Absorption and Scattering of Light by Small Particles
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Chapter 6

Rayleigh–Gans Theory

If a particle has other than a regular geometrical shape then it is difficult, if not essentially impossible, to solve the scattering problem in its most general form. There are, however, frequently encountered situations, particularly in laboratory investigations of scattering, in which the particles are suspended in a medium with similar optical properties. If the particles, which are sometimes referred to as "soft" or "tenuous," are not too large (but they may be larger than in the Rayleigh theory discussed in the preceding chapter), it is possible to obtain relatively simple approximate expressions for the scattering matrix elements. Within the limits of this approximation, these expressions are valid for particles of arbitrary shape.

6.1 AMPLITUDE SCATTERING MATRIX ELEMENTS

If the amplitude scattering matrix elements (5.4) for a homogeneous, isotropic sphere of radius a are divided by the volume v, the resulting quotients approach finite limits as the sphere radius tends to zero:

$$s_1 = \lim_{a\to 0} \frac{S_1}{v} = -\frac{3ik^3}{4\pi}\frac{m^2-1}{m^2+2},$$

$$s_2 = \lim_{a\to 0} \frac{S_2}{v} = -\frac{3ik^3}{4\pi}\frac{m^2-1}{m^2+2}\cos\theta. \tag{6.1}$$

The quantities s_1 and s_2 may be interpreted as the scattering matrix elements per unit particle volume, and it is physically plausible that under certain conditions the matrix elements for an arbitrarily shaped particle may be approximated by a suitable integration of the s_j over the volume of the particle. This assumption is the basis of what is often called the Rayleigh–Gans theory. However, Kerker (1969, p. 414) has argued that Debye, not Gans, should share honors with Rayleigh. Rocard sometimes trails Rayleigh and Gans (Acquista, 1976). And in quantum-mechanical scattering, the analogous approximation is called the *Born approximation* (to be precise, the *first* Born approximation) (Merzbacher, 1970, p. 229); the name of Kirchhoff sometimes appears in tandem with that of Born (Saxon, 1955a). Buried in obscure journals there undoubtedly rest papers the authors of which—or their heirs—could legitimately lay claim to having been first in print. Any day now we can expect scholars to announce that the theory has been found scribbled in the margins of one of Gauss's unpublished manuscripts; or in the notebooks of Leonardo; or implicit in the writings of Aristotle; or painted in brilliant colors on the walls of a French cave by Paleolithic men. Referring to the RGDRKBU approximation—the U is reserved for as yet unknown claimants—seems a bit unwieldly, although it assiduously avoids offense to anyone. Instead, we shall content ourselves with the somewhat more prosaic Rayleigh–Gans theory. What it lacks in historical accuracy it makes up for in brevity; moreover, it is probably the term most familiar to the majority of readers.

The conditions for the validity of the Rayleigh–Gans approximation are

$$|m - 1| \ll 1, \tag{6.2}$$

$$\mathrm{k}d|m - 1| \ll 1, \tag{6.3}$$

where d is a characteristic linear dimension of the particle and m is its complex refractive index relative to that of the surrounding medium. It may be shown rigorously from an integral equation formulation of the scattering problem (Saxon, 1955a) that the Rayleigh–Gans approximation is obtained if the field inside the particle is approximated by the incident field. Therefore, by analogy with the problem of reflection and transmission by a homogeneous slab (Section 2.8), we may interpret condition (6.2) as the requirement that the incident wave is not appreciably "reflected" at the particle–medium interface; condition (6.3) may be interpreted as the requirement that the incident wave not undergo appreciable change of phase or amplitude after it enters the particle. We emphasize, however, that this reasoning is heuristic.

