Springer Theses
Recognizing Outstanding Ph.D. Research

Llorenç Cremonesi

Light Scattering From Micrometric Mineral Dust and Aggregate Particles

Effects of Structure and Shape Applied to Paleoclimate Studies

Springer

Springer Theses

Recognizing Outstanding Ph.D. Research

Aims and Scope

The series "Springer Theses" brings together a selection of the very best Ph.D. theses from around the world and across the physical sciences. Nominated and endorsed by two recognized specialists, each published volume has been selected for its scientific excellence and the high impact of its contents for the pertinent field of research. For greater accessibility to non-specialists, the published versions include an extended introduction, as well as a foreword by the student's supervisor explaining the special relevance of the work for the field. As a whole, the series will provide a valuable resource both for newcomers to the research fields described, and for other scientists seeking detailed background information on special questions. Finally, it provides an accredited documentation of the valuable contributions made by today's younger generation of scientists.

Theses are accepted into the series by invited nomination only and must fulfill all of the following criteria

- They must be written in good English.
- The topic should fall within the confines of Chemistry, Physics, Earth Sciences, Engineering and related interdisciplinary fields such as Materials, Nanoscience, Chemical Engineering, Complex Systems and Biophysics.
- The work reported in the thesis must represent a significant scientific advance.
- If the thesis includes previously published material, permission to reproduce this must be gained from the respective copyright holder.
- They must have been examined and passed during the 12 months prior to nomination.
- Each thesis should include a foreword by the supervisor outlining the significance of its content.
- The theses should have a clearly defined structure including an introduction accessible to scientists not expert in that particular field.

More information about this series at http://www.springer.com/series/8790

Llorenç Cremonesi

Light Scattering From Micrometric Mineral Dust and Aggregate Particles

Effects of Structure and Shape Applied to Paleoclimate Studies

Doctoral Thesis accepted by
University of Milan, Milan, Italy

Springer

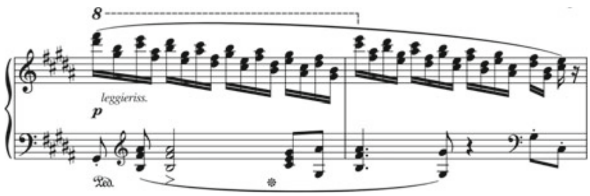
Author
Dr. Llorenç Cremonesi
Earth and Environmental
Sciences Department
University of Milano-Bicocca
Milano, Italy

Physics Department
University of Milan
Milan, Italy

Supervisor
Prof. Marco A. C. Potenza
Physics Department
University of Milan
Milan, Italy

ISSN 2190-5053 ISSN 2190-5061 (electronic)
Springer Theses
ISBN 978-3-030-56786-6 ISBN 978-3-030-56787-3 (eBook)
https://doi.org/10.1007/978-3-030-56787-3

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland



Chopin, Frédéric. Étude Op.25, No.6 mm 27–28, ca. 1836.

To the dearest Colour, the deepest Hue in my days and nights.

Supervisor's Foreword

The current understanding of systems dominated by radiative transfer is often limited by incomplete knowledge of the interaction of micrometric and nanometric particles with visible and infrared light. A relevant example is represented by the contribution of aeolian dust to the global radiative balance: the impact of aerosol on climate is still unclear and has been attracting considerable attention, prompted by the need of understanding its role in climate change. Substantial efforts are also devoted to tracking the sources of airborne particles emitted from natural and anthropogenic sources worldwide. A relevant contribution comes from the study of meltwater from alpine and polar ice cores, storing the solid contents of the atmosphere even for millennia. This provides a unique archive to be examined with as many techniques as possible. In this framework, the optical properties of small particles play a prominent role and our ability to interpret instrumental data is of utmost importance in the inversion of light scattering data. This is one of the big challenges for the interpretation of laboratory data. Although considerable progress has been achieved in the last decades, a growing amount of literature is questioning the actual reliability of simple models and approximations of objects endowed with a remarkable level of complexity. Several studies have been establishing that approximating aerosol particles as homogeneous spheres leads to rampant discrepancies with experimental observations. The theoretical and instrumental tools to refine the characterization of such particles are still under investigation. Numerical methods prove to be very effective while being much more demanding in terms of resources and computation time, especially for borderline scattering regimes that are also the most relevant in terms of radiative transfer.

This topic constituted the basis of the Ph.D. thesis of Dr. Llorenç Cremonesi. It provides results obtained on a high professional level both from the experimental and theoretical point of view. This thesis deals with the radiative effects of the morphology of scatterers, both shape and internal inhomogeneities, in view of interpreting experimental data with a model-independent approach when investigating samples with non-invasive optical techniques. Meltwater samples from the Alps, Greenland and Antarctica have been studied with several experimental methods, including the recently introduced Single Particle Extinction and

Scattering. The ice core data per se can serve as an optical characterization of samples complementary to chemical analyses. A novel approach to model scatterers endowed with internal inhomogeneities is introduced and validated by comparing to experimental results and extensive numerical simulations. The highlight is the discussion of the predictive potential of different theoretical models supported by experimental observations. Different kinds of samples have been studied, collected in the environment and produced in the laboratory. The obtained results and conclusions are supported by extensive numerical simulations. Both the fundamental background of the underlying physics and the optical techniques adopted are formulated and presented in clear form and convenient for being comprehensible for a readership that might not be familiar to these topics. The presented methods can be readily used to interpret data from laboratory optical methods and remote sensing, as well as to feed radiative transfer codes.

