THE SCATTERING OF LIGHT

AND OTHER ELECTROMAGNETIC RADIATION

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Preface

In writing this book, I have endeavored to summarize the theory of electromagnetic scattering, as well as to describe some of the practical applications, particularly to light scattering. The treatment is extensive, and yet it is hardly exhaustive, for the field is vast. The selection of topics, described in the introductory chapter, is biased very much in favor of my own interests.

A perusal of the list of references will show that although the theory is mainly more than half a century old, the applications have occurred almost entirely during the past two decades. This recent spate of research activity has opened up vast new possibilities for applications to the physics of particulate systems, the physical chemistry of solutions including those containing macromolecules, bio-colloids, and detergents, the morphology of solids, critical opalescence, low angle X-ray scattering, atmospheric and space optics, radar meteorology, and plasma physics including radiowave scattering by plasmas generated in the upper atmosphere by rapidly moving objects.

MILTON KERKER

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Most important of all has been the support throughout this endeavor of my wife, Reva. This book is affectionately dedicated to her, to each of our parents, and to our children, Ruth Ann, Martin, Susan, and Joel.

Glossary of Principal Symbols

A	albedo
A	Helmholtz free energy
A_1	semi-axis of a polarization ellipse
A_{ij}	co-factor of the determinant $\lvert a_{ij} \rvert$
$\mathbf{B}$	magnetic induction
B	second virial coefficient
B_1	semi-axis of polarization ellipse
C_{sca}, C_{ext}, C_{abs}	cross sections for scattering, extinction, absorption
C_τ, $C(\theta)$	Cabannes factors for turbidity and Rayleigh ratio
$\mathbf{D}$	dielectric displacement
d	diameter
D	divergence of a tube of rays
D	factor appearing in multi-component theory for poly-electrolytes
$\mathbf{E}$	electric field intensity
$F_a^2(h)$	intensity factor
G	gain
G	Gibbs free energy
G_{ij}	derivative of chemical potential
G_n	solution of radial equation for inhomogeneous sphere
$G(s)$	probability density function
$\mathbf{H}$	magnetic field intensity
H, H', H''	factors involving optical para-meters
$H_n(kr)$	Hankel function
I	intensity
$J_n(kr)$	Bessel function
K	factor in expression for Rayleigh ratio
L	persistence length
$\mathbf{M}$	magnetic polarization
M	molecular weight
M_w	weight average molecular weight
N	number of particles or molecules per unit volume
N_A	Avogadro's number
$N_n(kr)$	Neumann function
O.D.	optical density
$\mathbf{P}$	electric polarization
P_e	depolarization factor of ellipsoid
P	radiation pressure
P	form factor
P_n	radial function in scattering by inhomogeneous cylinder
$P_n^m(\cos\theta)$	associated Legendre polynomial
$p(\theta)$	degree of polarization
Q_{pr}	efficiency for radiation pressure
Q_{sca}, Q_{ext}, Q_{abs}	efficiencies for scattering, extinction, absorption
R	molar gas constant
R_g	radius of gyration
R_θ	Rayleigh ratio
$\mathbf{S}$	Poynting vector
S	surface of interfacial area
S_1, S_2	scattering amplitudes for sphere
S_{sp}	specific surface
T	absolute temperature
T	transmission
T_1, T_2	scattering amplitudes for cylinder
T_n	radial function in scattering by inhomogeneous cylinder
V	volume
V_h, H_v	Rayleigh ratio with polarizer in the horizontal position and analyzer in the vertical position, and vice versa