Because of condition (6.2) it is customary (but not necessary) to write the scattering matrix elements (6.1) as

$$s_1 = -\frac{i\mathrm{k}^3}{2\pi}(m - 1), \qquad s_2 = -\frac{i\mathrm{k}^3}{2\pi}(m - 1)\cos\theta, \tag{6.4}$$

where we have used

$$\frac{m^2 - 1}{m^2 + 2} = \frac{(m - 1)(m + 1)}{m^2 + 2} \simeq \frac{2}{3}(m - 1).$$

Consider an arbitrary particle illuminated by a plane wave propagating in the z' direction (Fig. 6.1). The contribution of a volume element Δv located at a point O' to the field scattered by the particle in a direction specified by the unit vector $\hat{\mathbf{e}}_r$ is

$$\begin{pmatrix} \Delta E_{\parallel s} \\ \Delta E_{\perp s} \end{pmatrix} = \frac{e^{i\mathrm{k}(r' - z')}}{-i\mathrm{k}r'}\Delta v \begin{pmatrix} s_2 & 0 \\ 0 & s_1 \end{pmatrix} \begin{pmatrix} E'_{\parallel i} \\ E'_{\perp i} \end{pmatrix}, \tag{6.5}$$

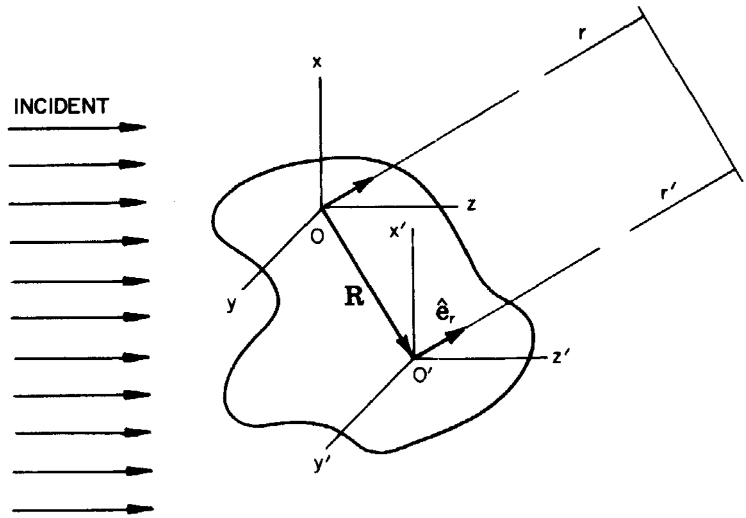

Figure 6.1 Coordinate systems for determining scattering by an arbitrary particle in the Rayleigh–Gans approximation.

where

$$E'_{\parallel i} = E'_{\parallel 0} e^{ikz'}, \qquad E'_{\perp i} = E'_{\perp 0} e^{ikz'}, \tag{6.6}$$

and the amplitudes $E'_{\parallel 0}$ and $E'_{\perp 0}$ are independent of position. A rectangular coordinate system (x', y', z') is centered at O'; let $-Z$ be the z' coordinate of the origin O of a reference coordinate system (x, y, z) the axes of which are parallel to those of the (x', y', z') system. The incident field at O is

$$E_{\parallel 0} = E'_{\parallel i}(-Z) = E'_{\parallel 0} e^{-ikZ},$$

$$E_{\perp 0} = E'_{\perp i}(-Z) = E'_{\perp 0} e^{-ikZ}. \tag{6.7}$$

It follows from (6.6) and (6.7) that $E'_{\parallel i} = E_{\parallel 0} e^{ik(Z+z')}$ and $E'_{\perp i} = E_{\perp 0} e^{ik(Z+z')}$. If we use the relations $r' = r - \mathbf{R} \cdot \hat{\mathbf{e}}_r$, $Z = \mathbf{R} \cdot \hat{\mathbf{e}}_z$, then (6.5) can be written

$$\begin{pmatrix} \Delta E_{\parallel s} \\ \Delta E_{\perp s} \end{pmatrix} = \frac{e^{ik(r-z)}}{-ikr} \Delta v e^{i\delta} \begin{pmatrix} S_2 & 0 \\ 0 & S_1 \end{pmatrix} \begin{pmatrix} E_{\parallel i} \\ E_{\perp i} \end{pmatrix}, \tag{6.8}$$

