particles are to the limit on bin size, we sized three additional quartz fractions ranging the gamut of wide PSDs (Pitman et al., 2005, in press\(^1\)). We present recently acquired laboratory emissivity spectra of three new samples (Fig. 4.4). The three additional pure SiO\(_2\) angular quartz grain fractions, representing small (\( d < 63 \mu \)m), medium (\( d = 90-125 \mu \)m), and large (\( d = 500-710 \mu \)m) sizes with wide particle size distributions were kindly provided by Dr. Marsha Presley, Arizona State University, from her study on thermal conductivity of quartz grains (Presley, 1995). These laboratory proxy quartz size fractions had been separated with 8" Gilson brass mesh sieves. Through microscopy and particle size distribution analysis, we found a trend in our Presley (1995) 90-125 \( \mu \)m diameter fraction similar to that of the MC95 samples separated by sieving. For particle size distributions of the Presley (1995) samples, we calculate frequency abundance profiles in summation form, where cumulative percent less than (CPLT) a certain grain diameter \( i \) is

\[
(CPLT)_i = \sum_{j=1}^{i-1} \frac{\#counts[j]}{\text{total}\#counts} \times 100\%.
\]

(4.2)

\(^1\)Reproduced by permission of American Geophysical Union.
Figure 4.3: $e = 0^\circ$ laboratory emissivity spectra of $\alpha$-quartz particulates (multiple sizes), prepared using the method of Cadle (1955). All diameters reported are in $d_{st}$ except $d = 160-180$ $\mu$m and 180-250 $\mu$m which are $d_A$ values (ref. Table 4.2). These previously unrecorded spectra add to the set of laboratory quartz spectra which can be modeled.
Figure 4.4: Laboratory thermal IR emissivity spectra of Presley (1995) small ($d < 63 \mu m$), medium ($d = 90-125 \mu m$), and large ($d = 500-710 \mu m$) sized quartz particulate samples, acquired with the Nicolet Nexus 670 spectrometer at ASU, c. 2003. Medium and large sizes are offset by 0.5 and 1.0 in emissivity, respectively.

We determined the frequency abundance profiles for the Presley (1995) small and medium sized natural quartz particulates (panels A, C, D, Fig. 4.5) from electrical sensing zone method (Coulter Counter Technique) analyses performed by Micromeritics Instruments Corporation (Norcross, GA).

The large quartz particulates (panel B, Fig. 4.5) were sized with the OptiSizer 5400. The particle size distribution fits for the three new samples are summarized in Table 4.4. Column 3 of Table 4.4 gives the effective radius $r_{eff}$, i.e., area-weighted mean, Eq. 4.3,

$$r_{eff} \equiv a = \frac{\int_{r_1}^{r_2} r^2 n(r) r dr}{\int_{r_1}^{r_2} r^2 n(r) dr}.$$ (4.3)

Column 4 of Table 4.4 gives the (dimensionless) effective variance, i.e., the width of the size distribution (Eq. 4.4),
Figure 4.5: Frequency abundance profiles (Eq. 4.2) as a function of radius for Presley (1995) small, medium, and large sized quartz particulate samples. Panel A. Eq. 4.5 fit (dashed line) to laboratory particle size distribution measured via Electrozone analyzer (solid line) for $d < 63 \mu m$ quartz samples. Panel B. Eq. 4.5 fit (dotted line) to laboratory measured particle size distribution via OptiSizer 5400 (diamonds) for $d = 500-710 \mu m$ quartz samples. Fits obtained via combinations of Eq. 4.5 (dashed line, panel C) and Eq. 4.6 (dashed line, panel D) successfully reproduce electrical sensing zone method laboratory bimodal particle size distributions (solid line, panels C and D) for the 90-125 $\mu m$ diameter quartz samples.
Table 4.4: Presley (1995) α-Quartz Model Run Parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Predicted Diameter Range (µm)</th>
<th>( r_{\text{eff}} ) (µm)</th>
<th>( v_{\text{eff}} ) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>small</td>
<td>&lt; 63</td>
<td>10.43(^a)</td>
<td>0.26(^a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.49</td>
<td>0.37</td>
</tr>
<tr>
<td>medium</td>
<td>90–125</td>
<td>51.00(^a)</td>
<td>0.03(^a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>52.00</td>
<td>0.03</td>
</tr>
<tr>
<td>large</td>
<td>500-710</td>
<td>308.38(^a)</td>
<td>0.07(^a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>304.17</td>
<td>0.06</td>
</tr>
</tbody>
</table>

\(^a\) Plain text values are calculated directly from lab size distribution measurements; italicized values are derived from functional fits.

\(^b\) Single sample with bimodal grain size distribution.

\[ v_{\text{eff}} \equiv b = \frac{\int_{r_1}^{r_2} (r - r_{\text{eff}})^2 r^2 n(r)dr}{\int_{r_1}^{r_2} r^2 n(r)dr}. \]  (4.4)

For the Presley (1995) small and large quartz samples, we fit the PSD curves (panels A, B, Fig. 4.5) using the functional form

\[ n(r) = A_0 e^{-\frac{r^2}{2}} + A_3 + A_4 r + A_5 r^2, \]  (4.5)

where coefficients \( A_0, A_1, A_2 \) specify the height, center, and width of a Gaussian, and \( A_3, A_4, A_5 \) represent constant, linear, and quadratic terms. The term \( z \) is given by \( (r - A_1)/A_2 \). We treated the medium sized quartz sample (panels C, D, Fig. 4.5) as a bimodal distribution, combining Eq. 4.5 and the functional form for the gamma size distribution given by Mishchenko et al. (2002) (Eq. 4.6),

\[ n(r) = (\text{constant}) r^{(1-3b)/b} \exp\left(\frac{-r}{ab}\right), b \in (0, 0.5), \]  (4.6)

Fig. 4.6 illustrates that supplying well-quantified PSDs for widely binned particulate samples can produce qualitatively reasonable \( \varepsilon \) spectral shapes for mid- to large-sized particles. While we do not suggest that these are satisfactory model-lab fits (packing is ignored; RMS values exceed the acceptable range defined in Chapter 3), Fig. 4.6 indicates that perhaps bin sizes may be increased beyond 5 µm in radius without producing highly detrimental results in the resulting \( \varepsilon \) spectra.
Figure 4.6: Model (dashed line) and laboratory measured (solid line) nadir quartz emissivity spectra for three samples with widely binned particle size distributions. Mie + discrete ordinates RT models were generated with (1/3-2/3) weighted optical constants of Wenrich & Christensen (1996). Panel A: The $d < 63 \, \mu m$ sample, with an extremely wide PSD, cannot be satisfactorily modeled on the basis of either shape or feature depth. Panels B and C: Shape is qualitatively reproduced better than expected for the bimodal size distribution (clinging fines and peak of the size distribution treated separately) in the $d = 90-125 \, \mu m$ quartz sample. Panel D: The 500-710 $\mu m$ diameter quartz model also shows promise in matching the shape of the $\epsilon$ feature at 1300-1100 cm$^{-1}$.
4.3 Particle Shape

