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S. Ramaseshan

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edited by P. W. Barber & R. K. Chang

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by P. W. Barber & S. C. Hill

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PREFACE

The optical properties associated with small particles, which include aerosols and hydrosols, impact several areas of science and engineering. Particles in outer space in the form of interstellar dust are of interest to astrophysicists. Water droplets in the form of clouds impact optical propagation and scattering in the atmosphere and affect environmental issues in the form of acid rain. Liquid sprays in diesel engines modify combustion and affect pollution in the form of particulates. Oceans are full of small particles in the form of plankton and other microorganisms. Hydrosols in the form of colloids are important to chemical engineers and interfacial scientists. Further, particles flowing through the blood vessels of our bodies influence our health. The impact of small particles in our daily lives is immense and has motivated a large number of investigators to study matter in the form of small particles. Applied scientists and engineers constantly attempt to modify such small particles to suit a particular task. Although this book is limited to the interaction of light with matter in the form of small particles, the fundamental diagnostic techniques presented here will be useful to many researchers who are not directly involved in the optical scattering, absorption, and emission aspects of aerosols and hydrosols.

Since the advent of high-speed computers and lasers, the interaction of light with matter in the form of small particles with a discontinuous optical boundary relative to the surroundings has been much better understood. Furthermore, the combined use of computers for calculations and lasers for experiments has continued to reward investigators with exciting new science and significant applications of optical diagnostic techniques for in-situ and real-time monitoring of aerosols and hydrosols in fields ranging from atmospheric science to combustion engineering and from oceanography to microbiology.

The most interesting and significant recent finding in this field is undoubtedly the existence of resonance peaks in linear and nonlinear optical spectra. Such resonance peaks

are solely dependent on the particle morphology (size, shape, and refractive index). Even though the mathematical formalism needed to predict the existence of such resonance peaks has been in place since 1908, it took the advent of high-speed computers and monochromatic lasers to fully demonstrate that the presence of such morphology-dependent resonances (MDR's) seems to affect every aspect of optical interactions with particles with sizes larger than the wavelength. Thus, in this book, such MDR's are discussed in depth in three chapters and mentioned in all five chapters. Because of the ubiquity of these resonances, they have been referred to by many names, including structural resonances, dimensional resonances, ripple structures, partial wave resonances, whispering modes or whispering gallery modes, creeping waves, circumferential waves, surface modes, and virtual modes. All of these names refer to the same phenomena. MDR's can become important when the particle size (radius a) approaches and exceeds the wavelength of the electromagnetic wave (λ) and the refractive index of the particle is greater than that of the surrounding medium. Such resonances are easiest to observe from a single particle with high symmetry, such as a sphere, spheroid, or cylinder. From a ray optics viewpoint, each spherical particle, for example, can be envisioned as a microlens to concentrate the electromagnetic fields inside and outside the particle and as an optical cavity to trap some of the external waves incident on the particle and to provide optical feedback to the internal waves. In the case of an ensemble of particles with different sizes and shapes, these resonances are "washed out" in some of the detected signals even though the presence of such resonances within each particle can greatly modify the optical interactions.

The validity of using the bulk refractive index when the particle size continues to decrease is another major research topic, especially in the field of condensed matter physics. The "quantum size" effects of extremely small particles (e.g., less than 50 Å) can alter the dielectric constant or refractive index and thereby their optical properties. Even though such

small particles can be simply treated from an electromagnetic point of view (e.g., within the Rayleigh limit), the quantum mechanics needed to consider the optical constant must take into consideration the confinement of the electrons by the particle boundary and the scattering at the interface.

We have asked several of the most active researchers in the field of optical interactions with small particles to contribute comprehensive reviews describing the fundamental approaches as well as the latest developments and discoveries in their respective research areas. Because of the excitement and competition in this field, many of the current research findings have appeared only in the form of brief reports intended for rapid communication (e.g., *Physical Review Letters*, *Optics Letters*, *Chemical Physics Letters*, *Solid State Communications*, *Rapid Communications in Applied Optics*, and *Applied Physics Letters*). Page restrictions of such brief reports sometimes make it necessary to sacrifice completeness and to curtail the necessary background material of the findings. The reading of these brief reports can at times be frustrating, especially for scientists and engineers not directly in the field and for graduate students interested in entering the field. We have asked researchers who authored many of the recent brief reports to integrate into one chapter their numerous research findings along with complementary results from other groups. In addition, keeping in mind the needs and interests of a much wider group of readers, we requested that all authors provide the essential introduction and necessary background information to make their subject more understandable as well as to capture the enthusiasm of their original results. Finally, we requested that the titles of all papers be included in the reference section of each chapter to help the readers decide whether a particular referenced article is of further interest. Most of all, those of us involved with the book want to share the beauty and enthusiasm of this field with a much wider group in the

hope that, by attracting more researchers to the field, our own work on small particles will be enriched and made even more exciting.

