Absorption and Scattering of Light by Small Particles
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Chapter 3

Absorption and Scattering by an Arbitrary Particle

When a particle is illuminated by a beam of light with specified characteristics, the amount and angular distribution of the light scattered by the particle, as well as the amount absorbed, depends in a detailed way on the nature of the particle, that is, its shape, size, and the materials of which it is composed. This presents us with an almost unlimited number of distinct possibilities. Nevertheless, there are some features common to the phenomena of scattering and absorption by small particles. In this chapter, therefore, our goal is to say as much as possible about such phenomena without invoking any specific particle. This will establish the mathematical and physical framework underlying all the specific problems encountered in later chapters.

3.1 GENERAL FORMULATION OF THE PROBLEM

Our fundamental problem is as follows: Given a particle of specified size, shape and optical properties that is illuminated by an arbitrarily polarized monochromatic wave, determine the electromagnetic field at all points in the particle and at all points of the homogeneous medium in which the particle is embedded. Although we limit our consideration to plane harmonic waves, this is less of a restriction than it might seem at first glance: in Section 2.4 we showed that an arbitrary field can be decomposed into its Fourier components, which are plane waves. Therefore, regardless of the illumination we can obtain the solution to the scattering–absorption problem by superposition.

The field inside the particle is denoted by $(\mathbf{E}_1, \mathbf{H}_1)$; the field $(\mathbf{E}_2, \mathbf{H}_2)$ in the medium surrounding the particle is the superposition of the incident field $(\mathbf{E}_i, \mathbf{H}_i)$ and the scattered field $(\mathbf{E}_s, \mathbf{H}_s)$ (Fig. 3.1):

$$\mathbf{E}_2 = \mathbf{E}_i + \mathbf{E}_s, \qquad \mathbf{H}_2 = \mathbf{H}_i + \mathbf{H}_s,$$

where

$$\mathbf{E}_i = \mathbf{E}_0 \exp(i\mathbf{k}\cdot\mathbf{x} - i\omega t), \qquad \mathbf{H}_i = \mathbf{H}_0 \exp(i\mathbf{k}\cdot\mathbf{x} - i\omega t),$$

and $\mathbf{k}$ is the wave vector appropriate to the surrounding medium. The fields

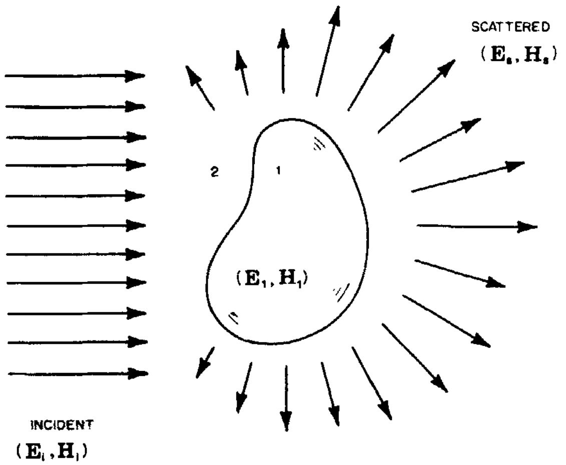

Figure 3.1 The incident field ($\mathbf{E}_i, \mathbf{H}_i$) gives rise to a field ($\mathbf{E}_1, \mathbf{H}_1$) inside the particle and a scattered field ($\mathbf{E}_s, \mathbf{H}_s$) in the medium surrounding the particle.

must satisfy the Maxwell equations

$$\nabla \cdot \mathbf{E} = 0, \tag{3.1}$$

$$\nabla \cdot \mathbf{H} = 0, \tag{3.2}$$

$$\nabla \times \mathbf{E} = i\omega\mu\mathbf{H}, \tag{3.3}$$

$$\nabla \times \mathbf{H} = -i\omega\varepsilon\mathbf{E}, \tag{3.4}$$

at all points where ε and μ are continuous. The curl of (3.3) and (3.4) is

$$\nabla \times (\nabla \times \mathbf{E}) = i\omega\mu\nabla \times \mathbf{H} = \omega^2\varepsilon\mu\mathbf{E},$$

$$\nabla \times (\nabla \times \mathbf{H}) = -i\omega\varepsilon\nabla \times \mathbf{E} = \omega^2\varepsilon\mu\mathbf{H},$$

and if we use the vector identity

$$\nabla \times (\nabla \times \mathbf{A}) = \nabla(\nabla \cdot \mathbf{A}) - \nabla \cdot (\nabla\mathbf{A}) \tag{3.5}$$

we obtain

$$\nabla^2\mathbf{E} + \mathrm{k}^2\mathbf{E} = 0, \qquad \nabla^2\mathbf{H} + \mathrm{k}^2\mathbf{H} = 0, \tag{3.6}$$

where $\mathrm{k}^2 = \omega^2\varepsilon\mu$ and $\nabla^2\mathbf{A} = \nabla \cdot (\nabla\mathbf{A})$. Thus, **E** and **H** satisfy the *vector wave equation*. Any vector field with zero divergence that satisfies the vector wave equation is an admissible electric field; the associated magnetic field is related to the curl of the electric field through (3.3). Caution: The symbol ∇^2 in (3.6) should be looked upon as shorthand notation for the *vector* operator $\nabla \cdot \nabla$; that is, $\nabla \mathbf{A}$ is a dyadic which when operated on by the divergence operator $\nabla \cdot$ yields a vector. Alternatively, we can consider (3.5) to define $\nabla^2 \mathbf{A}$. It is *not* true that the components of $\mathbf{E}$ separately satisfy the *scalar wave equation*

$$\nabla^2 \psi + k^2 \psi = 0,$$

as a superficial glance at (3.6) might lead one to believe, except in the special case where $\mathbf{E}$ is specified relative to a rectangular Cartesian coordinate system.

3.1.1 Boundary Conditions

The electromagnetic field is required to satisfy the Maxwell equations at points where ε and μ are continuous. However, as one crosses the boundary between particle and medium, there is, in general, a sudden change in these properties. This change occurs over a transition region with thickness of the order of atomic dimensions. From a macroscopic point of view, therefore, there is a discontinuity at the boundary. At such boundary points we impose the following conditions on the fields:

$$\left.\begin{aligned} [\mathbf{E}_2(\mathbf{x}) - \mathbf{E}_1(\mathbf{x})] \times \hat{\mathbf{n}} = 0, \\ [\mathbf{H}_2(\mathbf{x}) - \mathbf{H}_1(\mathbf{x})] \times \hat{\mathbf{n}} = 0, \end{aligned}\right. \qquad \mathbf{x} \text{ on } S, \tag{3.7}$$

where $\hat{\mathbf{n}}$ is the outward directed normal to the surface S of the particle. The boundary conditions (3.7) are the requirement that the *tangential components* of $\mathbf{E}$ and $\mathbf{H}$ are continuous across a boundary separating media with different properties.