V_v, H_h	Rayleigh ratio with polarizer and analyzer vertical and horizontal respectively
W_n	solution of radial equation for inhomogeneous sphere
Z_0	intrinsic impedance
Z_i	ionic charge
$Z_n(z)$	cylinder function
a	radius
a'	absorption coefficient
a_i	activity of ith component
a_{ij}	matrix element in multi-component theory
a_M	modal value of radius
a_n	scattering coefficient
b	radius of coated sphere
b_n	scattering coefficient
c	concentration in gm/ml.
c	velocity of light in free space
e	electronic charge
e_s	eccentricity of spheroid
f_i	activity coefficient (based on mole fraction)
$g(s)$	radial distribution function
i	$\sqrt{-1}$
i_1, i_2	angular intensity functions
g	concentration in grams per gram of water
g	wavelength exponent
g_{os}	rational osmotic coefficient
h	$(4\pi/\lambda)\sin\theta/2$
h	$k_0 \sin\phi$
j	$(m^2k_0^2 - h^2)^{1/2}$
k	Boltzmann constant
k	propagation constant
l	$k_0 \cos\phi$
l	path length
l	range of molecular forces
$\bar{l}$	characteristic length
l_c	coherence length
m_a	aggregation number for micelle, polyion
m	molality
m	refractive index
m_e	mass of the electron
$\mathbf{n}$	unit vector normal to surface
n	real part of refractive index
n_i	number of ions per unit volume
$\mathbf{p}$	dipole moment
p	micellar charge
p	pressure
$p(a)$	size distribution function
q	ratio of α/v or of a/b
r	radial distance
r_1, r_2	Fresnel reflection coefficients
s	intra-particle distance
s_0, s_1, s_2, s_3	Stokes' parameters
t	time
t_1, t_2	Fresnel transmission coefficients
u	any scalar component of E or H
u	ha
v	velocity of light in medium
x_i	mole fraction of ith component
$z(\theta)$	dissymmetry of angular scattering
α	degree of dissociation
α	dimensionless size parameter
α'	polarizability
α_M	modal value of size parameter α
α_n	phase angle
α_p	volume expansion coefficient
β	$m\alpha$
β_{ij}	interaction coefficient
β_n	phase angle
β_T	isothermal compressibility
γ	anisotropy factor
γ_i	activity coefficient
$\gamma(s)$, $\gamma_0(s)$	correlation function
δ	phase difference
ε	dielectric constant
$\zeta_n(kr)$	Ricatti–Bessel function
$\overline{\eta^2}$	mean square of the variation of the local dielectric constant
$\overline{\eta_A\eta_B}$	correlation distance
$\eta_n(kr)$	logarithmic derivative of Ricatti–Bessel function
θ	scattering angle
θ_i, θ_t	angles of incidence and refraction
κ	index of absorption
κ	reciprocal length in Debye–Hückel theory
κ_1, κ_2	factors of propagation constant
λ	wavelength
μ	magnetic permeability
μ	refractive index of a scattering medium
μ_i	chemical potential of ith component

ν	frequency
v	size parameter of coated sphere
ν_n	number of ions into which an electrolyte dissociates
$\mathbf{\Pi}$, Π	Hertz vector, potential
π	osmotic pressure
$\pi_n(\cos\theta)$	angular function
ρ	density
ρ	dimensionless radial distance kr
ρ	phase shift parameter
ρ_e	electron density
ρ_u, ρ_v, ρ_h	depolarization factors
$\rho(\theta)$	polarization ratio
σ	back scatter cross section
σ	specific conductance
σ	standard deviation or other measure of width of distribution
σ_0	breadth parameter of ZOLD
τ	turbidity
$\tau_n(\cos\theta)$	angular function
ϕ	tilt angle for cylindrical symmetry
ϕ_{os}	practical osmotic coefficient
ϕ, ϕ_i	volume fraction of scattering material
$\chi_n(kr)$	Ricatti–Bessel function
ψ	angle between scattering direction and incident electric vector
ψ_e	inclination of polarization ellipse
ψ_i	refractive index increment of ith component
$\psi_n(kr)$	Ricatti–Bessel function
ω	circular frequency
ω'	weight fraction of scattering material

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CHAPTER 1

Introduction

The optical properties of a medium are characterized by its refractive index, and as long as this is uniform, light will pass through the medium undeflected. Whenever there are discrete variations in the refractive index due to the presence of particles or because there are small scale density fluctuations, part of the radiation will be scattered in all directions.