where $\delta = k\mathbf{R} \cdot (\hat{\mathbf{e}}_z - \hat{\mathbf{e}}_r)$, $E_{\parallel i} = E_{\parallel 0} e^{ikz}$, and $E_{\perp i} = E_{\perp 0} e^{ikz}$. Because the particle is much smaller than the distance to the point of observation, we may approximate the factor $1/kr'$ by $1/kr$. The total field $\mathbf{E}_s$ scattered in the direction $\hat{\mathbf{e}}_r$ is obtained by integrating (6.8) over the particle volume v:

$$\begin{pmatrix} E_{\parallel s} \\ E_{\perp s} \end{pmatrix} = \frac{e^{ik(r-z)}}{-ikr} \begin{pmatrix} S_2 & 0 \\ 0 & S_1 \end{pmatrix} \begin{pmatrix} E_{\parallel i} \\ E_{\perp i} \end{pmatrix},$$

$$S_1 = -\frac{ik^3}{2\pi}(m-1)vf(\theta,\phi),$$

$$S_2 = -\frac{ik^3}{2\pi}(m-1)vf(\theta,\phi)\cos\theta. \tag{6.9}$$

The *form factor* $f(\theta, \phi)$ is

$$f(\theta,\phi) = \frac{1}{v}\int_v e^{i\delta}\,dv. \tag{6.10}$$

Implicit in the derivation of (6.9) is the assumption that the particle is homogeneous. This is not necessary, however; the particle may be composed of several distinct regions. The generalization of (6.9) to a heterogeneous particle is straightforward:

$$S_1 = -\frac{ik^3}{2\pi}\sum_j (m_j - 1)v_j f_j(\theta,\phi),$$

$$S_2 = -\frac{ik^3}{2\pi}\sum_j (m_j - 1)v_j f_j(\theta,\phi)\cos\theta,$$

where m_j is the relative refractive index of the jth region in the particle, v_j is its volume, and the associated form factor is

$$f_j = \frac{1}{v_j}\int_{v_j} e^{i\delta}\,dv.$$

In the forward direction ($\theta = 0°$) $\hat{\mathbf{e}}_r = \hat{\mathbf{e}}_z$ and, therefore, $f(0°) = 1$ for all particles; this, in turn, implies that $S_1(0°) = S_2(0°)$. Because our point of departure was the Rayleigh theory for an infinitesimal sphere, the Rayleigh–Gans theory shares some of its features. For example, the form of the 4×4 scattering matrix corresponding to (6.9) is the same as that for a Rayleigh sphere (5.5); the dependence of the individual scattering matrix elements on the scattering direction is, however, different in general.

The optical theorem yields the absorption cross section

$$C_{\text{abs}} = 2kv\,\text{Im}\{m\} \tag{6.11}$$

independent of the polarization of the incident light and the orientation of the particle. Equation (6.11) can be written in a more interesting form

$$C_{\text{abs}} = \alpha v,$$

where $\alpha = 4\pi k_1/\lambda$ is the absorption coefficient and k_1 is the imaginary part of the refractive index of the particle. The irradiance transmitted by a homogeneous slab of thickness h and absorption coefficient α is

$$I_t = I_i e^{-\alpha h},$$

where we have assumed that the reflectance is small (see Section 2.8). Therefore, the amount of energy W_{abs} absorbed by the slab is

$$W_{\text{abs}} = I_i(1 - e^{-\alpha h})A,$$

where A is the cross-sectional area. If we assume that $\alpha h \ll 1$, then

$$\frac{W_{\text{abs}}}{I_i} = \alpha V,$$

where V is the volume of the slab. Therefore, under conditions similar to (6.2) and (6.3), the absorption cross section W_{abs}/I_i of a slab has the same form as that of a tenuous particle. This strengthens the heuristic arguments at the beginning of this chapter which were made to give a physical basis to the conditions (6.2) and (6.3).

The scattering cross section, unlike the absorption cross section, depends on the state of polarization of the incident light unless S_1 and S_2 are independent of the azimuthal angle ϕ, which will be true for spherically symmetrical particles. Regardless of the shape of the particle, however, the degree of polarization of the scattered light is the same as that for a Rayleigh sphere; this follows from the fact that f merely multiplies the Rayleigh amplitude scattering matrix elements. The major difference between the Rayleigh and Rayleigh–Gans theories is the angular distribution of the scattered light.