Within the five chapters of this book, optical interactions with small particles are discussed by experts in the fields of electromagnetics related to MDR's, optical spectroscopy applicable to a single droplet or aerosol, thermodynamic and hydrodynamic properties of a droplet upon irradiation by high-intensity and/or high-energy laser beams, and condensed matter physics in the examination of the applicability of bulk optical constants to small particles. Each of these chapters was written with the aim of presenting in one volume a review of the present status of optical effects with small particles, making certain that each chapter contains the necessary introduction and fundamental background for those not directly doing research in this field, and for those who want to apply segments of the various approaches to their specific applications, as well as for those we wish to attract to this exciting field.

In Chapter 1, the mathematical formalism (commonly referred to as the Lorenz-Mie theory) is developed in detail with particular emphasis on the MDR's pertaining to a transparent sphere with $a > \lambda$. These MDR's are considered in view of and related to specific observed resonance peaks in linear optics experiments (e.g., elastic scattering, IR absorption, optical levitation, spectroscopy, fluorescence, energy transfer between fluorescent molecules, optical bistability, and Raman scattering) and in nonlinear optics experiments (e.g., lasing, stimulated Raman scattering, coherent anti-Stokes Raman scattering, and the intensity-dependent refractive index). The authors of this chapter have brought together for the first time various mathematical treatments of MDR's and have made the difficult connection between these treatments with the ray optics picture of radiation propagating within the particle interface. The analogy of MDR's with the more familiar RLC resonances in electrical circuits is presented in terms of pole locations in the real and

the imaginary frequency plane and in terms of the Q-factor for each MDR. Particularly useful are the simple formulas pertaining to MDR's in the asymptotic limit of large size, e.g., the approximate frequency separation between MDR's of the same order and polarization. This theoretical chapter was written with the experimentalists in mind, since they will be interested in such quantities as the width and density of MDR's within a frequency interval dictated by the natural linewidth of the fluorescence or Raman emission. Those interested in the computation and techniques to extract the particle sizes from MDR's in the experimental spectra will find this chapter most helpful. In addition, the T-matrix method techniques for rapid calculation of the MDR's from spheroids are also clearly presented.

One convenient way to "hold" the single particle in an experiment is to use a levitator by either electrical or optical forces. Levitation methods for single particles are presented in Chapter 2, starting with a historical review dating back to the classic experiment in 1917 by Millikan and his student, Fletcher. Once the limitation of an electrostatic levitator is presented, the author proceeds to work out in detail the trapping forces associated with an electrodynamic levitator with hyperbolic electrodes. The unique and innovative design of a spherical void electrodynamic levitator (a limiting case of the hyperbolic electrodes for the particle in the center of the sphere) is presented. This spherical geometry not only is simple to construct (with a standard ball end mill) but also at the same time proves to be valuable when used as an integrating sphere for the light scattered and/or emitted by the levitated particle. The following sensitive spectroscopic techniques applicable to a single levitated particle are reviewed: (1) photoemission excitation spectroscopy which results in the ejection of discrete charges from the particle as the incident photon energy is swept; (2) photophoretic spectroscopy which is sensitive to the motion of the particle due to radiometric forces associated with the recoil of molecules from the heated surface of the

particle; (3) infrared spectroscopy which is based on the slight radius change of the particle when the IR radiation is tuned to a vibrational mode of the medium and on the shift of MDR's in the scattering coefficient of the visible radiation when the radius is changed; and (4) fluorescence spectroscopy, particularly on the observed enhanced energy transfer between two different types of molecules embedded in the particle and on the intensity ratios of the fluorescence emission when TE or TM MDR's are excited by the incident radiation. The energy transfer results are of current interest to a large group of chemical physicists who are studying the spatial extent of this coupling between molecules. The fluorescence intensity ratio experiments have demonstrated that precise information on the orientation of fluorescent molecules bridged to the host material at the interface can be inferred.