At this point we depart from the traditional derivation of (3.7)—what might be called the "pharmaceutical approach" of constructing pillboxes and loops that straddle the boundary and taking various limits—and give a physical justification of these boundary conditions by appealing to conservation of energy. Consider a closed surface A, with outward normal $\hat{\mathbf{n}}$, which is the boundary between regions 1 and 2 (Fig. 3.2). There are no restrictions on the properties of these regions. The rate at which electromagnetic energy is transferred across a closed surface arbitrarily near A in region 1 (shown by the dashed line in Fig. 3.2) is

$$\int_A \mathbf{S}_1 \cdot \hat{\mathbf{n}} \, dA = \int_A \hat{\mathbf{n}} \cdot (\mathbf{E}_1 \times \mathbf{H}_1) \, dA, \tag{3.8}$$

where the electromagnetic field $(\mathbf{E}_1, \mathbf{H}_1)$ is not restricted to be time harmonic. Similarly, the rate of electromagnetic energy transfer across a closed surface arbitrarily near A in region 2 (shown by the dotted line in Fig. 3.2) is

$$\int_A \mathbf{S}_2 \cdot \hat{\mathbf{n}} \, dA = \int_A \hat{\mathbf{n}} \cdot (\mathbf{E}_2 \times \mathbf{H}_2) \, dA. \tag{3.9}$$

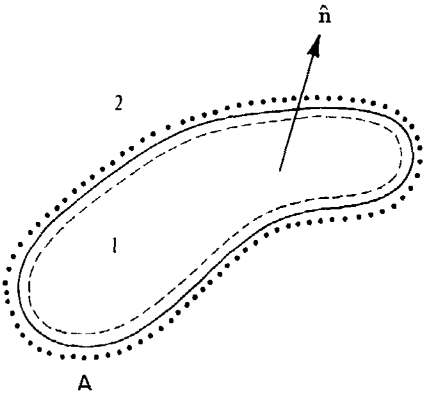

Figure 3.2 Closed surface separating regions 1 and 2.

If the boundary conditions (3.7) are imposed, then $\mathbf{E}_2 \times \hat{\mathbf{n}} = \mathbf{E}_1 \times \hat{\mathbf{n}}$, $\mathbf{H}_2 \times \hat{\mathbf{n}} = \mathbf{H}_1 \times \hat{\mathbf{n}}$, and the integrals (3.8) and (3.9) may be written

$$\int_A \mathbf{S}_1 \cdot \hat{\mathbf{n}}\, dA = \int_A \mathbf{H}_1 \cdot (\hat{\mathbf{n}} \times \mathbf{E}_1)\, dA = \int_A \mathbf{H}_1 \cdot (\hat{\mathbf{n}} \times \mathbf{E}_2)\, dA,$$

$$\int_A \mathbf{S}_2 \cdot \hat{\mathbf{n}}\, dA = \int_A \mathbf{E}_2 \cdot (\mathbf{H}_2 \times \hat{\mathbf{n}})\, dA = \int_A \mathbf{H}_1 \cdot (\hat{\mathbf{n}} \times \mathbf{E}_2)\, dA,$$

where we have used the permutation rule for the triple scalar product: $\mathbf{A} \cdot (\mathbf{B} \times \mathbf{C}) = \mathbf{B} \cdot (\mathbf{C} \times \mathbf{A}) = \mathbf{C} \cdot (\mathbf{A} \times \mathbf{B})$. Therefore, there are no sources or sinks of electromagnetic energy on A:

$$\int_A \mathbf{S}_1 \cdot \hat{\mathbf{n}}\, dA = \int_A \mathbf{S}_2 \cdot \hat{\mathbf{n}}\, dA.$$

Thus, the requirement that the tangential components of the electromagnetic field are continuous across a boundary of discontinuity is a *sufficient* condition for energy conservation across that boundary.

3.1.2 Superposition

Our fundamental task is to construct solutions to the Maxwell equations (3.1)–(3.4), both inside and outside the particle, which satisfy (3.7) at the boundary between particle and surrounding medium. If the incident electromagnetic field is arbitrary, subject to the restriction that it can be Fourier analyzed into a superposition of plane monochromatic waves (Section 2.4), the solution to the problem of interaction of such a field with a particle can be obtained in principle by superposing fundamental solutions. That this is possible is a consequence of the *linearity* of the Maxwell equations *and* the boundary conditions. That is, if $\mathbf{E}_a$ and $\mathbf{E}_b$ are solutions to the field equations, their sum $\mathbf{E}_a + \mathbf{E}_b$ is also a solution; and if

$$(\mathbf{E}_{a2} - \mathbf{E}_{a1}) \times \hat{\mathbf{n}} = 0, \qquad (\mathbf{E}_{b2} - \mathbf{E}_{b1}) \times \hat{\mathbf{n}} = 0,$$

then

$$(\mathbf{E}_2 - \mathbf{E}_1) \times \hat{\mathbf{n}} = 0,$$

where $\mathbf{E}_2 = \mathbf{E}_{a2} + \mathbf{E}_{b2}$ and $\mathbf{E}_1 = \mathbf{E}_{a1} + \mathbf{E}_{b1}$. This, therefore, is our justification for considering only scattering of plane monochromatic waves. An arbitrarily polarized wave can be expressed as the superposition of two orthogonal polarization states (Section 2.11). Therefore, we need only solve each scattering problem twice (for a given direction of propagation) in order to determine the scattering of an arbitrarily polarized plane wave.

3.2 THE AMPLITUDE SCATTERING MATRIX

Consider an arbitrary particle that is illuminated by a plane harmonic wave (Fig. 3.3). The direction of propagation of the incident light defines the z axis, the *forward direction*. Any point in the particle may be chosen as the origin O of a rectangular Cartesian coordinate system (x, y, z), where the x and y axes are orthogonal to the z axis and to each other but are otherwise arbitrary. The orthonormal basis vectors $\hat{\mathbf{e}}_x, \hat{\mathbf{e}}_y, \hat{\mathbf{e}}_z$ are in the directions of the positive x, y, and z axes. The scattering direction $\hat{\mathbf{e}}_r$ and the forward direction $\hat{\mathbf{e}}_z$ define a plane called the *scattering plane*, which is analogous to the plane of incidence in problems of reflection at an interface (Section 2.7). The scattering plane is uniquely determined by the azimuthal angle ϕ except when $\hat{\mathbf{e}}_r$ is parallel to the z axis. In these two instances $(\hat{\mathbf{e}}_r = \pm \hat{\mathbf{e}}_z)$ any plane containing the z axis is a suitable scattering plane. It is convenient to resolve the incident electric field $\mathbf{E}_i$, which lies in the xy plane, into components parallel $(E_{\parallel i})$ and perpendicular $(E_{\perp i})$ to the scattering plane:

$$\mathbf{E}_i = \left(E_{0\parallel}\hat{\mathbf{e}}_{\parallel i} + E_{0\perp}\hat{\mathbf{e}}_{\perp i}\right)\exp(ikz - i\omega t) = E_{\parallel i}\hat{\mathbf{e}}_{\parallel i} + E_{\perp i}\hat{\mathbf{e}}_{\perp i},$$

where $k = 2\pi N_2/\lambda$ is the wave number in the medium surrounding the particle, N_2 is the refractive index, and λ is the wavelength of the incident light *in vacuo*. The orthonormal basis vectors $\hat{\mathbf{e}}_{\parallel i}$ and $\hat{\mathbf{e}}_{\perp i}$, where

$$\hat{\mathbf{e}}_{\perp i} = \sin\phi\hat{\mathbf{e}}_x - \cos\phi\hat{\mathbf{e}}_y, \qquad \hat{\mathbf{e}}_{\parallel i} = \cos\phi\hat{\mathbf{e}}_x + \sin\phi\hat{\mathbf{e}}_y,$$

form a right-handed triad with $\hat{\mathbf{e}}_z$:

$$\hat{\mathbf{e}}_{\perp i} \times \hat{\mathbf{e}}_{\parallel i} = \hat{\mathbf{e}}_z.$$

We also have

$$\hat{\mathbf{e}}_{\perp i} = -\hat{\mathbf{e}}_\phi, \qquad \hat{\mathbf{e}}_{\parallel i} = \sin\theta\hat{\mathbf{e}}_r + \cos\theta\hat{\mathbf{e}}_\theta,$$

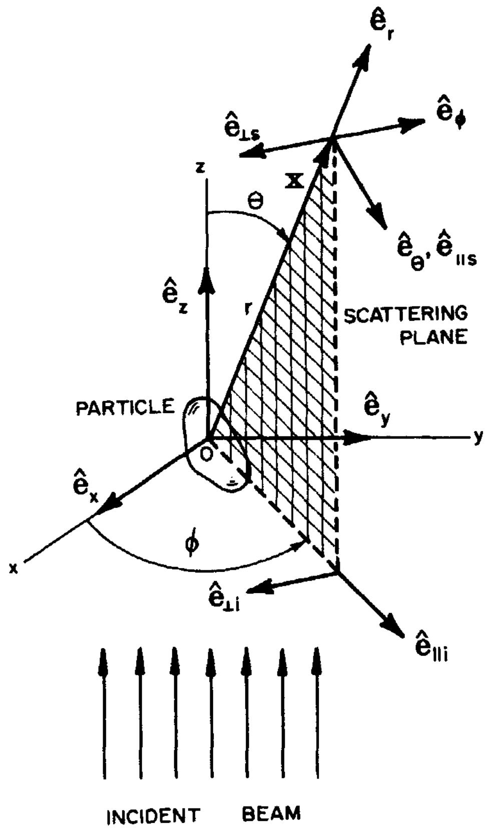

Figure 3.3 Scattering by an arbitrary particle.

where $\hat{\mathbf{e}}_r$, $\hat{\mathbf{e}}_\theta$, $\hat{\mathbf{e}}_\phi$ are the orthonormal basis vectors associated with the spherical polar coordinate system (r, θ, ϕ). If the x and y components of the incident field are denoted by E_{xi} and E_{yi}, then

$$E_{\|i} = \cos\phi E_{xi} + \sin\phi E_{yi},$$

$$E_{\perp i} = \sin\phi E_{xi} - \cos\phi E_{yi}.$$

At sufficiently large distances from the origin ($kr \gg 1$), in the *far-field region*, the scattered electric field $\mathbf{E}_s$ is approximately *transverse* ($\hat{\mathbf{e}}_r \cdot \mathbf{E}_s \simeq 0$) and has the asymptotic form (see, e.g., Jackson, 1975, p. 748)

$$\mathbf{E}_s \sim \frac{e^{ikr}}{-ikr}\mathbf{A} \qquad kr \gg 1, \tag{3.10}$$

where $\hat{\mathbf{e}}_r \cdot \mathbf{A} = 0$. Therefore, the scattered field in the far-field region may be written

$$\mathbf{E}_s = E_{\|s}\hat{\mathbf{e}}_{\|s} + E_{\perp s}\hat{\mathbf{e}}_{\perp s},$$

$$\hat{\mathbf{e}}_{\|s} = \hat{\mathbf{e}}_\theta, \qquad \hat{\mathbf{e}}_{\perp s} = -\hat{\mathbf{e}}_\phi, \qquad \hat{\mathbf{e}}_{\perp s} \times \hat{\mathbf{e}}_{\|s} = \hat{\mathbf{e}}_r. \tag{3.11}$$

The basis vector $\hat{\mathbf{e}}_{\|s}$ is parallel and $\hat{\mathbf{e}}_{\perp s}$ is perpendicular to the scattering plane. Note, however, that $\mathbf{E}_s$ and $\mathbf{E}_i$ are specified relative to *different* sets of basis vectors. Because of the linearity of the boundary conditions (3.7) the amplitude of the field scattered by an arbitrary particle is a linear function of the amplitude of the incident field. The relation between incident and scattered fields is conveniently written in matrix form

$$\begin{pmatrix} E_{\|s} \\ E_{\perp s} \end{pmatrix} = \frac{e^{ik(r-z)}}{-ikr} \begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix} \begin{pmatrix} E_{\|i} \\ E_{\perp i} \end{pmatrix}, \tag{3.12}$$

where the elements $S_j (j = 1, 2, 3, 4)$ of the *amplitude scattering matrix* depend, in general, on θ, the *scattering angle*, and the azimuthal angle ϕ.

Rarely are the real and imaginary parts of the four amplitude scattering matrix elements measured for all values of θ and ϕ. To do so requires measuring the amplitude *and* phase of the light scattered in all directions for two incident orthogonal polarization states, a measurement impeded by the elusiveness of the latter quantity. Hart and Gray (1964) have described a procedure by which phases might be measured from the interference between light scattered by the particle of interest and a nearby particle with known scattering properties. But few such experiments have been performed, a notable exception being the microwave experiments of Greenberg et al. (1961). However, the amplitude scattering matrix elements are related to quantities the measurement of which poses considerably fewer experimental problems than phases; this will be explored in the following two sections.