Milan, Italy
May 2020

Prof. Marco A. C. Potenza

Abstract

Atmospheric aerosol is known to impact the radiative energy balance of the Earth and the local temperature in the atmosphere by interacting with both solar and terrestrial radiation. The extent of this direct and indirect contribution has not to date been determined with adequate accuracy. The present work examines the scattering of visible light from non-spherical particles in the micrometric size range, such as mineral dust and colloidal aggregates, with a focus on the effect of their shape and morphology. Lorenz–Mie scattering and effective medium approximations are currently the main theoretical approaches to model the optical properties of aerosol particles, although their effectiveness has been recently called into question. This thesis provides an overview of the experimental results from analyzing Antarctic and Alpine ice cores using optical techniques with a particle-by-particle approach. Particular attention is also given to the study of colloidal aggregates as a model for complex particles. Specifically, we rely on Single Particle Extinction and Scattering and Near Field Scattering on flowing samples, which give model-independent results. On the theoretical side, an interpretation of scattering data is given in terms of the structure factor of the particles, beyond the spherical approximation. The experimental findings are also supported by extensive simulations based on the Discrete Dipole Approximation. By measuring two optical parameters simultaneously, it is possible to distinguish compact particles from aggregates of smaller particles occurring in deep ice cores. While some scattering parameters are correctly predicted by well-established models such as the Rayleigh–Debye–Gans approximation, it is found that particle shape and internal structure have a significant effect on their complex scattering amplitude. Similarly, the discrepancy between the results obtained from two different experimental approaches for particle sizing can be ascribed to particle shape. Moreover, there is evidence that effective medium approximations cannot be applied to aggregates, as a result of the contribution of correlations among the fields radiated by the particles in the aggregate.

Acknowledgements

I would like to acknowledge my advisor Prof. Marco Potenza, Dr. Barbara Delmonte, Dr. Marius Simonsen, Prof. Alberto Parola and Prof. Fabio Ferri for their precious help and guidance throughout these years.

I also wish to thank the Referees: the accurate criticisms and suggestions by Prof. Paul Vallelonga and Dr. Dario Massabò contributed to ameliorate this text considerably.

My loved ones contributed to this work perhaps more indirectly, but it certainly meant a lot to me. To them I extend my deepest gratitude.

Contents

Chapter 1
Introduction

In the present work, we focus on the scattering of visible light from non-spherical particles in the micrometric size range, such as mineral dust and colloidal aggregates. Beyond the interest for paleoclimate studies, we restrict ourselves to the visible spectrum for practical reasons. From a merely theoretical standpoint, such limitation is not of primary importance, since one can discuss and generalise many scattering properties provided that the particle size and the wavelength are conveniently scaled (see for example [39]). The frequency (wavelength) of the incoming radiation, nonetheless, must be taken into account if the material of the scatterer is to be considered to any extent. To our purposes, the relevance of visible and near-infrared light lies in the unique point of view it provides on our natural environment: atmospheric aerosol is unavoidably exposed to both solar and terrestrial radiation (see for example [14, 36, 46, 61]).

Briefly, aerosols are known to impact the Earth's climate by altering the spectral solar irradiance, effectively reflecting a portion of the incoming radiation from the Sun (backscattering). On the other hand, they are also involved in scattering and absorption of light reflected by the surface of the Earth, as well as thermal infrared radiation, which has a warming effect. Moreover, a significant contribution to the total aerosol radiative forcing is given by efficient absorbing particles such as soot, much of which is of anthropogenic origin. Beyond the radiative energy balance standpoint, these phenomena also affect the local temperature in the atmosphere, which in turn affects the stability of water droplets and ice crystals, hence the formation of clouds and the occurring of precipitations [10]. We should mention that aerosols are essential as nucleation sites for water molecules in clouds [7], albeit this remarkable feature is beyond the scope of this thesis.

The properties of aerosols and micrometric particles have a considerably general scope due to their ubiquity. For example, the processes described above have been observed in extraterrestrial environments and they are the driver of some atmospheric dynamics on Mars [6, 20, 33, 38]. The extent of direct and indirect effects of aerosols on climate is still a relevant line of research for radiative balance and

L. Cremonesi, *Light Scattering From Micrometric Mineral Dust and Aggregate Particles*, Springer Theses, https://doi.org/10.1007/978-3-030-56787-3_1

paleoclimate studies [1, 19, 28, 49, 60]. More broadly, the optical properties of a system may be leveraged as a probe for studying the physics of a system. For instance, the scattering of electromagnetic radiation is the only possible way of studying tropospheric aerosol and cosmic dust in its natural environment, overcoming by remote sensing the distance between the observer and the object [21, 30, 31, 34]. On the other hand, optical properties are also an interesting feature *per se*, since in many settings they directly determine the extent to which the system is able to interact with its surroundings [37]. Referring to glaciology, it is worth mentioning that particles deposited on mid-latitude glaciers, polar snow and sea ice alter the ability of such surfaces to scatter light (albedo) by significantly enhancing absorption, hence melting [4, 18].