In-situ absorption and fluorescence spectroscopy in aerosol analysis are reviewed in Chapter 3. Aerosols are dispersions of particular matter suspended in the gas phase and thus involve an ensemble of particles of different sizes for liquid droplets and oftentimes different shapes for solid particles. Absorption spectroscopy is primarily concentrated on photothermal schemes. A comprehensive treatment is therefore presented of the heat conduction equation for a sphere in a gaseous medium which is appropriate in the input low intensity limit when heat conduction from the particle is the dominant effect and when convection leading to explosive vaporization can be neglected. All the photothermal techniques presented in this chapter rely on the particular heat patterns developed in the gas near the laser-illuminated particle surface or on the heat-induced changes in the size of the laser-illuminated particle. Of the three absorption techniques considered (photothermal interferometry, photothermal modulation of Mie scattering, and photophoretic spectroscopy), a variation of the photothermal interferometric technique appears to have the greatest sensitivity. The connection is made between these laboratory techniques and the realistic problems of high-energy laser beam propagation in the atmosphere where thermal

blooming of the laser beam profile is unavoidable. Fluorescence techniques with single particles are also presented in terms of the quantum yield and decay time of fluorescence emission as a result of energy transfer between dye molecules within a liquid droplet. Furthermore, this chapter reviews the application of using the changes in the MDR-related fluorescence peaks to monitor the droplet size changes (resulting from evaporation or condensation) and the shape oscillations (resulting from surface tension restoration and viscous damping of the deformation amplitude). The section on lasing droplets develops the unique properties of the droplet as a microlens and as an optical cavity. Again, the connection is made between MDR's and the ray optics picture of waves propagating inside the droplet and experiencing pumping and feedback.

The problem of light-induced droplet heating is thoroughly treated in Chapter 4 for two cases. First is the low irradiance case in which droplet heating and vaporization are considered. The isobaric vaporization is assumed in the calculation for both the transient and the steady-state temperature rise within the droplet and the droplet size decrease due to vaporization. Second is the high irradiance case which includes explosive vaporization results and hydrodynamics, plasma formation due to laser-induced breakdown, and nonlinear optical phenomena. The rapid deposition of energy within the droplet results in the generation of pressure waves within it. These over-pressure waves or shock waves can cause material ablation, which is usually referred to as an explosive plume. To treat such an explosive vaporization event, the author develops the hydrodynamic equations involving the conservation of mass, momentum, and energy and discusses the difficult boundary conditions across the droplet interface. Graphic solutions are presented for the high irradiance case in which the heating is uniform or has spherical symmetry (e.g., for small particles in the Rayleigh limit) and in which diffusion is either considered or neglected. The underlying physics resulting from nonuniform heating of larger absorbing particles and of

larger transparent particles is also discussed. The nonuniform heating of a droplet requires a computer code capable of solving the two-dimensional hydrodynamic equations along with the associated boundary considerations. For transparent droplets, absorption results from plasma generated by the laser-induced breakdown process within the liquid or in the gas just outside the shadow face. Once the plasma is generated, theoretical treatment must account for the coupling of EM and hydrodynamic effects since the EM fields polarize the medium and alter the medium density which, in turn, perturbs the polarization that affects the EM fields. The author has selectively cited a large number of references from the Russian literature and placed them in the proper context in terms of thermodynamic and hydrodynamic development. This chapter forms the foundation for those interested in high-intensity and high-energy laser propagation in the atmosphere.

Chapter 5 asks the difficult question, "As the particle size decreases, when do bulk optical constants cease to be valid?" The author, who is the coauthor of the book Absorption and Scattering of Light by Small Particles by Bohren and Huffman, chose to consider the subject related to the experimental evidence for quantum size effects. The last chapter reviews the investigations he and several international groups conducted to answer the above question. Examples on carbon, olivine silicate, and silver submicrometer size particles are based on the author's experimental endeavors. Additional examples of CdS and ZnS semiconductor colloids with sizes in the tens of angstrom range are also discussed. Particle clumping often gives rise to apparent size-dependent optical constants. In addition, depolarization effects associated with the particle boundary can frequently cause an apparent optical constant change with size. This chapter leads the readers through the various difficulties which demand the utmost care and restraint on the part of the experimentalist not to mistakenly conclude that true quantum size effects have been observed. As the particle size continues to decrease to the tens of angstrom range, new phenomena involving

quantum physics, electromagnetics, and hydrodynamics are still to be explored.

We thank the authors for contributing to this comprehensive book which clearly expresses the current excitement in this extremely active field.

Peter W. Barber and Richard K. Chang
Editors

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