A quantitative description of particle shape, the aspect ratio, may be obtained by dividing the measured maximum dimension by the measured minimum dimension (Macke et al., 1995). To obtain this quantity and to obtain additional quantitative data on real-world particle sizes, shapes, and surface roughness, scanning electron microscopy on the three representative Presley (1995) samples was conducted at the Center for Advanced Microstructures & Devices (CAMD), Baton Rouge, LA. The instrument used for imaging was a Hitachi S-4500 II field emission SEM. The advantage to using a field emission SEM over a JEOL model SEM is that at low accelerating voltage (~5 kV), non-metallic samples analyzed by a field emission SEM do not have to be gold coated, thus keeping the sample particulates pristine for future diagnostic work. Imaging of a field of ~20 particles or individual particles were obtained from 20X up to 100X magnification. For particles on the order of 50 microns in (linear) diameter, particle axial ratios (aspect ratios) can be determined via SEM using X-Y cross hairs (e.g., Figs. 4.7, 4.8, 4.9). The accuracy on cross hair measurements was originally estimated to be 5-10%. Error bars on field emission SEM horizontal, vertical, and diagonal (≡X, Y, D) crosshair measurements were further estimated by comparing (X, Y, D) measurements of an electroplated Ni mask of known size (~105 µm by [205, 405, 805, 1205] µm rectangles; see Fig. 4.10) via field emission SEM to (X, Y) measurements determined via optical microscopy. Combined measurement and instrument error was determined to be <5%. For particles on the order of 100-1000 µm in linear diameter and for increased accuracy, the optical profiler\(^2\) was used for measuring (X, Y, D). Particle dimensions and aspect ratios for selected grains in the three samples are presented in Tables 4.5, 4.6, and 4.7.

4.4 Discussion and Conclusions

Based on the preceding laboratory analyses, I have determined the following:

1. To model single scattering properties with the methods outlined in Chapter 3, use of natural quartz grains is preferable for laboratory proxies. In Section 4.1, I showed that any advantages for the model potentially offered by synthetic silica grinding media (e.g., more uniform, spherical shapes among particles in a single sample) are strongly outweighed by the deviation from pure SiO\(_2\) composition as evidenced in laboratory emissivity spectra. To that end, I have collected additional size fractions of α-quartz (Table 4.1) and acquired nadir

\(^2\)For future analytical work, we acquired 3-D output surface topology maps of representative particles from each sample with the optical profiler; these 3-D outputs include particle roughness measurements, averaged over the entire particle, with the option to enlarge areas of interest.
Figure 4.7: SEM images of representative α-quartz grains from the $d < 63 \mu m$ Presley (1995) sample. Particle shape is decidedly nonspherical for all grains presented in Table 4.5, trending toward ellipsoidal particle shapes.
Figure 4.8: SEM images of representative $\alpha$-quartz grains from the $d = 90$-$125 \, \mu m$ Presley (1995) sample. Particle shapes are more equant throughout the sample, with some grains presenting prismatic behavior.
Figure 4.9: SEM images of representative $\alpha$-quartz grains from the $d = 500$-$710 \ \mu m$ Presley (1995) sample. Equal populations of equant grains (upper panel) and irregular, highly fractured grains (lower panel) are observed.
Figure 4.10: Electroplated Ni mask used in calculating error bars on the field emission SEM (X, Y, D) crosshair measurements. Example shown is the 205 μm rectangle. Combined measurement and instrument error was estimated to be < 5%.

laboratory emissivity spectra for these samples to add to the list of available laboratory comparison spectra that can be modeled.

2. The choice of particle size definition and the laboratory technique used to obtain the distribution of particle sizes strongly impacts the values of model inputs for particle size. Modelers expect that “size” is defined as equivalent spherical volume diameter, however, that is not necessarily what is measured directly in the lab. In Section 4.2.1, I noted that use of a laboratory sizing technique which provides information on both numeric and volume mean particle sizes maximizes the utility of a PSD dataset among both physics and planetary science single scattering models. One such sizing technique, the electrical sensing zone method, gives PSD results which do not depend on particle shape; use of these results as model inputs will allow for the introduction of nonspherical shapes into the model at a later date.
Table 4.5: Particle Dimensions and Aspect Ratios: $d < 63 \mu m \alpha$-Quartz

<table>
<thead>
<tr>
<th>Sample</th>
<th>X</th>
<th>Y</th>
<th>D</th>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d &lt; 63 \mu m$</td>
<td>29.760</td>
<td>33.600</td>
<td>44.890</td>
<td>1.129</td>
</tr>
<tr>
<td></td>
<td>21.330</td>
<td>28.900</td>
<td>35.920</td>
<td>1.355</td>
</tr>
<tr>
<td></td>
<td>33.720</td>
<td>44.330</td>
<td>55.700</td>
<td>1.315</td>
</tr>
<tr>
<td></td>
<td>74.990</td>
<td>84.440</td>
<td>112.900</td>
<td>1.126</td>
</tr>
<tr>
<td></td>
<td>9.024</td>
<td>4.980</td>
<td>10.310</td>
<td>1.812</td>
</tr>
<tr>
<td></td>
<td>10.310</td>
<td>7.550</td>
<td>12.780</td>
<td>1.366</td>
</tr>
<tr>
<td></td>
<td>17.060</td>
<td>9.960</td>
<td>19.760</td>
<td>1.713</td>
</tr>
<tr>
<td></td>
<td>57.970</td>
<td>72.380</td>
<td>92.720</td>
<td>1.249</td>
</tr>
<tr>
<td></td>
<td>86.040</td>
<td>107.100</td>
<td>137.400</td>
<td>1.245</td>
</tr>
<tr>
<td></td>
<td>113.200</td>
<td>73.250</td>
<td>134.800</td>
<td>1.545</td>
</tr>
<tr>
<td></td>
<td>26.090</td>
<td>45.870</td>
<td>52.770</td>
<td>1.758</td>
</tr>
<tr>
<td></td>
<td>59.180</td>
<td>89.750</td>
<td>107.750</td>
<td>1.517</td>
</tr>
<tr>
<td></td>
<td>41.290</td>
<td>54.920</td>
<td>68.700</td>
<td>1.330</td>
</tr>
<tr>
<td></td>
<td>43.130</td>
<td>54.270</td>
<td>69.310</td>
<td>1.258</td>
</tr>
<tr>
<td></td>
<td>113.200</td>
<td>75.420</td>
<td>136.000</td>
<td>1.501</td>
</tr>
<tr>
<td></td>
<td>79.470</td>
<td>52.360</td>
<td>95.160</td>
<td>1.518</td>
</tr>
<tr>
<td></td>
<td>55.530</td>
<td>55.850</td>
<td>78.750</td>
<td>1.006</td>
</tr>
<tr>
<td></td>
<td>39.090</td>
<td>48.230</td>
<td>62.080</td>
<td>1.234</td>
</tr>
<tr>
<td></td>
<td>40.350</td>
<td>46.220</td>
<td>61.350</td>
<td>1.145</td>
</tr>
<tr>
<td></td>
<td>16.230</td>
<td>15.650</td>
<td>22.550</td>
<td>1.037</td>
</tr>
</tbody>
</table>