6.2 HOMOGENEOUS SPHERE

The form factor for a particle of arbitrary shape can be calculated by numerical integration of (6.10). However, for certain regular geometrical shapes, it is possible to obtain analytical expressions for f. In this section we consider one such particle, a homogeneous sphere.

The vector $\hat{\mathbf{e}}_z - \hat{\mathbf{e}}_r$ is normal to planes $\mathbf{R} \cdot (\hat{\mathbf{e}}_z - \hat{\mathbf{e}}_r) = \text{constant}$, over which the phase δ is constant; we can write the phase as

$$\delta = 2k \sin\frac{\theta}{2} R \cos(\mathbf{R}, \hat{\mathbf{e}}_z - \hat{\mathbf{e}}_r) = 2k\xi \sin\frac{\theta}{2},$$

where $|\xi| = |R\cos(\mathbf{R}, \hat{\mathbf{e}}_z - \hat{\mathbf{e}}_r)|$ is the distance from the origin to a plane of constant phase. Thus, the form factor can be expressed as an integral over the variable ξ:

$$f = \frac{1}{v}\int \exp\left(i2k\xi\sin\frac{\theta}{2}\right)A(\xi)\,d\xi, \tag{6.12}$$

where $A(\xi)$ is the area of that portion of the plane $R\cos(\mathbf{R}, \hat{\mathbf{e}}_z - \hat{\mathbf{e}}_r) = \xi$ which lies within the boundaries of the particle. In general, the limits on ξ and the functional form of $A(\xi)$ depend on the direction $\hat{\mathbf{e}}_r$ of the scattered wave. However, for a sphere we have $A(\xi) = \pi(a^2 - \xi^2)$, $-a \le \xi \le a$, for all scattering directions, and it is not difficult to integrate (6.12):

$$f(\theta) = \frac{3}{u^3}(\sin u - u\cos u), \qquad u = 2x\sin\frac{\theta}{2}.$$

Note that f vanishes at those values of θ for which

$$\tan u - u = 0. \tag{6.13}$$

The zeros u_n of (6.13) are to good approximation given by

$$u_n^2 = \left(n + \tfrac{1}{2}\right)^2\pi^2 - 2, \qquad n = 1, 2, \ldots$$

from which, together with the inequalities $0 \le u \le 2x$, $u_1 < u_2 < u_3 \cdots$, it follows that f does not vanish for any angle θ unless $x > 2.25$.

6.3 FINITE CYLINDER

In Chapter 8 we shall derive the field scattered by an infinite cylinder of arbitrary radius and refractive index; we shall also consider scattering by a finite cylinder in the diffraction theory approximation. Although the finite cylinder scattering problem is not exactly soluble, we can obtain analytical expressions for the amplitude scattering matrix elements in the Rayleigh–Gans approximation.

Consider a cylinder of radius a and length $2L$, subject to the conditions (6.2) and (6.3), which is illuminated by a beam making an angle ζ with its axis (Fig. 6.2). The directions of the incident and scattered waves are specified by the unit vectors $\hat{\mathbf{e}}_i$ and $\hat{\mathbf{e}}_r$, respectively, where $\hat{\mathbf{e}}_i = \sin\zeta\hat{\mathbf{e}}_z - \cos\zeta\,\hat{\mathbf{e}}_x$, $\hat{\mathbf{e}}_r = \sin\theta\cos\phi\hat{\mathbf{e}}_x + \sin\theta\sin\phi\hat{\mathbf{e}}_y + \cos\theta\hat{\mathbf{e}}_z$; the position vector $\mathbf{R}$ of a point in the particle with cylindrical polar coordinates (ρ, ψ, x) is $x\hat{\mathbf{e}}_x + \rho\cos\psi\hat{\mathbf{e}}_y + \rho\sin\psi\hat{\mathbf{e}}_z$. Therefore, the form factor (6.10) is

$$f = \frac{1}{\pi a^2 2L}\int_{-L}^{L} e^{-ikAx}\,dx\int_0^a \rho\,d\rho\int_0^{2\pi} e^{-ik\rho(B\cos\psi + C\sin\psi)}\,d\psi,$$