3.3 SCATTERING MATRIX

Once we have obtained the electromagnetic fields inside and scattered by the particle, we can determine the Poynting vector at any point. However, we are usually interested only in the Poynting vector at points outside the particle. The time-averaged Poynting vector $\mathbf{S}$ at any point in the medium surrounding the particle can be written as the sum of three terms:

$$\mathbf{S} = \tfrac{1}{2}\,\mathrm{Re}\{\mathbf{E}_2 \times \mathbf{H}_2^*\} = \mathbf{S}_i + \mathbf{S}_s + \mathbf{S}_{\mathrm{ext}},$$

$$\mathbf{S}_i = \tfrac{1}{2}\,\mathrm{Re}\{\mathbf{E}_i \times \mathbf{H}_i^*\}, \qquad \mathbf{S}_s = \tfrac{1}{2}\,\mathrm{Re}\{\mathbf{E}_s \times \mathbf{H}_s^*\}, \tag{3.13}$$

$$\mathbf{S}_{\mathrm{ext}} = \tfrac{1}{2}\,\mathrm{Re}\{\mathbf{E}_i \times \mathbf{H}_s^* + \mathbf{E}_s \times \mathbf{H}_i^*\}.$$

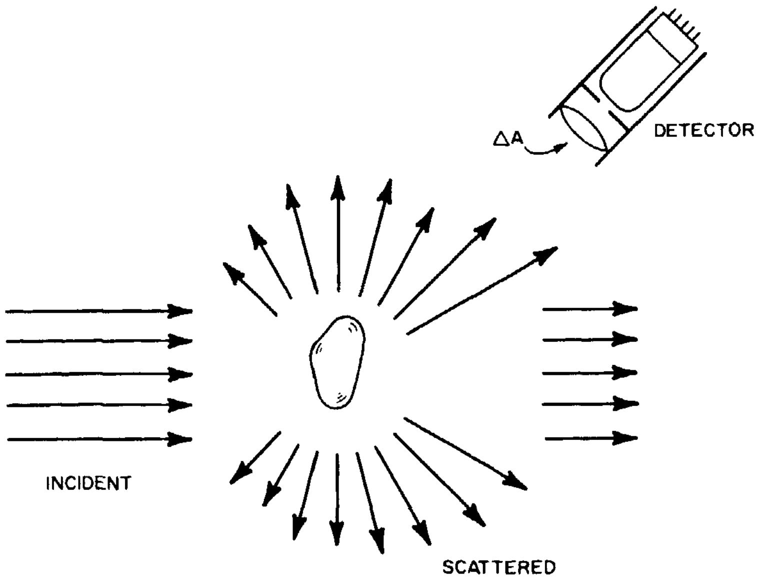

Figure 3.4 The collimated detector responds only to the scattered light.

$\mathbf{S}_i$, the Poynting vector associated with the incident wave, is independent of position if the medium is nonabsorbing; $\mathbf{S}_s$ is the Poynting vector of the scattered field; and we may interpret $\mathbf{S}_{ext}$ as the term that arises because of interaction between the incident and scattered waves.

Suppose that a detector is placed at a distance r from a particle in the far-field region, with its surface ΔA aligned normal to $\hat{\mathbf{e}}_r$ (Fig. 3.4). If the detector is suitably collimated, and if $\hat{\mathbf{e}}_r$ is not too near the forward direction $\hat{\mathbf{e}}_z$, the detector will record a signal proportional to $\mathbf{S}_s \cdot \hat{\mathbf{e}}_r \Delta A$ (ΔA is sufficiently small so that $\mathbf{S}_s$ does not vary greatly over the detector). The detector "sees" only the scattered light provided that it does not "look at" the source of incident light. From (3.10) and (3.13) it follows that

$$\mathbf{S}_s \cdot \hat{\mathbf{e}}_r \Delta A = \frac{k}{2\omega\mu} \frac{|\mathbf{A}|^2}{k^2} \Delta\Omega, \tag{3.14}$$

where $\Delta\Omega = \Delta A / r^2$ is the solid angle subtended by the detector. Thus, we can obtain $|\mathbf{A}|^2$ as a function of direction, to within a solid angle $\Delta\Omega$, by recording the detector response at various positions on a hemisphere surrounding the particle.

By interposing various polarizers between particle and detector and recording the resulting irradiances in a manner identical to that discussed for a plane wave in Section 2.11, we obtain the Stokes parameters of the light scattered by a particle:

$$
\begin{aligned}
I_s &= \langle E_{\parallel s} E_{\parallel s}^* + E_{\perp s} E_{\perp s}^* \rangle, \\
Q_s &= \langle E_{\parallel s} E_{\parallel s}^* - E_{\perp s} E_{\perp s}^* \rangle, \\
U_s &= \langle E_{\parallel s} E_{\perp s}^* + E_{\perp s} E_{\parallel s}^* \rangle, \\
V_s &= i \langle E_{\parallel s} E_{\perp s}^* - E_{\perp s} E_{\parallel s}^* \rangle.
\end{aligned}
\tag{3.15}
$$

We again omit the multiplicative factor $k/2\omega\mu$. The relation between incident and scattered Stokes parameters follows from the amplitude scattering matrix (3.12):

$$
\begin{pmatrix} I_s \\ Q_s \\ U_s \\ V_s \end{pmatrix} = \frac{1}{k^2 r^2} \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{pmatrix} \begin{pmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{pmatrix}
\tag{3.16}
$$

$$
\begin{aligned}
S_{11} &= \tfrac{1}{2}\left(|S_1|^2 + |S_2|^2 + |S_3|^2 + |S_4|^2\right), \\
S_{12} &= \tfrac{1}{2}\left(|S_2|^2 - |S_1|^2 + |S_4|^2 - |S_3|^2\right), \\
S_{13} &= \operatorname{Re}\{S_2 S_3^* + S_1 S_4^*\}, \\
S_{14} &= \operatorname{Im}\{S_2 S_3^* - S_1 S_4^*\}, \\
S_{21} &= \tfrac{1}{2}\left(|S_2|^2 - |S_1|^2 - |S_4|^2 + |S_3|^2\right), \\
S_{22} &= \tfrac{1}{2}\left(|S_2|^2 + |S_1|^2 - |S_4|^2 - |S_3|^2\right), \\
S_{23} &= \operatorname{Re}\{S_2 S_3^* - S_1 S_4^*\}, \\
S_{24} &= \operatorname{Im}\{S_2 S_3^* + S_1 S_4^*\}, \\
S_{31} &= \operatorname{Re}\{S_2 S_4^* + S_1 S_3^*\}, \\
S_{32} &= \operatorname{Re}\{S_2 S_4^* - S_1 S_3^*\}, \\
S_{33} &= \operatorname{Re}\{S_1 S_2^* + S_3 S_4^*\}, \\
S_{34} &= \operatorname{Im}\{S_2 S_1^* + S_4 S_3^*\}, \\
S_{41} &= \operatorname{Im}\{S_2^* S_4 + S_3^* S_1\}, \\
S_{42} &= \operatorname{Im}\{S_2^* S_4 - S_3^* S_1\}, \\
S_{43} &= \operatorname{Im}\{S_1 S_2^* - S_3 S_4^*\}, \\
S_{44} &= \operatorname{Re}\{S_1 S_2^* - S_3 S_4^*\}.
\end{aligned}
$$

The 4×4 matrix in (3.16), the *scattering matrix*, is the Mueller matrix for scattering by a single particle; the term *phase matrix* is also used, a particularly inappropriate choice of terminology because the "phase" matrix relates scattered to incident irradiances. The 16 scattering matrix elements for a single particle are not all independent; only seven of them can be independent, corresponding to the four moduli $|S_j|$ $(j = 1, 2, 3, 4)$ and the three differences in phase between the S_j. Thus, there must be nine independent relations among the S_{ij}; these are given by Abhyankar and Fymat (1969).