3. We note that the particulate proxies produced in the lab by sieving and Stokes settling techniques may not in fact be true monodispersions. The terms “monodispersion” and “polydispersion” of particle sizes relate to how narrow or wide the spread in diameters in a sample is as compared to the mean particle diameter. Defining the coefficient of variation as $\sigma_d/\mu_d \times 100\%$, for nanometer-scale particles, a sample is considered monodisperse if the coefficient of variation is $< 5$-$10\%$ (Hunter et al., 1987). However, for the micron-scale MC95 laboratory quartz proxies presented in Table 3.1, the coefficients of variation are on the order of $15$-$20\%$, implying that the samples are slightly polydisperse. In Section 4.2.2, we have shown that using effective radii and effective variances of laboratory comparison emissivity spectra for mid-sized to large grained samples with coefficients of variation $> 10\%$ and $> 20\%$ does not seem to affect the overall shape of modeled emissivity.
4. In Chapter 3, we introduced the idea that Mie theory poorly approximates grain shape. To better quantify the true particle shape of the laboratory proxies, in Section 4.3, aspect ratios for three size fractions of natural quartz grains were measured. The aspect ratio values for all three sample fall between 1.0 and 2.0. Based on SEM imaging, ellipsoids appear to be better approximations to the shapes of the

spectra in the absence of packing corrections. Therefore, when packing is excluded, using mean diameter and standard deviation values for slightly polydisperse laboratory particulate samples as model inputs poses no problems. When packing corrections are introduced, the modeler must be aware that the assumption of monodispersion is being violated when using these size and variance inputs.
Table 4.7: Particle Dimensions and Aspect Ratios: $d = 500$-$710 \mu$m $\alpha$-Quartz

<table>
<thead>
<tr>
<th>Sample $d = 500$-$710 \mu$m</th>
<th>X</th>
<th>Y</th>
<th>D</th>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>907.300</td>
<td>1166.000</td>
<td>1477.000</td>
<td>1.285</td>
<td></td>
</tr>
<tr>
<td>929.600</td>
<td>1323.000</td>
<td>1617.000</td>
<td>1.423</td>
<td></td>
</tr>
<tr>
<td>943.300</td>
<td>934.900</td>
<td>1328.000</td>
<td>1.009</td>
<td></td>
</tr>
<tr>
<td>898.300</td>
<td>1056.000</td>
<td>1387.000</td>
<td>1.176</td>
<td></td>
</tr>
<tr>
<td>921.800</td>
<td>851.000</td>
<td>1255.000</td>
<td>1.083</td>
<td></td>
</tr>
<tr>
<td>890.600</td>
<td>942.100</td>
<td>1296.000</td>
<td>1.058</td>
<td></td>
</tr>
<tr>
<td>503.900</td>
<td>1110.000</td>
<td>1219.000</td>
<td>2.203</td>
<td></td>
</tr>
<tr>
<td>1564.000</td>
<td>1103.000</td>
<td>1913.000</td>
<td>1.418</td>
<td></td>
</tr>
<tr>
<td>1045.000</td>
<td>1134.000</td>
<td>1542.000</td>
<td>1.085</td>
<td></td>
</tr>
<tr>
<td>197.100</td>
<td>226.800</td>
<td>300.500</td>
<td>1.151</td>
<td></td>
</tr>
<tr>
<td>250.300</td>
<td>288.000</td>
<td>381.600</td>
<td>1.151</td>
<td></td>
</tr>
<tr>
<td>1179.000</td>
<td>1297.000</td>
<td>1752.000</td>
<td>1.100</td>
<td></td>
</tr>
<tr>
<td>1045.000</td>
<td>854.200</td>
<td>1349.000</td>
<td>1.223</td>
<td></td>
</tr>
<tr>
<td>930.700</td>
<td>1157.000</td>
<td>1485.000</td>
<td>1.243</td>
<td></td>
</tr>
<tr>
<td>927.400</td>
<td>1060.000</td>
<td>1408.000</td>
<td>1.143</td>
<td></td>
</tr>
<tr>
<td>1692.000</td>
<td>1016.000</td>
<td>1974.000</td>
<td>1.665</td>
<td></td>
</tr>
<tr>
<td>857.100</td>
<td>945.600</td>
<td>1276.000</td>
<td>1.103</td>
<td></td>
</tr>
<tr>
<td>1526.000</td>
<td>1458.000</td>
<td>2110.000</td>
<td>1.047</td>
<td></td>
</tr>
</tbody>
</table>

real-world angular quartz grains. This finding warrants a future theoretical investigation of single scattering particle geometries more complex than spheres. Substituting nonspherical particle shapes for model planetary regolith grains is not expected to significantly alter integrated single scattering properties (e.g. albedo, scattering cross sections) from those of volume-equivalent spheres (Lumme & Rahola, 1998). However, changing the particle shape of model planetary regolith grains can affect the single scattering phase function and the asymmetry parameter. In future work, we intend to quantify how much these quantities change in response to changes in particle shape in the geometric optics and $d \gg \lambda$ limits and determine if the changes in the phase functions and asymmetry parameters noticeably manifest in the modeled emissivity spectra. Reflectance models using the static structure factor packing correction with randomly oriented spheroids as compared to laboratory quartz grains have shown promising agreement for single scattering phase functions in the geometric optics regime ($d \gg \lambda$) (Petrova
et al., 2001). For our future geometric optics exploration, we intend to utilize codes originally developed for studies of atmospheric ice crystals (Macke 1993; Macke et al., 1995; Macke & Mishchenko, 1996; Macke et al., 1996) to model single scattering properties for prolate and oblate spheroids as per Petrova et al. (2001), ellipsoids to match our SEM imaging and aspect ratio measurements, and cylinders for increased geometrical complexity.
5. Conclusions

As discussed in the introduction, radiative transfer and scattering models developed for physics and astronomy applications can provide insight into the microphysical properties of the Martian surface (i.e., grain size, grain shape, and degree of packing in Martian regolith) as inferred from satellite and rover emissivity spectra. In Chapter 2, I showed that directional effects observed in MGS-TES thermal infrared emissivity observations taken at different angles of emergence over moderate to high albedo surfaces on Mars are in fact real, based on evidence from previous modeling attempts and field studies in the literature and on recent field and laboratory studies I conducted on Mars terrestrial analog sites in Death Valley, CA. The finding that sand and playa samples showed the most promising evidence of directional emissivity effects in the Mars terrestrial analog sites supports previous modeling attempts in the literature while contradicting MGS-TES EPF observation sequences. In Chapter 3, I assessed the efficacy of a particular type of model, the Mie theory + (analytical or numerically exact) radiative transfer solution, for calculating thermal infrared emissivity spectra of micron-sized particles with a well-quantified dielectric function (i.e., composition): α-quartz. My collaborators and I established (previously undefined) quantitative standards for what constitutes a successful model fit to laboratory-measured emissivity spectra and targeted several assumptions which are inconsistent with real-world characteristics of the scattering particles, as analyzed in Chapter 4. From simple numerical experiments, it is clear that the assumptions of monodisperse or widely spaced spheres as supplied to radiative transfer solutions do not adequately represent the single scattering particles in these laboratory proxy samples. Because grain shape assumptions cannot easily be decoupled from packing assumptions, moving beyond spheroidal geometry means that packing correction methods must also reflect more sophisticated grain shapes. In future work, packing methods with more sophisticated grain shapes and also the influence of coherent effects on the single scattering albedo as a function of packing distance must be investigated. In order to realistically model planetary regolith fines, future efforts should carefully treat assumptions about the fundamental scatterer and packing.
Allen, T. 1981, Particle Size Measurement (New York: Chapman and Hall)
Bandfield, J. L., Hamilton, V. E., & Christensen, P. R. 2000, Science, 287, 1626
Bandfield, J. L., & Smith, M. D. 2003, Icarus, 161, 1, 47, doi:10.1016/S0019-1035(02)00025-8
Bandfield, J. L., Glotch, T. D., & Christensen, P. R. 2003, Science, 301, 5636, 1084
Cadle, R. D. 1955, Particle size determination (Stanford, CA: Stanford Research Institute)
Chandrasekhar, S. 1960, Radiative Transfer (New York: Dover)
Christensen, P. R., & Harrison, S. T. 1993, J. Geophys. Res., 98, B11, 19819