A large number of studies has established that the optical properties of a particle, namely the fraction of the incoming radiation absorbed by the particle, the amount of power which is instead scattered, and ultimately the angular and spectral dependence of light scattering, all exhibit a strong relationship with the geometrical structure and composition of the scatterer, as well as its size (see for example [8, 25, 42, 43, 47, 64, 65]). These complex physical phenomena are usually defined in terms of measurable quantities such as the scattering and absorption cross sections, albedo and asymmetry parameter. From an experimental point of view, the measurement of these parameters can be achieved in many ways. The difficulty lies in the interpretation of data, given the variety of particle characteristics which affect them. Similarly, the number of parameters that come into play encourages researchers to deploy a variety of instrumentation to collect data.

Optical techniques are a versatile and non-invasive probe, lending themselves to be designed for in situ, routine or in-line applications [29, 65]. They can either be applied to bulk samples, nanocomposites, suspensions of an ensemble of particles or be used in particle-by-particle approaches [22, 41, 52–54, 58]. Some examples include Light Detection and Ranging o Laser Imaging Detection and Ranging (LIDAR) [14], hyperspectral imaging [16], optical scattering techniques [5, 35, 45], laser sensing particle detectors [56].

At present, the major problem affecting the interpretation of scattering data lies with the mathematical models linking the optical properties of a particle to its morphology. The very fact that a particle is a system of limited size is the origin of a completely different level of complexity and interaction capabilities compared to the corresponding bulk case, beyond what is ascribable to the surface to volume ratio [2]. Moreover, even in particles with a homogeneous composition, the polarizability can differ from its value for bulk [25].

As it might be expected, care should be also given to the environment of the particle, since the scattering centre can hardly be considered isolated from its surroundings in most situations. A particle may be deposited on a surface or on a larger particle, the density of particles dispersed in a medium might be high to the point that the optical properties of the system are no longer linear, or the particles themselves may bound together forming an aggregate which should be considered as a whole.

The rigorous solution of the Maxwell equations for an isolated sphere interacting with a monochromatic plane wave was first given by Gustav Mie [40]. These calculations of the absorption and scattering by a particle of arbitrary polarizability are the basis of aerosol optics [23, 63]. Lorenz–Mie scattering and effective medium approximations are, to date, the common theoretical approaches to model the optical properties of aerosol particles [13]. Notwithstanding their widespread use, it has conclusively been shown that in some specific cases applying the Lorenz–Mie model results in poor agreement with experimental data [17, 42, 49, 51]. It should be pointed out that the Achilles heel of this approach consists in the limited accuracy in the depiction of irregularly shaped particles that inherently comes with modelling them as homogeneous spheres. More importantly, this approximation also brings about the need for an estimate of the *effective* polarizability, which is open to many possible definitions. These two shortcomings combined give fundamentally model-dependent interpretations and can cause theoretical predictions to deviate significantly from experimental data.

Along these lines, many works have shown a preference for numerical methods over theoretical approximations, also as a tool to interpret experimental data [44, 50, 59]. While retaining some practical advantages, approximate methods fail to reproduce the entire range of observations at all wavelengths as accurately as more computationally intensive exact approaches do [65]. Moreover, recent advancements in computing capabilities have surely allowed fast and accurate numerical calculations of complex particles. It should be noted, however, that such methods tend to be case-specific since they require a detailed modelling of the scatterer.

The general consensus of researchers in the field is that to understand the radiative properties of complex non-spherical particles it is necessary to go beyond the coarse-grained models on which approximate approaches are based (see for example [8, 24] and references therein for a focus on absorbing aggregates and [15, 48] for mineral dust). Critical aspects of morphology affecting absorption and scattering need to be identified: non-spherical shape has been observed to have an impact comparable to surface roughness [26]. On the experimental side, a particle-by-particle approach provides a more detailed picture which paves the way for inverting scattering data. The trend is to collect experimental data burdened by as few free parameters as possible, in order to lay down the guidelines for more sophisticated mathematical models and feed efficient parameters into climate models [3]. Atmospheric circulation and radiative transfer models are also supported by satellite, airborne and ground-based remote sensing measurements, whereby to characterise atmospheric and aerosol composition in situ [9, 11, 14, 21]. Such approaches allow researchers to quantify with a remarkable spatial and temporal resolution the (vertically integrated) optical thickness of the atmosphere, backscattering and downwelling radiation, and also give insight on the essential contribution of water vapour and clouds [37]. While direct measurements provide invaluable information on which to widen our knowledge of radiative balance processes, they are clearly restricted to the current state of the atmosphere, although a considerable amount of data has been gathered over the last three decades.

Reconstructing atmospheric composition and radiative balance in the past is a question of great interest. As we will see in greater detail in Chap. 4, glaciers and especially polar ice cores provide a unique archive of the climate fingerprint over