The Stokes parameters of the light scattered by a collection of randomly separated particles are the sum of the Stokes parameters of the light scattered by the individual particles. Therefore, the scattering matrix for such a collection is merely the sum of the individual particle scattering matrices (we assume that the linear dimensions of the volume occupied by the scatterers is small compared with the distance r at which the scattered light is observed). In general, there are 16 nonzero, independent matrix elements, although this number may be reduced because of symmetry. We shall return to this matter of symmetry in later chapters when we consider specific scattering matrices and experimental means for their measurement. For the moment, we consider the most general scattering matrix. The S_{ij} must be independent of ϕ for any particle or collection of particles that is invariant with respect to arbitrary rotation about the z axis.

If unpolarized light of irradiance I_i is incident on one or more particles, the Stokes parameters of the scattered light are

$$\frac{I_s}{I_i} = S_{11}, \qquad \frac{Q_s}{I_i} = S_{21}, \qquad \frac{U_s}{I_i} = S_{31}, \qquad \frac{V_s}{I_i} = S_{41};$$

for convenience we omit the factor $(kr)^{-2}$. Therefore, S_{11} specifies the angular distribution of the scattered light given unpolarized incident light. This scattered light is, in general, partially polarized with degree of polarization

$$\sqrt{\left(S_{21}^2 + S_{31}^2 + S_{41}^2\right)/S_{11}^2}\,.$$

This clearly demonstrates a very general aspect of scattering by particles regardless of their nature: scattering is a mechanism for polarizing light. S_{ij} depends on the scattering direction and, therefore, so does the degree of polarization.

If the incident light is right-circularly polarized, then the irradiance I_R of the scattered light is $S_{11} + S_{14}$ (this notation should not mislead the reader that the scattered light is also right-circularly polarized: it is not, in general). Similarly, the irradiance I_L of the scattered light, given incident left-circularly polarized light, is $S_{11} - S_{14}$. Therefore, S_{14} is readily interpretable in terms of the difference of the irradiances of scattered light for incident right-circularly and left-circularly polarized light:

$$S_{14} = \frac{1}{2}\frac{I_R - I_L}{I_i}.$$

At this point, it is well to remind ourselves that as the scattering direction varies, so does the scattering plane and, as a consequence, the Stokes parameters Q_i and U_i (although $Q_i^2 + U_i^2$ is independent of the scattering plane). If, for a given scattering direction, we consider incident light polarized parallel and perpendicular to the associated scattering plane, it follows that S_{12} is

$$S_{12} = \frac{1}{2}\frac{I_{\parallel} - I_{\perp}}{I_i},$$

where $I_{\parallel}$ and $I_{\perp}$ are the scattered irradiances for incident light polarized parallel and perpendicular to the scattering plane.

By considering incident light polarized obliquely to the scattering plane ($+45°$ and $-45°$), we obtain a straightforward physical interpretation of the matrix element S_{13}. The remaining matrix elements are a bit more difficult to interpret individually, although various combinations of them are related to *changes* in the state of polarization of incident light. As an example, let us consider the change in degree of polarization of incident light that is completely polarized parallel to a particular scattering plane. The Stokes parameters of the scattered light are $I_s = (S_{11} + S_{12})I_i$, $Q_s = (S_{21} + S_{22})I_i$, $U_s = (S_{31} + S_{32})I_i$, $V_s = (S_{41} + S_{42})I_i$, and the degree of polarization is

$$\frac{\sqrt{(S_{21} + S_{22})^2 + (S_{31} + S_{32})^2 + (S_{41} + S_{42})^2}}{S_{11} + S_{12}}. \tag{3.17}$$

If we are considering scattering by a *single* particle or a collection of *identical* particles (by identical is meant identical in size, shape, composition, and orientation relative to the incident beam), it follows from (3.16) and (3.17) that the scattered light is completely polarized. Although we chose a particular example, this general conclusion is true for arbitrary incident light that is completely polarized. Scattering by a single particle or collection of identical particles does not decrease the *degree* of polarization of 100% polarized incident light. Note, however, that the *nature* of the polarization will, in general, be changed; for example, linearly polarized incident light will be transformed into elliptically polarized light upon scattering. If, on the other hand, the collection is composed of *nonidentical* particles, then (3.17) will be less than (or at most, equal to) 100%. Therefore, scattering by a collection of nonidentical particles results in *depolarization* of incident polarized light. This is another general feature of scattering that is independent of the specific nature of the particles.

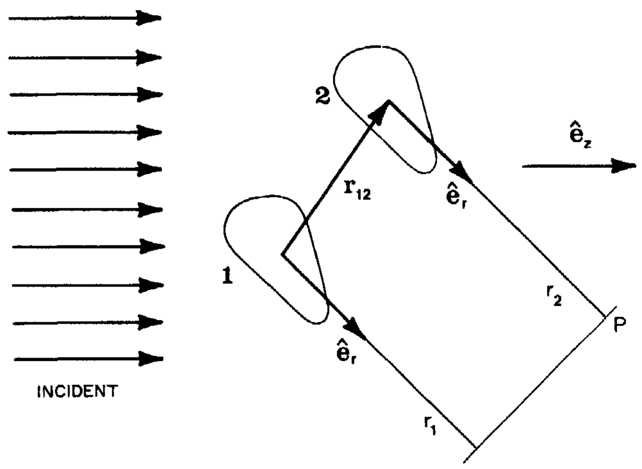

Figure 3.5 Scattering by two identical particles.