Goguen, J. D. 1993, Lunar Planet. Sci. XXIV, 541


Howard, A. 2001, Lecture Notes from Field Trip and Workshop on the Martian Highlands and Mojave Desert Analogs, Las Vegas, Nevada, and Barstow, California, Lunar & Planetary Institute


Mishchenko, M. I. et al. 1999, J. Quant. Spectrosc. Radiat. Transfer, 63, 2-6, 409
van de Hulst, H. C. 1957, Light Scattering by Small Particles (New York: Dover)
Wyatt, M. B., et al. 2004, Geology, 32, 8, 654
Appendix A: Photographs, Field and Laboratory Emissivity Spectra of Martian Analog Sites

The following appendix contains photographs of field site conditions, field emissivity spectra, and laboratory emissivity spectra for Mars terrain analog sites in and around Death Valley, CA (see Chapter 2).

Figure A.1: Smooth clay mud, Devil’s Speedway, Death Valley, CA, 2003/12/02. Weather conditions: ~15°C, less overcast than on Day 1, with some cirrus clouds overhead. Photo credit: K. Pitman.
Figure A.2: Field emissivity spectra of the Devil’s Speedway smooth mud site at two angles of emergence: $e = 0^\circ$ and $40^\circ$. Little variation in $\epsilon$ spectral profile with change in $e$ was noted at this site.
Figure A.3: Upper panel: Field conditions for white particulate material on evaporites, Devil’s Speedway, Death Valley, CA, 2003/12/02. This possibly organic layer was distinct from the underlying salts. Photo credit: K. Pitman. Lower panel: A single field emissivity spectrum of the Devil’s Speedway white (organic?) material was acquired at $e = 0^\circ$ to record influence of these white grains on other salt flat spectra.
Figure A.4: Upper panel: Field conditions for evaporite minerals, Badwater Basin, Death Valley, CA, 2003/12/02. The dominant mineral was presumably halite. Photo credit: K. Pitman. Lower panel: Field emissivity spectra of the Badwater Basin evaporite assemblage at $\epsilon = 0^\circ$ and $85^\circ$ illustrate a relatively flat behavior in the nadir $\epsilon$ spectrum (i.e., a poor initial baseline for comparison for directional $\epsilon$ effects) and implausible high angle $\epsilon$ spectra.
Figure A.5: Upper panel: Field conditions for sulfate deposits at Shorty’s Well, Death Valley, CA, 2003/12/02. Spectra were acquired at ambient temperatures of \(\sim 10^0C\), with the sun low in the sky behind the mountains. Photo credit: K. Pitman. Lower panel: A reference field emissivity spectrum of the sulfate deposits at Shorty’s Well: \(e = 0^\circ\).
Figure A.6: Upper panel: Field conditions for brown dirt underlying the sulfate deposits at Shorty’s Well, Death Valley, CA, 2003/12/02. Photo credit: K. Pitman. Lower panel: Field emissivity spectra of the brown dirt underlying the sulfate deposits at Shorty’s Well: $e = 0^\circ$, $55^\circ$, and $85^\circ$. 
Figure A.7: Upper panel: Field conditions for Silver Lake Playa, 2003/12/03. Weather conditions during measurements: \(\sim 18^\circ\text{C}\) air temperature, partly cloudy skies, with sun to the left of the instrument. Lower panel: Target site selection. What appears to be a relatively smooth surface in the upper panel is in fact crossed by extensive mudcracks, thus limiting the choices of areas favorable for emissivity spectral measurements. Photo credit: K. Pitman.
Figure A.8: Upper panel: $e = 0^\circ$ field $\epsilon$ spectra of two sites at Silver Lake Playa. The “field” and “rough” spectra represent undisturbed terrain and an overturned surface of particulate layers. Lower panel: $e = 60^\circ$ field $\epsilon$ spectra of the undisturbed site, taken at the beginning (in blue) and end (black) of the measurements. Slight changes in $L_{\text{sky} \lambda}$ did not affect the spectra; the relative spectral differences in Fig. 2.5 are due to angular effects.
Figure A.9: Field conditions for quartz-feldspar sand, Dumont Dunes (located off I-172, halfway between Baker and Shoshone, CA), 2003/12/03. Weather conditions during spectral measurements: \( \sim 50^\circ F \) air temperature and overcast skies. Photo credit: K. Pitman.
Figure A.10: Multiple emergence angle field emissivity spectra of quartz-feldspar sand at Dumont Dunes: $e = 0^\circ$, $30^\circ$, $40^\circ$, and $50^\circ$ (upper panel) and $e = 0^\circ$, $20^\circ$, $40^\circ$, and $60^\circ$ (lower panel).
Figure A.11: Multiple emergence angle emissivity spectra for lab sample EVAP-4: $e = 0^\circ$ (solid black line), $10^\circ$ (red), $20^\circ$ (purple), $40^\circ$ (blue), and $50^\circ$ (magenta). While the emissivity spectra for different angles of emergence keep the same relative trend across all wavelengths, a monotonic decrease in $\epsilon$ with increasing $e$ is not observed.
Figure A.12: Nadir laboratory emissivity spectra of white (organic?) grains (≡ FUZZ-5) collected at site # 5, Devil’s Speedway, Death Valley, CA, 2003/12/02. The red and black spectra only were averaged to obtain the nadir $\epsilon$ spectrum in the following figure.
Figure A.13: Multiple emergence angle emissivity spectra for lab sample FUZZ-5: $e = 0^\circ$ (solid black line), $10^\circ$ (red), $20^\circ$ (purple), $40^\circ$ (blue), and $50^\circ$ (magenta). Trends in emissivity with angle of emergence are not present.
Figure A.14: Multiple emergence angle emissivity spectra for lab sample SLP-1b: $e = 0^\circ$ (solid black line), 10$^\circ$ (red), 20$^\circ$ (purple), 30$^\circ$ (blue), 40$^\circ$ (magenta), 50$^\circ$ (green), and 60$^\circ$ (cyan). As a function of emergence angle $e$, results are highly variable.
Figure A.15: Nadir laboratory emissivity spectra for an additional section of the hand sample obtained from the south end of Silver Lake Playa (≡ SLP-3), Baker, CA, 2003/12/03. All $\epsilon$ spectra were included in the averaged $\epsilon = 0^\circ$ spectrum for this sample.
Figure A.16: Multiple emergence angle emissivity spectra for lab sample SLP-3: $e = 0^\circ$ (solid black line), $10^\circ$ (red), $20^\circ$ (purple), $30^\circ$ (blue), $40^\circ$ (magenta), $50^\circ$ (green), $60^\circ$ (cyan), and $70^\circ$ (tan). Results are highly variable and do not suggest a clear trend with $e$. 
Figure A.17: Nadir laboratory emissivity spectra of quartz-feldspar sand (≡ DUNE-6) obtained from Dumont Dunes, Baker, CA, 2003/12/03. All $\epsilon$ spectra pictured were included in the averaged $\epsilon = 0^\circ$ spectrum.
Appendix B: Single Scattering Phase Function

The volume single scattering phase function \( p(\theta) \) is defined as the angular distribution of scattered light after it has encountered a dust grain, divided by the scattering cross-section \( C_{\text{sca}} \):

\[
p(\theta) \propto \frac{1}{C_{\text{sca}}} \frac{dC_{\text{sca}}}{d\Omega}.
\]

The phase function may be generated using a variety of numerical tools; however, not all of these codes directly output the phase function. In the following, I extract the phase function from the quantities output by the new Mie code in Chapter 3. I also present verification that the phase functions generated by the new Mie code compare well with what is expected using alternate numerical routines.