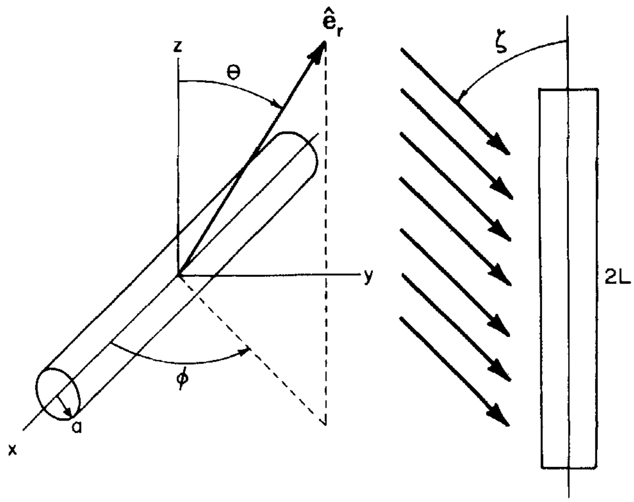

Figure 6.2 A finite cylinder illuminated obliquely.

where $A = \cos\zeta + \sin\theta\cos\phi$, $B = \sin\theta\sin\phi$, and $C = \cos\theta - \sin\zeta$. The integral over x is trivial:

$$\int_{-L}^{L} e^{-ikAx}dx = \frac{2\sin(kAL)}{kA}.$$

If we write $B = M\cos\mu$, $C = M\sin\mu$, where $M = \sqrt{B^2 + C^2}$ and $\tan\mu = C/B$, then the integral over ψ is

$$\int_0^{2\pi} e^{-ik\rho M\cos(\psi-\mu)}\,d\psi = \int_0^{2\pi} e^{-ik\rho M\cos\psi}\,d\psi. \tag{6.14}$$

It follows from the integral representation of the Bessel function $J_0(z)$,

$$J_0(z) = \frac{1}{2\pi}\int_0^{2\pi} e^{-iz\cos\psi}\,d\psi,$$

where z is real, that the integral (6.14) is $2\pi J_0(k\rho M)$. The last integral,

$$\int_0^a \rho J_0(k\rho M)\,d\rho,$$

can be evaluated if we recall that $d(zJ_1)/dz = zJ_0$. Therefore, the form factor for a given angle of incidence ζ is

$$f(\theta,\phi;\zeta) = \frac{2\sin(x\mathcal{L}A)}{x\mathcal{L}A}\,\frac{J_1(xM)}{xM}, \tag{6.15}$$

where $x = \mathrm{k}a$, and $\mathcal{L} = L/a$ is the ratio of cylinder length to diameter. If the incident light is normal to the cylinder axis ($\zeta = \pi/2$), then for scattering directions in a plane normal to the axis ($\phi = \pi/2$ or $3\pi/2$), (6.15) reduces to

$$f(\theta) = \frac{2J_1(u)}{u}, \qquad u = 2x\sin\frac{\theta}{2}.$$

NOTES AND COMMENTS

Chapter 8 of Kerker (1969) is a more thorough treatment of Rayleigh-Gans (RG) theory that we have given here. There is a good concise derivation of this theory in the appendix of a paper by Wyatt (1968).

Turner (1973) and McKellar (1976) applied RG theory to ensembles of randomly oriented particles of arbitrary shape; the former author included spheres with anisotropic optical constants. Optically active particles have been treated within the framework of the RG approximation by Bohren (1977).

Beginning with an integral equation, Acquista (1976) obtained an iterative solution to the problem of scattering by an arbitrary particle. The first iteration is just the RG expression. Agreement between approximate and exact theories of scattering by a sphere is considerably improved by a second iteration.