Light scattered in the forward direction ($\hat{\mathbf{e}}_r = \hat{\mathbf{e}}_z$) has unique characteristics not possessed by light scattered in all other directions. No matter how small the solid angle $\Delta\Omega$ subtended by the detector, it is not possible to separate the incident beam from the light scattered in the forward direction: the detector unavoidably responds to a superposition of incident and forward scattered fields. There is another singular aspect of the forward scattering direction. Consider a collection of *identical* particles, two of which are shown in Fig. 3.5. For a given scattering direction $\hat{\mathbf{e}}_r$, there is a difference in phase $\Delta\phi$ between the fields $\mathbf{E}_{s1}(\hat{\mathbf{e}}_r)$ and $\mathbf{E}_{s2}(\hat{\mathbf{e}}_r)$ scattered by particles 1 and 2:

$$\mathbf{E}_{s2}(\hat{\mathbf{e}}_r) \simeq \mathbf{E}_{s1}(\hat{\mathbf{e}}_r)e^{i\Delta\phi},$$

where $\mathbf{E}_s$ is evaluated in the far-field region at points on the plane P normal to $\hat{\mathbf{e}}_r$, and the phase difference is

$$\Delta\phi = k[\mathbf{r}_{12}\cdot(\hat{\mathbf{e}}_z - \hat{\mathbf{e}}_r)]. \tag{3.18}$$

We have also assumed that $r_1 \gg |\mathbf{r}_{12}|$, $r_2 \gg |\mathbf{r}_{12}|$. Except near the forward direction, there is a random distribution of phase differences for light scattered by randomly separated identical particles in a large collection. As we approach the forward direction ($\hat{\mathbf{e}}_r \to \hat{\mathbf{e}}_z$), however, the phase difference (3.18) approaches zero *regardless of the particle separation*. Therefore, scattering near the forward direction is *coherent*. If the particles are not identical, the difference in phase between light scattered by various pairs of particles, does not, in general, vanish in the forward direction, although it is independent of particle separation; the phase difference may, however, depend on the relative orientation of the two particles. It is clear that scattering in or near the forward direction is sufficiently singular to require careful consideration.

3.4 EXTINCTION, SCATTERING, AND ABSORPTION

Suppose that one or more particles are placed in a beam of electromagnetic radiation (Fig. 3.6). The rate at which electromagnetic energy is received by a detector D downstream from the particles is denoted by U. If the particles are removed, the power received by the detector is U_0, where $U_0 > U$. We say that the presence of the particles has resulted in *extinction* of the incident beam. If the medium in which the particles are embedded is nonabsorbing, the difference $U_0 - U$ is accounted for by *absorption* in the particles (i.e., transformation of electromagnetic energy into other forms) and *scattering* by the particles. This extinction depends on the chemical composition of the particles, their size, shape, orientation, the surrounding medium, the number of particles, and the polarization state and frequency of the incident beam. Although the specific details of extinction depend on all these parameters, certain general features are shared in common by all particles.

Let us now consider extinction by a single arbitrary particle embedded in a nonabsorbing medium (not necessarily a vacuum) and illuminated by a plane wave (Fig. 3.7). We construct an imaginary sphere of radius r around the particle; the net rate at which electromagnetic energy crosses the surface A of this sphere is

$$W_a = -\int_A \mathbf{S}\cdot\hat{\mathbf{e}}_r\,dA.$$

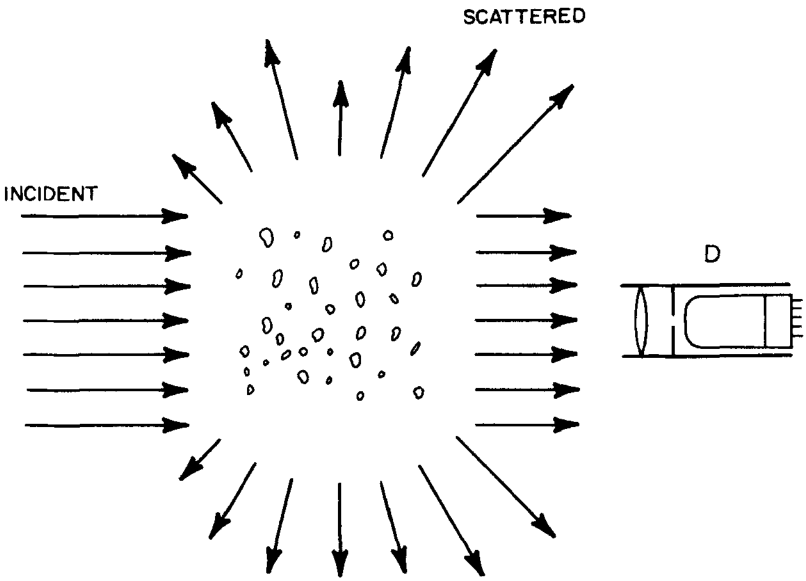

Figure 3.6 Extinction by a collection of particles.

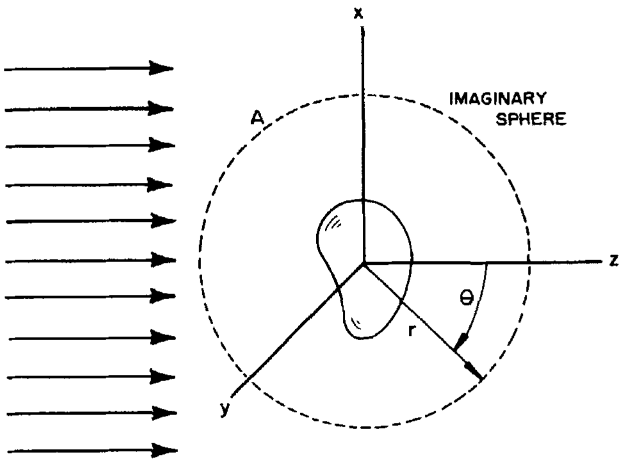

Figure 3.7 Extinction by a single particle.

If $W_a > 0$ (if W_a is negative, energy is being created within the sphere, a possibility we exclude from consideration), energy is absorbed within the sphere. But the medium is nonabsorbing, which implies that W_a is the rate at which energy is absorbed by the particle. Because of (3.13) W_a may be written as the sum of three terms: $W_a = W_i - W_s + W_{\text{ext}}$, where

$$W_i = -\int_A \mathbf{S}_i \cdot \hat{\mathbf{e}}_r \, dA, \qquad W_s = \int_A \mathbf{S}_s \cdot \hat{\mathbf{e}}_r \, dA, \qquad W_{\text{ext}} = -\int_A \mathbf{S}_{\text{ext}} \cdot \hat{\mathbf{e}}_r \, dA. \tag{3.19}$$