The scattering of light is a ubiquitous natural phenomenon. We perceive the blue of the sky because of the scattering of the solar rays by the air molecules; were it not for this, the heavens would be black. Something close to the correct explanation was suggested more than four and a half centuries ago by da Vinci (ca. 1500) when he wrote:

> "I say that the blueness we see in the atmosphere is not intrinsic color, but is caused by warm vapor evaporated in minute and insensible atoms on which the solar rays fall, rendering them luminous against the infinite darkness of the fiery sphere which lies beyond and includes it . . . . If you produce a small quantity of smoke from dry wood and the rays of the sun fall on this smoke and if you place (behind it) a piece of black velvet on which the sun does not fall, you will see that the black stuff will appear of a beautiful blue color . . . . Water violently ejected in a fine spray and in a dark chamber where the sunbeams are admitted produces then blue rays . . . . Hence it follows, as I say, that the atmosphere assumes this azure hue by reason of the particles of moisture which catch the rays of the sun."

Other optical phenomena in the atmosphere such as the colors of the sunset, the rainbow, the glory, the corona, and the halo are due to scattering either by aerosols, by ice crystals, or by water droplets. The transparency of the atmosphere varies according to the extent that there is scattering of light by aerosol or fog. In interstellar space there are huge clouds of colloidal particles which scatter starlight directly to us, or by the same scattering process, alter the starlight which is transmitted through them. The zodiacal light seen in the western sky is due to scattering by interplanetary dust.

The turbidity of liquids and of solids, and in some cases their color, results from the scattering of the light in which they are viewed, either by their constituent molecules or by suspended particles. The brilliant colors of metal sols or of certain precious stones are derived from the preferential scattering and absorption of certain wavelengths by the suspended particles. The color of the sea is, in part, a light scattering phenomenon.

The scientific study of light scattering may be said to have commenced with the experiments on aerosols by Tyndall (1869), which were followed from 1871 onwards by Lord Rayleigh's great body of theoretical work. The problem is to relate the properties of the scatterer—its shape, its size, and its refractive index—to the angular distribution of the scattered light. The incident beam of known intensity and wavelength is usually taken to be parallel and linearly polarized. If the scatterer is absorptive, part of the light will be absorbed within it as heat, another part will be scattered, and the remainder will be transmitted unperturbed along the incident direction. A complete description of the scattered light entails a knowledge of the wavelength, amplitude, phase, and polarization of the radiation emanating in each direction from the scatterer. This also provides the information necessary to calculate the amount of absorption and the light pressure upon the particle.

Scattering is hardly restricted to the optical part of the spectrum, and the scattering laws apply with equal validity to all wavelengths. Interestingly, these depend upon the ratio of a characteristic dimension of the particle to the wavelength rather than explicitly upon the size. Thus, there is a built-in scaling factor. The scattering of radiowaves by artificial earth satellites, the scattering of microwaves by raindrops, and the scattering of light by aerosols are quite similar phenomena because in each case the wavelength is of the same magnitude as that of the scatterer.

The study of electromagnetic scattering is an interdisciplinary activity. The scattering of starlight by interstellar and interplanetary dust is of interest to astrophysicists. Meteorologists are concerned with the whole range of atmospheric optical phenomena mentioned earlier. In addition, the technique of observing the backscatter of microwaves by rain, snow, and hail has given rise to the science of radar meteorology. The radar technique is also utilized to observe meteors and artificial objects in the atmosphere as well as the plasmas created in the wake of these rapidly moving bodies. There are collateral laboratory studies using microwaves.

The transhorizon propagation of radiowaves along the surface of the earth is one of the classical problems of electromagnetic scattering, going back to the early days of radio at the turn of the century. In addition, there is considerable interest in the scattering and consequent attenuation of radiowaves due to density fluctuations in the atmosphere. The variety of scattering shapes encountered in both the microwave and the radiowave work has stimulated a considerable amount of theoretical activity by electrical engineers, mathematicians, and physicists.

Chemists, physicists, biochemists, and various engineers utilize light scattering to study a whole range of materials including gases, pure liquids, solutions of both ordinary molecules and particularly of macromolecules, colloidal suspensions, glasses, and polymers. In some cases X-ray scattering may be used. Also, there is considerable interest in the light scattering effects observed in the neighborhood of the critical point of pure substances or at the critical mixing point of partially miscible solutions.