B.1 Electromagnetic Scattering Matrices

B.1.1 Amplitude Scattering Matrix

The electric field vector for a time-independent, monochromatic electromagnetic plane wave incident upon an arbitrary particle in the \( \hat{z} \) direction, following the convention of van de Hulst (1957) and Bohren & Huffman (1983), is given by Eq. B.2,

\[
\tilde{E}^{\text{inc}}(\vec{r}) = (E^{\text{inc}} e_{\parallel} + E^{\text{inc}} e_{\perp}) \times \exp(i\xi z),
\]

In Eq. B.2, \( \xi = \frac{2\pi}{\lambda} \) is the wavenumber in vacuum for wavelength \( \lambda \) and \( \vec{r} \) is the radius vector originating from the laboratory coordinate system origin. The behavior of the scattered wave in the far field region (\( \xi r \gg 1, r = |\vec{r}| \)) is spherical. To obtain the components of the scattered electric field in that limit, one uses the \( 2 \times 2 \) amplitude scattering matrix (the S-matrix in Eq. B.3), i.e., a linear transformation acting on the incident electric field vector,

\[
\begin{pmatrix}
E^{\text{scat}}_{\parallel} \\
E^{\text{scat}}_{\perp}
\end{pmatrix}
= \begin{pmatrix}
S_2 & S_3 \\
S_4 & S_1
\end{pmatrix}
\begin{pmatrix}
E^{\text{inc}}_{\parallel} \\
E^{\text{inc}}_{\perp}
\end{pmatrix}.
\]

Each element in the amplitude scattering matrix carries a dependence on scattering angle \( \theta \) and azimuthal angle \( \phi \).
B.1.2 Real-World Measurements: Phase Matrix

The components of the incident electric field described by Eq. B.2 cannot be directly measured by optical instruments; however, quadratic combinations of $E_\parallel$ and $E_\perp$ can be measured. These quadratic combinations ($I \equiv$ net monochromatic energy flux, $Q, U, V \equiv$ linear and circular polarizations) are collectively called the Stokes parameters $I$,

$$I = \begin{pmatrix} I \\ Q \\ U \\ V \end{pmatrix}. \quad (B.4)$$

Stokes parameters carry dimensions of energy per unit area per unit time per unit wavelength. Analogously to Eq. B.3, one may define a matrix, like the amplitude scattering matrix, that transforms the Stokes parameters for the incident electric field into the Stokes parameters for the scattered electric field,

$$I^{\text{scat}} = \frac{1}{r^2} Z I^{\text{inc}}. \quad (B.5)$$

This analog to the $2 \times 2$ amplitude scattering matrix is the $4 \times 4$ phase matrix ($Z$). $Z$ is the convention of Mishchenko et al. (2000) and is calculated by the FORTRAN77 code spher.F (Mishchenko et al., 1999). The FORTRAN77 code coatsph.F used in Chapter 3 calculates the phase matrix of Bohren & Huffman (1983), denoted here by $S_{BH}$. $S_{BH}$ is a $4 \times 4$ matrix whose elements are linear combinations of the amplitude scattering matrix elements $S_1, S_2, S_3$, and $S_4$. Note that

$$Z = \frac{S_{BH}}{\xi^2}. \quad (B.6)$$

To avoid confusion with the amplitude scattering matrix, I use $Z$ to denote phase matrix in the remainder of the section.

B.1.3 Desired Quantity: Scattering Matrix

To define the Stokes parameters relative to the plane of scattering (not relative to some meridional plane, which is what applying $Z$ to $I^{\text{inc}}$ gives), a third matrix is required: the $4 \times 4$ scattering matrix $F$. Applying two rotation matrices, one on either side of $F$, results in the phase matrix $Z$. The matrix elements of $F$ are dependent upon particle orientations with respect to incident and scattered light and are typically nonzero. In the case of macroscopically symmetric media with random particle orientations, the scattering matrix $F$ depends only on the scattering angle $\theta$. The single scattering phase function $p(\theta)$ is by definition the $(1,1)$ element of the scattering matrix $F$. 
B.2 Normalized $F_{11}$ In Terms of $Z_{11}$ and $S_{11BH}$

Numerical tools such as spher.F (Mishchenko et al., 1999) and the Mie algorithm used in Chapter 3 return phase matrix elements, leaving the user to calculate $p(\theta) \equiv F_{11}(\theta)$. The normalization coefficients for these formalisms are slightly different. Mishchenko defines single scattering phase function as

$$p(\theta) = \frac{4\pi}{C_{sca}} \frac{dC_{sca}}{d\Omega}$$

i.e. (eq. 57, Mishchenko et al. 2000),

$$p(\theta) = F_{11}(\theta) = \frac{4\pi}{C_{sca}} Z_{11}(\theta, 0; 0, 0),$$

and is normalized under the following condition:

$$\frac{1}{2} \int_{\cos \theta = -1}^{1} d(\cos \theta) p(\theta) = 1.$$  

This definition and normalization is required by all codes created by M. Mishchenko, including the codes that recalculate single scattering properties for packing via the monodisperse static structure factor. The equivalent expression for the phase function in the Bohren & Huffman (1983) scheme (used in Chapter 3), is given by

$$p(\theta) = \frac{2\pi}{C_{sca}} \frac{S_{11BH}}{\xi^2}.$$  

By plotting normalized phase function $\equiv F_{11}$ versus scattering angle $\theta$ for both formalisms, I have shown that both of the FORTRAN77 Mie scattering theory routines tested here supply the same information to the radiative transfer codes (Figs. B.1, B.2).
Figure B.1: Comparison of phase functions generated by spher.F (ref. Mishchenko et al., 1999; dashed lines) and coatsph.F (ref. Chapter 3; solid lines) for \( r_{\text{eff}} = 5.0 \, \mu m \), \( v_{\text{eff}} = 0.1 \), \( \lambda = 5 \, \mu m \) (top panel), 14 \( \mu m \) (middle panel), and 50 \( \mu m \) (lower panel).
Figure B.2: Comparison of phase functions generated by spher.F (ref. Mishchenko et al., 1999; dashed lines) and coatsph.F (ref. Chapter 3; solid lines) for $r_{eff} = 500.0$ $\mu$m, $v_{eff} = 0.1$, $\lambda = 5$ $\mu$m (top panel), 14 $\mu$m (middle panel), and 50 $\mu$m (lower panel).
Appendix C: Mie/Hapke (1993b) Model Reconstruction

A straightforward improvement to the Mie/Hapke (1993b) hybrid solution of MC95 can be made by replacing the part of the code which calculates single scattering particle properties (e.g., single scattering albedo, target particle scattering phase function) with a computationally superior Mie algorithm. I use a routine which employs the Mie algorithm DMiLay (ftp://climate.gsfc.nasa.gov/wiscombe/Single_Scatt/Coated_Sphere/), which has excellent convergence properties within and well beyond the wavenumber region of interest.