W_i vanishes identically for a nonabsorbing medium; W_s is the rate at which energy is scattered across the surface A. Therefore, W_{ext} is just the sum of the energy absorption rate and the energy scattering rate:

$$W_{\text{ext}} = W_a + W_s. \tag{3.20}$$

For convenience we take the incident electric field $\mathbf{E}_i = E\hat{\mathbf{e}}_x$ to be x-polarized. Because the medium is nonabsorbing, W_a is independent of the radius r of the imaginary sphere. Therefore, we may choose r sufficiently large such that we are in the far-field region where

$$\mathbf{E}_s \sim \frac{e^{ik(r-z)}}{-ikr}\mathbf{X}E, \qquad \mathbf{H}_s \sim \frac{k}{\omega\mu}\hat{\mathbf{e}}_r \times \mathbf{E}_s, \tag{3.21}$$

and $\hat{\mathbf{e}}_r \cdot \mathbf{X} = 0$. As a reminder that the incident light is x-polarized we use the symbol $\mathbf{X}$ for the *vector scattering amplitude*, which is related to the (scalar) amplitude scattering matrix elements S_j as follows:

$$\mathbf{X} = (S_2 \cos\phi + S_3 \sin\phi)\hat{\mathbf{e}}_{\parallel s} + (S_4 \cos\phi + S_1 \sin\phi)\hat{\mathbf{e}}_{\perp s}. \tag{3.22}$$

After a considerable amount of algebraic manipulation we obtain

$$\begin{aligned} W_{\text{ext}} = \frac{-\mathrm{k}}{2\omega\mu} |E|^2 \operatorname{Re}\bigg\{ & \frac{e^{-ikr}}{ikr} \int_A e^{ikz} \hat{\mathbf{e}}_x \cdot \mathbf{X}^* \, dA \\ & - \frac{e^{ikr}}{ikr} \int_A e^{-ikz} \cos\theta \hat{\mathbf{e}}_x \cdot \mathbf{X} \, dA \\ & + \frac{e^{ikr}}{ikr} \int_A e^{-ikz} \sin\theta \cos\phi \hat{\mathbf{e}}_z \cdot \mathbf{X} \, dA \bigg\}. \end{aligned} \tag{3.23}$$

Equation (3.23) contains integrals of the form

$$\int_{-1}^{1} e^{ikr\mu} f(\mu) \, d\mu,$$

where $\mu = \cos\theta$, which can be integrated by parts to yield

$$\frac{e^{ikr} f(1) - e^{-ikr} f(-1)}{ikr} + O\left(\frac{1}{\mathrm{k}^2 r^2}\right),$$

provided that $df/d\mu$ is bounded. The limiting value of W_{ext} as $\mathrm{k}r \to \infty$ is therefore

$$W_{\text{ext}} = I_i \frac{4\pi}{\mathrm{k}^2} \operatorname{Re}\{(\mathbf{X} \cdot \hat{\mathbf{e}}_x)_{\theta=0}\},$$

where I_i is the incident irradiance. The ratio of W_{ext} to I_i is a quantity with dimensions of area:

$$C_{\text{ext}} = \frac{W_{\text{ext}}}{I_i} = \frac{4\pi}{\mathrm{k}^2} \operatorname{Re}\{(\mathbf{X} \cdot \hat{\mathbf{e}}_x)_{\theta=0}\}. \tag{3.24}$$

It follows from (3.20) that the *extinction cross section* C_{ext} may be written as the sum of the *absorption cross section* C_{abs} and the *scattering cross section* C_{sca}:

$$C_{\text{ext}} = C_{\text{abs}} + C_{\text{sca}}, \tag{3.25}$$

where $C_{\text{abs}} = W_{\text{abs}}/I_i$ and $C_{\text{sca}} = W_s/I_i$. From (3.19) and (3.21) we have

$$C_{\text{sca}} = \int_0^{2\pi} \int_0^{\pi} \frac{|\mathbf{X}|^2}{\mathrm{k}^2} \sin\theta \, d\theta \, d\phi = \int_{4\pi} \frac{|\mathbf{X}|^2}{\mathrm{k}^2} d\Omega. \tag{3.26}$$

The quantity $|\mathbf{X}|^2/k^2$ is sometimes called the *differential scattering cross section*, a familiar term in atomic and nuclear physics, and denoted symbolically by $dC_{\text{sca}}/d\Omega$; this should not be interpreted as the derivative of a function of Ω: the differential scattering cross section is *formally* written as a derivative merely as an aid to the memory. Physically, $dC_{\text{sca}}/d\Omega$ specifies the angular distribution of the scattered light: the amount of light (for unit incident irradiance) scattered into a unit solid angle about a given direction. In light scattering theory one commonly encounters the term *phase function*, defined as $|\mathbf{X}|^2/k^2 C_{\text{sca}}$ and denoted by the symbol p; it is normalized:

$$\int_{4\pi} p \, d\Omega = 1.$$

We previously voiced our objection to the term phase used to designate irradiances. A less commonly encountered, although perhaps better term for the phase function is the *scattering diagram*.

The average cosine of the scattering angle, or the *asymmetry parameter* g is

$$g = \langle \cos \theta \rangle = \int_{4\pi} p \cos \theta \, d\Omega.$$

For a particle that scatters light *isotropically* (i.e., the same in all directions), g vanishes; g also vanishes if the scattering is symmetric about a scattering angle of 90°. If the particle scatters more light toward the forward direction ($\theta = 0°$), g is positive; g is negative if the scattering is directed more toward the back direction ($\theta = 180°$).

We may define *efficiencies* (or efficiency factors) for extinction, scattering, and absorption:

$$Q_{\text{ext}} = \frac{C_{\text{ext}}}{G}, \qquad Q_{\text{sca}} = \frac{C_{\text{sca}}}{G}, \qquad Q_{\text{abs}} = \frac{C_{\text{abs}}}{G},$$

where G is the particle cross-sectional area projected onto a plane perpendicular to the incident beam (e.g., $G = \pi a^2$ for a sphere of radius a). The word "efficiency," together with our intuitive notions molded by geometrical optics, might lead us to believe that extinction efficiencies can never be greater than unity. Indeed, *if* geometrical optics were a completely trustworthy guide into the world of small particles, the extinction efficiency of *all* particles would be identically equal to unity: all rays incident on a particle are either absorbed or deflected by reflection and refraction. In later chapters we shall see that there are very many particles of a rather common sort which can scatter and absorb *more* light, often much more, than is geometrically incident upon them. So the wisest course is to look on the efficiencies as merely dimensionless cross sections and not hobble our thinking with imagined constraints on the values they can take.

The expressions for C_{ext} and C_{sca} were derived under the assumption of x-polarized incident light. It is clear, however, that the form of these expressions is the same for arbitrary linearly polarized incident light: we need merely reinterpret what is meant by the x direction. We must keep in mind, however, that $\mathbf{X}$ depends on the direction of polarization $\hat{\mathbf{e}}_x$.