There are two classes of problems—the direct problem and the inverse problem. The direct problem is to calculate theoretically or to observe experimentally the scattering by a known, well-defined system. The inverse problem is to characterize the system from a knowledge of the scattering, usually obtained by experiment or, in the case of natural phenomena, from observations. A most elusive and difficult example of the inverse problem is the goal of astrophysicists to describe the interstellar particles by analysis of the scattered and transmitted light. A much less ambitious but far from trivial program is to determine the size distribution of a suspension of colloidal spheres of known refractive index by light scattering experiments.

The treatment in this book reflects the bias of the author as a physical chemist. Most of the examples of practical applications and most of the experimental studies deal with light scattering from colloidal and macromolecular systems. However, the theoretical treatment in Chapters 2 to 6 is quite general and applies equally well to all parts of the electromagnetic spectrum. Furthermore, much of the discussion in this part of the book relates directly to topics in microwave and radiowave physics. Indeed, a perusal of the bibliography will show that a considerable body of electrical engineering, applied physics, and meteorology literature has been incorporated into the discussion, and we hope that at least this part of the book will be of some interest to workers in these and related fields.

Only single scattering and elastic scattering are treated. The latter condition means that there is no shift of frequency between the incident and the scattered radiation. This excludes quantum mechanical phenomena such as the Raman effect and fluorescence or Brillouin scattering which arises from the Doppler shifts associated with the motion of the scattering particles.

The restriction to single scattering implies that the scattering particle is unaffected by the presence of neighboring particles. Also, there is an absence of multiple scattering. After the encounter between the incident beam and the particle, the scattered radiation proceeds directly to the observer without any further scattering encounters. In the laboratory, the necessary conditions for single scattering can usually be attained by working with dilute systems and with small volumes. On the other hand, in the atmosphere and in space, multiple scattering can become the predominant effect.

Still a third gap is the absence of any consideration of laboratory procedures. The art of obtaining light scattering data is simple in principle but fraught with difficulties in practice and we have not attempted to treat laboratory technique in this volume.

1.1 Résumé

Chapter 2 is a review of electromagnetic waves and of optics. It introduces some of the physical concepts and quantities upon which the rest of the book will build. The treatment is brief and is hardly intended to substitute for a general introduction to the broader subject. Rather, it serves only to define and to interrelate the main physical quantities and the physical concepts of optics.

Chapters 3 to 6 deal with the theory of scattering by spheres and infinitely long cylinders. We are fortunate in having an exact theory in the sense of classical physics. The only restrictions are that the substance of which the particle is composed be isotropic and that any variations in the refractive index be radially symmetric.

In Chapter 3, after an historical introduction, there is an exposition of Rayleigh's theory of scattering by spheres which are small compared to the wavelength. This is followed by the theory of homogeneous spheres of arbitrary size. Although this is frequently called the Mie theory, it is quite clear that Mie's (1908) paper was preceded by the independent solutions of a number of workers, starting with the very elegant work of Lorenz (1890). Our treatment follows that of Debye (1909a). Chapter 3 continues with a discussion of the Bessel and Legendre functions needed to calculate the various scattering quantities and a very brief review of the point-matching method. This recently developed technique which solves for the boundary conditions at only a finite number of points upon the particle surface can readily be extended to nonspherical particles. Finally, there is an exposition of the theory of light pressure which is intimately connected with light scattering.

The dependence of the numerical values of the scattering functions upon the particle size, the refractive index, and the scattering angle is reviewed in Chapter 4. The first function dealt with is the scattering coefficient from which all of the other quantities are derived. The scattering cross section which is the total intensity scattered in all directions and the scattering efficiency which is the ratio of the scattering cross section to the geometrical cross section of the particle are considered next. When the particles are absorptive, there is a corresponding cross section for absorption and an efficiency for absorption. The cross section for extinction and the efficiency for extinction measure the total effect and each of these is the sum of the respective quantities for scattering and absorption. Finally, there is the intensity scattered at various angles with particular emphasis upon the backscatter. Two approximations are compared numerically with the exact theory. These are the theory of anomalous diffraction and ray optics. The latter interprets scattering as the result of reflection, refraction, and diffraction.