I will first demonstrate that the new Mie theory (single scattering) code performs comparably to the 1991 updated Hansen & Travis (1974) Mie algorithm used by MC95. This requires a reconstruction of the multiple scattering algorithm of MC95 (the “Hapke” part of the hybrid). The desired quantity is emissivity as a function of incident wavelength (ε(λ)), which requires an integration over the field of view of the laboratory spectrometer,

$$\epsilon(\lambda) = \int_\omega \gamma H(w_{\text{diff}}, \mu) d\omega.$$  \hfill (C.1)

In Eq. C.1, $\gamma = \sqrt{1 - w_{\text{diff}}}$ and $H(w_{\text{diff}}, \mu)$ is Chandrasekhar’s H function. To account for the reduction in diffraction due to close packing of particles, the single scattering albedo calculated by the Mie algorithm ($w_{\text{mie}}$) must be modified to arrive at single scattering albedo $w_{\text{diff}}$ in the expression for $\gamma$; to reproduce MC95 values, I accomplish this by use of the “diffraction subtraction” equation of Wald (1994),

$$w_{\text{diff}} = 2w_{\text{mie}} - 1. \hfill (C.2)$$

Rather than use Hapke’s 1993 approximation to calculate Chandrasekhar’s H functions, MC95 opted to use the exact values for H from Table XI of Chandrasekhar (1960) with a bilinear interpolation on $(1 - w)^{\frac{1}{2}}$ and $\mu$. The second order analytical approximation to $H(w, \mu)$ of Hapke (2002) has a less than 1% disagreement with Chandrasekhar’s numerically evaluated exact H functions, so I substitute the Hapke (2002) formulation for the exact values,

$$H(w_{\text{diff}}, \mu) = (1 - w_{\text{diff}})(r_0 + \frac{1 - 2r_0}{2} \ln(\frac{1 + \mu}{\mu}))^{-1}, \hfill (C.3)$$

where $r_0 = \frac{1 - \gamma}{1 + \gamma}$ and $\mu = \cos \theta$. Explicitly,

$$\epsilon(\lambda) = \frac{\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\theta_{\text{max}}} \gamma H(w, \mu) \sin \theta d\theta d\phi}{\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\theta_{\text{max}}} \sin \theta d\theta d\phi}. \hfill (C.4)$$
MC95 mathematically treated the spectrometer field of view as circular, so I preserved that assumption when calculating the integral in Eq. C.1. In actuality, the field of view of the Mattson Cygnus spectrometer used to measure the laboratory quartz spectra of MC95 is an ellipse with a major axis that is variable between 1 and 5 cm; its replacement (Nicolet Nexus 670) has a spot size of 1 cm. The Mattson Cygnus detector’s field of view was $42^\circ$ ($\theta_{\text{max}} = 21^\circ$; Fig. C.1); to simplify the integral in Eq. C.1, MC95 broke the field of view into 10 equal angle annuli, calculated $\epsilon(\epsilon = \theta)$ for each annulus, then combined results in an average weighted by the area of each annulus to get the final desired result for $\epsilon(\lambda)$. Because I used the Hapke (2002) approximation for the H functions, I did not have to perform such a weighting to integrate Eq. C.1.

Using the (1/3-2/3) approximation with the quartz infrared dielectric function of Spitzer & Kleinman (1961) in the new Mie routine + reconstructed emissivity expression, I was able to successfully reproduce the emissivity values produced by the Mie/Hapke (1993b) model of MC95 (Fig. 3.1).
Figure C.1: Schematic drawing of laboratory spectrometer’s field of view. A 1-5 cm ellipse is projected onto the “SAMPLE,” i.e., the target surface (either particulates in a sample cup of diameter 1-3” or a hand sample with maximum dimension < 11 cm). The “SAMPLE CHAMBER” is a double-walled Cu cylinder with diameter = 20 cm (Ruff et al., 1997) and height = 14 cm (Christensen & Harrison, 1993). Figure credit: V. Gokhale and K. Pitman.
Appendix D: Static Structure Factor
Corrected Scattering Properties

In order to fully understand how to arrive at Eqs. 3.15, 3.16 and the context of the assumptions made therein, I present the development of these equations from fundamental principles. For a packed medium, the first tool a physicist reaches for is the static structure factor. The static structure factor $S(\theta)$ is a quantity related to the isothermal compressibility of a medium; it measures the influence of non-local interactions on density fluctuation correlations. $S(\theta)$ carries dependencies on the scattering angle between incident and scattered beams, particle size distribution $n_d$, and particle shape (in this case, spherical). One must first assume that a regolith is an isotropic, homogeneous “fluid” medium. The individual particles in this “fluid” are hard, impenetrable, monodisperse spheres of radius $r$. To arrive at the expression for the static structure factor presented by Mishchenko (1994), one must invoke the Percus-Yevick approximation which is essentially a closure method for an integral equation: the Ornstein-Zernike equation for pair correlation.

D1. Pair Correlation and the Static Structure Factor

Let the average density for an isotropic, homogeneous “fluid” observed at any radius be $\rho$. The surplus of density (i.e., the average density of a given particle located at a particular radius minus the average density at any radius) $\rho(r) - \rho \equiv \rho h(r)$ is defined in terms of the total correlation function $h(r)$, as given by the Ornstein-Zernike equation, $h(r) = g(r) - 1 = c(r) + \rho \int dr' c(r') h(|r - r'|)$. (D.1)

In Eq. D.1, $g(r)$ is the radial distribution function, which measures the extent to which the structure of the “fluid” deviates from total randomness. For small $r$, $g(r) \to 0$ (because two particles cannot occupy the same position), while at large $r$, $g(r) \to 1$ (for $r > 0$, $g(r)$ is typically oscillatory). The right hand side of Eq. D.1 states that, given $N$ number of particles, the total correlation between particles 1 and 2 is due both to the direct correlation between particles 1 and 2 (the short range function $c(r)$) as well as the indirect correlation mediated via increasingly large numbers of intermediate particles (the integral expression). Applying the Percus-Yevick approximation for hard spheres sets $c(r) = 0$ at $r > d$.