Stratified spheres, which are the subject of Chapter 5, may consist of a series of concentric spherical shells of different media or the radial profile of the refractive index may vary continuously in some arbitrary fashion. These configurations can be solved exactly. In some cases the solutions can be represented analytically in terms of standard functions; otherwise numerical, albeit exact, solutions are obtained. Chapter 6 contains a discussion of circular cylinders at both perpendicular and oblique incidence. Solutions are available, just as for spheres, for any arbitrary radially varying refractive index. In addition, there are solutions for two particular anisotropies—the gyroelectric and the gyromagnetic media.

The application of light scattering to the determination of the size distribution of colloidal particles is reviewed in Chapter 7. There is a digression to consider the preparation of some of the colloids of narrow size distribution which have served as model systems for much of the experimental work as well as a discussion of some of the distribution functions which have been used to characterize the particle sizes. One useful technique for obtaining the particle size distribution is based upon a comparison of the experimental light scattering data with results computed for a large number of size distributions. That distribution for which the calculated and experimental results agree is chosen to characterize the colloid. This technique is successful only when the distribution is not too broad and when the particle size is comparable to the wavelength.

If the refractive index of a particle is sufficiently close to that of the external medium and if the particle is not too large, each volume element behaves as a Rayleigh scatterer. Each of the scattered wavelets, in turn, mutually interfere. The scattering for such a model was calculated precisely by Lord Rayleigh. Although this is frequently termed Rayleigh–Gans scattering, we have proposed that it should more appropriately be called Rayleigh–Debye scattering. This is the subject of Chapter 8. Rayleigh–Debye scattering may be applied to particles of any shape and has been particularly successful in elucidating the configuration of macromolecules in solution. The angular distribution at the forward angles leads directly to a value of the radius of gyration without any prior knowledge of the particle shape. When the particle shape is known, the forward scattering can sometimes be reduced directly to give the particle size distribution without any prior knowledge of the form of the distribution. The Rayleigh–Debye theory is also particularly useful in interpreting the scattering by nonparticulate media. These may be solids for which the scattering arises from a more or less continuous variation of the refractive index. Such internal structure can be described by a correlation function which can, in turn, be deduced directly from the angular distribution of the forward scattered radiation. Small angle X-ray scattering as well as light scattering is commonly utilized for this approach.

Chapter 9 deals with scattering by liquids. These may be considered to scatter light by virtue of the microscopic fluctuations of the density from the macroscopic value. If the density fluctuation has associated with it a fluctuation of the polarizability or the dielectric constant or the refractive index (each of these quantities being manifestations of the same optical property), there will be light scattering. The fluctuation in each volume element is assumed to take place independently of those in the neighboring elements, and since these volumes are also chosen to be small compared to the wavelength, Rayleigh's law for small particles serves to describe the scattering. The problem, which was solved by Einstein (1910), is to calculate the magnitude of the density fluctuations by the methods of statistical thermodynamics. The theory was extended from single component and binary systems to multicomponent systems by Zernike (1915).

This fluctuation theory has been particularly successful in its application to the study of the molecular weight and the thermodynamic interactions in solutions of macromolecules, polyelectrolytes, proteins, and surfactants. In conjunction with the Rayleigh–Debye theory, it has also been possible to obtain information about the configuration of such species. In the region of the critical point, the density fluctuations in neighboring volume elements are no longer independent but the mutual interference can be accounted for with the aid of a correlation function quite the same as that introduced in the treatment of Rayleigh–Debye scattering from inhomogeneous media.

The final chapter is concerned with anisotropy. Lord Rayleigh derived the scattering by ellipsoidal particles which are small compared to the wavelength in a manner similar to his treatment of small spheres. Such anisotropic particles scatter more intensely than spheres of the same volume by a factor known as the Cabannes factor. This can actually be determined from a measurement of the depolarization of the scattered light at a single angle without any prior knowledge of the configuration of the anisotropic particles. This chapter also considers the effect upon the light scattering of partial orientation of anisotropic particles in electrical and magnetic fields and in