From Hansen & McDonald (1986), the static structure factor is by definition $S(\xi) = 1 + \rho h(\xi)$, where $h(\xi)$ is the Fourier transform of Eq. D.1 into momentum space: $h(\xi) = c(\xi)/(1 - \rho c(\xi))$. We find $S(\xi) = 1/(1 - \rho c(\xi))$, which matches the expression of Mishchenko (1994),
Figure D.1: Static structure factor as a function of (particle size) \( u = 2\xi r \) for an incident light wavelength of 1 \( \mu m \). The height of oscillations in \( S \) increases with increasing values of the filling factor \( f \). Values are in agreement with Mishchenko (1994).

\[
S(\theta) \equiv S(\xi) = \frac{1}{1 - n_d K(\xi)}, \quad (D.2)
\]

In Eq. D.2, \( n_d \) is the number density of scattering particles, \( \xi = 4\pi \sin(\theta/2)/\lambda \) is the wavenumber (i.e., the absolute value of the momentum transfer in an elastic collision), \( \lambda \) is the incident wavelength of light, and \( K(\xi) \) is the Fourier transform of the direct correlation function \( c(r) \), the quantity that dictates how other particles can be arranged about a fixed particle without overlapping. For hard spheres where \( x \equiv \text{radius divided by hard sphere diameter} \), Wertheim (1963) has shown that the Percus-Yevick approximation is solved by

\[
-C(x) = \alpha + \beta x + \gamma x^2 + \delta x^3,
\]

from which it is straightforward to find that

\[
K(\xi) = 24 \frac{f}{n_d} \left[ \left( \frac{\alpha + \beta + \delta}{u^2} - \frac{2(\beta + 6\delta)}{u^4} + \frac{24\delta}{u^6} \right) \cos u \\
+ \left( \frac{24\delta}{u^6} - \frac{\alpha + 2\beta + 4\delta}{u^3} \right) \sin u + \frac{2\beta}{u^4} - \frac{24\delta}{u^6} \right]
\]

for \( \xi \neq 0 \), while for \( \xi = 0 \),

\[
K(0) = \frac{24f}{n_d} \left( \frac{\alpha + \beta + \delta}{u^2} - \frac{2(\beta + 6\delta)}{u^4} + \frac{24\delta}{u^6} \right)
\]
\[ K(0) = -24 \frac{f}{n_d} \left( \frac{\alpha}{3} + \frac{\beta}{4} + \frac{\delta}{6} \right). \]  

(D.3)

In the equations above, filling factor \( f = 1 - \text{(porosity)} \), \( u = 2 \xi r \), \( \alpha = (1 + 2f)^2/(1 - f)^4 \), \( \beta = -6f(1 + f/2)^2/(1 - f)^4 \), and \( \delta = (\alpha f)/2 \). The behavior of \( S \) as a function of \( u \) is plotted in Figure D.1.

**D2: Applying the Correction**

In the far-field zone, particles can be treated as independent scatterers, with mean interparticle distances on the order of \( \geq 3r \), so that electromagnetic field vectors add incoherently. In this independent scattering assumption, the coherent wave interactions between particles are entirely ignored. For a planetary regolith, particles will be touching and should be treated by an interaction potential. Using the static structure factor to modify single scattering properties (the single scattering albedo \( \omega \), asymmetry parameter \( g \), scattering cross-section \( C_{sca} \), extinction cross-section \( C_{ext} \), volume scattering phase function \( p(\mu) \)) incorporates the interaction terms to give scattering and extinction properties of a group of densely packed spheres (see Figs. D.2, D.3, and D.4 for illustrations of the impact on the phase function and the asymmetry parameter). The packing corrected quantities are

\[ \tilde{p}(\theta) = p(\theta)S(\theta), \]  

(D.4)

\[ g_{struc} \equiv \tilde{g} = \frac{\int_{-1}^{1} d(\cos \theta) p(\theta) \cos \theta}{\int_{-1}^{1} d(\cos \theta) p(\theta)} = \frac{\int_{-1}^{1} d(\cos \theta)[p(\theta)S(\theta)]\cos \theta}{\int_{-1}^{1} d(\cos \theta)[p(\theta)S(\theta)]}, \]  

(D.5)

\[ \tilde{C}_{sca} = \frac{1}{4\pi} \int_{\phi=0}^{2\pi} 2\pi \int_{\theta=0}^{\pi} \pi d\phi d\theta \sin \theta C_{sca} p(\theta) S(\theta), \]  

(D.6)

and

\[ \tilde{C}_{ext} = \frac{\tilde{C}_{sca}}{\tilde{\omega}(f)}. \]  

(D.7)

The expression for the single scattering albedo of a densely packed group of spheres, \( w_{struc} \equiv \tilde{\omega}(f) \), depends on a few key assumptions. Let \( B(f) \) be the ratio of the scattering cross-section of densely packed particles to that of isolated particles,

\[ B(f) = \frac{\tilde{C}_{sca}(f)}{\tilde{C}_{sca}(f = 0)} = \frac{1}{2} \int_{\cos \theta = -1}^{1} d(\cos \theta) p(\theta) S(\theta). \]  

(D.8)

Then an alternate definition for \( \tilde{C}_{sca} \) is
\[
\tilde{C}_{\text{sca}} = C_{\text{sca}} B(f). \tag{D.9}
\]
Assume that absorption cross-section is unaffected by packing density,
\[
\tilde{C}_{\text{abs}} = C_{\text{abs}} = \left(1 - \frac{w}{w}\right)C_{\text{sca}}, \tag{D.10}
\]
and extend the basic definition of the single scattering albedo to a densely packed group of spheres,
\[
\tilde{w} = \frac{\tilde{C}_{\text{sca}}}{C_{\text{ext}}} = \frac{\tilde{C}_{\text{sca}}}{\tilde{C}_{\text{sca}} + \tilde{C}_{\text{abs}}}. \tag{D.11}
\]
Substitute Eqs. D.9, D.10 into Eq. D.11 and reduce to yield
\[
\tilde{w} = \frac{C_{\text{sca}} B(f)}{C_{\text{sca}} B(f) + \left(1 - \frac{w}{w}\right)C_{\text{sca}}} = \frac{w B(f)}{w B(f) + (1 - w)}. \tag{D.12}
\]
The single scattering albedo (for 1 particle) may also be broken down into ray tracing and diffraction components,
\[
w = \frac{C_{\text{sca}}^{\text{ray}} + C_{\text{sca}}^{\text{diff}}}{C_{\text{ext}}^{\text{ray}} + C_{\text{ext}}^{\text{diff}}}. \tag{D.13}
\]
At this point, Mishchenko & Macke (1997) make three assumptions:

- \(C_{\text{ext}}^{\text{diff}} = C_{\text{sca}}^{\text{diff}}\) [sets the diffraction albedo component equal to 1]
- \(C_{\text{ext}}^{\text{diff}} = \frac{\pi d^2}{4} \equiv G\) [invokes the isolated particle assumption]
- \(C_{\text{ext}}^{\text{ray}} \equiv G\).

Using Assumption 3, then \(C_{\text{sca}}^{\text{ray}} = w_{\text{ray}} G\). Now
\[
w = \frac{w_{\text{ray}} G + G}{G + G} = \frac{1 + w_{\text{ray}}}{2}. \tag{D.14}
\]
Substituting Eq. D.14 into Eq. D.11 and reducing, we are left with the final expression for the scattering albedo of a group of densely packed spheres,
\[
w_{\text{struc}} \equiv \tilde{w}(f) = \frac{(1 + w_{\text{ray}}) B(f)}{(1 + w_{\text{ray}}) B(f) - w_{\text{ray}} + 1}. \tag{D.15}
\]
Figure D.2: Static structure factor packing corrected normalized phase function and asymmetry parameter for small particle radii and different packing fractions. Upper panel: For the same effective radius $r_{\text{eff}} = 5.0 \, \mu m$ and effective variance $v_{\text{eff}} = 0.1$ values, normalized phase functions (F11 element - ref. Mishchenko et al., 2002) are shown to be different for the cases of no packing (solid line: filling factor $f = 0$) and dense packing of grains (dashed line: $f = 0.6$) via the static structure factor packing corrections to single scattering properties. Composition is O-ray $\alpha$-quartz (Wenrich & Christensen, 1996). Lower panel: Behavior of asymmetry parameter as a function of incident wavenumber for $r_{\text{eff}} = 5.0 \, \mu m$, $v_{\text{eff}} = 0.1$ (diamonds: unpacked, asterisks: densely packed). Black dots represent the wavenumber (corresponding to $\lambda = 14 \, \mu m$) for which the normalized phase functions in upper panel were calculated.
Figure D.3: Static structure factor packing corrected normalized phase function for large particle radii and different packing fractions. For $r_{eff} = 500.0$, $v_{eff} = 0.1$, normalized phase functions are different for unpacked ($f = 0$, solid line) and densely packed ($f = 0.6$, dashed line) cases as well. Inset illustrates the roll-over in phase function at small scattering angles. Composition is defined by O-ray $\alpha$-quartz optical constants (Wenrich & Christensen, 1996).
Figure D.4: Static structure factor corrected asymmetry parameter as a function of incident wavenumber, corresponding to large particle radii \(r_{\text{eff}} = 500.0\), \(v_{\text{eff}} = 0.1\) and different packing fractions (diamonds: unpacked, asterisks: densely packed). Black dots represent the wavenumber (corresponding to \(\lambda = 14\ \mu\text{m}\)) for which the normalized phase functions in previous figure were calculated.
Appendix E: Copyright Permission Letters

E.1 Author Permission, Figure 1.1

Date: Mon, 18 Jul 2005 14:52:26 -0400
From: R. Todd Clancy <clancy@spacescience.org>
To: Karly Pitman <pitman@phys.lsu.edu>
Subject: figure reproduction

To: Karly M. Pitman
Dept. of Physics & Astronomy
Louisiana State University
Baton Rouge, LA 70803
(o) 225-578-8287
(e) pitman@baton.phys.lsu.edu

Dear Karly,

You have my permission to reproduce Figure 1 from my paper entitled “A New Look at Dust and Clouds in the Mars Atmosphere: Analysis of Emission-Phase-Function Sequences from Global Viking IRTM Observations” (Clancy & Lee 1991, Icarus, 93, 135) for inclusion in your dissertation.

R. Todd Clancy
Space Science Institute
P.O. Box 3075
Bald Head Island, NC 28461
(910) 457-6362

At 12:41 PM 7/18/2005 -0500, you wrote:

> Date: Mon, 18 Jul 2005 12:41:48 -0500 (CDT)
> From: Karly Pitman <pitman@theory.phys.lsu.edu>
> To: R. Todd Clancy <clancy@SpaceScience.org>
> Subject: permission to use Clancy & Lee 1991 figure
> 
> Dear Dr. Clancy,
> 
> I would like permission to reproduce Figure 1 from your paper entitled "A New Look at Dust and Clouds in the Mars Atmosphere: Analysis of Emission-Phase-Function Sequences from Global Viking IRTM

Please respond to this e-mail to confirm or deny permission. Both this e-mail request and your response will be shown in the dissertation’s Appendix.

Thank you,

Karly M. Pitman

Dept. of Physics & Astronomy
Louisiana State University
Baton Rouge, LA 70803
(o) 225-578-8287
(e) pitman@baton.phys.lsu.edu

E.2 Publisher Permission, Author’s Own Refereed Publication

Date: Wed, 20 Jul 2005 09:24:05 -0400
From: Michael Connolly <MConnolly@agu.org>
To: Karly Pitman <pitman@phys.lsu.edu>
Subject: Re: copyright permission to use manuscript # 2005JE002428

We are pleased to grant permission for the use of the material requested for inclusion in your thesis. The following non-exclusive rights are granted to AGU authors:

1. All proprietary rights other than copyright (such as patent rights).
2. The right to present the material orally.
3. The right to reproduce figures, tables, and extracts, appropriately cited.
4. The right to make hard paper copies of all or part of the paper for classroom use.
5. The right to deny subsequent commercial use of the paper.

Further reproduction or distribution is not permitted beyond that stipulated. The copyright credit line should appear on the first page of the article or book chapter. The following must also be included, “Reproduced by permission of American Geophysical Union.” To ensure that credit is given to the original source(s) and that authors receive full credit through appropriate citation to their papers, we recommend that the full bibliographic reference be cited in the reference list. The standard credit line for journal articles is: “Author(s), title of work, publication title, volume number, issue number, page number(s), year. Copyright [year] American Geophysical Union.”
If an article was placed in the public domain, in which case the words “Not subject to U.S. copyright” appear on the bottom of the first page or screen of the article, please substitute “published” for the word “copyright” in the credit line mentioned above.

Copyright information is provided on the inside cover of our journals. For permission for any other use, please contact the AGU Publications Office at AGU, 2000 Florida Ave., N.W., Washington, DC 20009.

Michael Connolly
Journals Publications Specialist

Date: Mon, 18 Jul 2005 14:24:24 -0500 (CDT)
From: Karly Pitman <pitman@theory.phys.lsu.edu>
To: mconnolly@agu.org
Subject: copyright permission to use manuscript # 2005JE002428

Dear Dr. Connolly,

I am the first author on the manuscript entitled ”Application of Modern Radiative Transfer Tools To Model Laboratory Quartz Emissivity” (MS# 2005JE002428), accepted in May 2005 for publication in JGR-Planets. I would like permission to reproduce this paper in its entirety for inclusion in my doctoral dissertation, ”Radiative Transfer Modeling of Thermal Infrared Emissivity Spectra: Applications to Martian Regolith Observations.”

The requested permission extends to any future revisions and editions of my dissertation, including non-exclusive world rights in all languages, and to the prospective publication of my dissertation by UMI Company. These rights will in no way restrict republishation of the material in any other form by you or by others authorized by you. Your authorization of this reproduction will also confirm that your company owns the copyright to the above-described material.

Please respond to this e-mail to confirm or deny permission. Both this e-mail request and your response will be shown in the dissertation’s Appendix.

Thank you,

Karly M. Pitman
Department of Physics and Astronomy
Louisiana State University
Baton Rouge, LA 70803
Vita

Karly Mariah Pitman was born in Fort McClellan, Alabama, on January 28, 1977. Karly graduated from Rock Bridge Senior High School in Columbia, Missouri, in 1995. In 1999, she graduated from Vassar College (Poughkeepsie, New York) with a double major in astronomy and geology and entered graduate school in the Department of Physics and Astronomy at Louisiana State University. Working with Dr. Geoffrey Clayton’s interstellar medium research group from 1999 onward, Karly developed an interest in light scattering of micron-sized dust particles in planetary and astrophysical environments, with emphasis on connections between theoretical models, laboratory data, and field spectra. She earned her master of science degree in physics from Louisiana State University in 2002 and began work on her primary research topic: radiative transfer modeling of planetary regolith. In addition, Karly has collaborated on projects ranging from interstellar dust in quasars to Martian atmospheric aerosols to meteorites. From 2003 to the present, Karly has been working remotely as a graduate research assistant for Dr. Michael Wolff at the Space Science Institute in Boulder, Colorado. Karly expects to receive her doctorate degree in December of 2005.