If the incident field $\mathbf{E}_i = E_x\hat{\mathbf{e}}_x + E_y\hat{\mathbf{e}}_y$ is arbitrarily polarized, the expressions for the cross sections are

$$C_{\text{ext}} = \frac{4\pi}{k^2|\mathbf{E}_i|^2}\operatorname{Re}\{(\mathbf{E}_i^* \cdot \mathbf{T})_{\theta=0}\},$$

$$C_{\text{sca}} = \int_{4\pi} \frac{|\mathbf{T}|^2}{k^2|\mathbf{E}_i|^2}\, d\Omega,$$

where $\mathbf{T} = E_x\mathbf{X} + E_y\mathbf{Y}$ and $\mathbf{Y}$ is the vector scattering amplitude for incident y-polarized light. For incident *unpolarized* light ($\langle E_x E_x^* \rangle = \langle E_y E_y^* \rangle$, $\langle E_x E_y^* \rangle = \langle E_x^* E_y \rangle = 0$), these expressions yield

$$C_{\text{ext}} = \tfrac{1}{2}\left(C_{\text{ext},x} + C_{\text{ext},y}\right), \qquad C_{\text{sca}} = \tfrac{1}{2}\left(C_{\text{sca},x} + C_{\text{sca},y}\right),$$

where subscripts x and y denote cross sections for incident x-polarized and y-polarized light.

Equation (3.24) is one particular form of the *optical theorem*, the 100-year history of which has been related by Newton (1976). This theorem, which is common to all kinds of seemingly disparate scattering phenomena involving acoustic waves, electromagnetic waves, and elementary particles, expresses a very curious fact: extinction depends only on the scattering amplitude *in the forward direction*. Yet extinction is the combined effect of absorption in the particle and scattering *in all directions* by the particle. To explain this, we must examine in more detail the measurement of extinction. In so doing, we shall rely heavily on a physically intuitive derivation of the optical theorem given by van de Hulst (1949).

Consider a single arbitrary particle interposed between a source of light (taken to be x-polarized) and a detector D (Fig. 3.6). The power U incident on the detector is

$$\begin{aligned} U &= \iint_D \mathbf{S}_i \cdot \hat{\mathbf{e}}_z \, dx\, dy + \iint_D \mathbf{S}_s \cdot \hat{\mathbf{e}}_z \, dx\, dy + \iint_D \mathbf{S}_{\text{ext}} \cdot \hat{\mathbf{e}}_z \, dx\, dy \\ &= U_i + U_s + U_{\text{ext}}, \end{aligned} \tag{3.27}$$

where integration is taken over the area of the detector. The first term in (3.27) is just $U_i = I_i A(D)$, where I_i is the incident irradiance and $A(D)$ is the area of the detector. We take the distance z between particle and detector to be sufficiently large ($kz \gg 1$) so that the detector is in the far-field region:

$$U_s = I_i \iint_D \frac{|\mathbf{X}|^2}{(kr)^2} \cos\theta \, dx \, dy. \tag{3.28}$$

If $R/z \ll 1$, where R is the maximum linear dimension of the detector, then $|\mathbf{X}|^2$, $\cos\theta$, and r are approximately constant on D, and (3.28) is

$$U_s \simeq I_i \frac{|\mathbf{X}|^2_{\theta=0}}{k^2} \Omega(D), \tag{3.29}$$

where $\Omega(D) \simeq A(D)/z^2$ is the solid angle subtended by the detector. The third term U_{ext} is

$$\begin{aligned} U_{\text{ext}} = I_i \text{Re}\Bigg\{ & \iint_D \frac{e^{-ik(r-z)}}{ikr} \cos\theta (\hat{\mathbf{e}}_x \cdot \mathbf{X}^*) \, dx \, dy \\ & - \iint_D \frac{e^{-ik(r-z)}}{ikr} \sin\theta \cos\phi (\hat{\mathbf{e}}_z \cdot \mathbf{X}^*) \, dx \, dy \\ & - \iint_D \frac{e^{ik(r-z)}}{ikr} (\hat{\mathbf{e}}_x \cdot \mathbf{X}) \, dx \, dy \Bigg\}. \end{aligned} \tag{3.30}$$

Equation (3.30) contains integrals of the form

$$J = \iint_D e^{ikzf(x,y)} g(x,y) \, dx \, dy, \tag{3.31}$$

the asymptotic behavior of which have been investigated extensively by Jones and Kline (1958) using the *method of stationary phase*. The value of J is determined by the behavior of f in the neighborhood of certain *critical points* interior to and on the boundary of D. The integrals in (3.30) are of the form (3.31) with $f = r/z - 1$. The only critical point in the interior of D is at $x = 0$, $y = 0$, where f is stationary ($\partial f/\partial x = \partial f/\partial y = 0$). If the detector is chosen so that there are no critical points on the boundary of D, then

$$J = \frac{2\pi i z}{k} g(0,0) + O\left(\frac{1}{k^2 z^2}\right). \tag{3.32}$$

In particular, a circular boundary (centered at $x = 0, y = 0$) for D is excluded. We also require that $kR^2/z \gg 4\pi$, which ensures that the domain of integration includes a large number of maxima and minima of the oscillatory function $\exp[ik(r - z)]$. If we use (3.32), then (3.30) becomes

$$U_{\text{ext}} = -I_i C_{\text{ext}},$$

for sufficiently large kz. Therefore, the power received by the detector is

$$U = I_i\left[A(D) - C_{\text{ext}} + \frac{|\mathbf{X}|^2_{\theta=0}}{k^2}\Omega(D)\right]. \tag{3.33}$$

The third quantity in brackets in (3.33) is the amount of energy scattered into a solid angle $\Omega(D)$ centered about the forward direction; if this solid angle is sufficiently small, consistent with the requirement that $kR^2/z \gg 4\pi$, then

$$U = I_i[A(D) - C_{\text{ext}}]. \tag{3.34}$$

Therefore, C_{ext} is a well-defined observable quantity: we measure U with and without the particle interposed between source and detector. Because C_{ext} is inherently positive, the effect of the particle is to reduce the detector area by C_{ext}; this, then, is the interpretation of C_{ext} as an area. In the language of geometrical optics we would say that the particle "casts a shadow" of area C_{ext}. However, as stated previously, this "shadow" can be considerably greater—or much less—than the particle's geometrical shadow. We note from (3.33) that C_{ext} is the *maximum* observable extinction. The scattering term $\Omega(D)|\mathbf{X}|^2_{\theta=0}/k^2$ cannot be greater than C_{sca} and is positive; therefore, the observed extinction C'_{ext} lies within the limits

$$C_{\text{abs}} \le C'_{\text{ext}} \le C_{\text{ext}}.$$

The full extinction C_{ext} will be observed only if the detector subtends a sufficiently small solid angle. As the detector is moved closer to the particle, however, the observed extinction will decrease. We shall see when we consider specific examples that light scattered by particles much larger than the wavelength of the incident light tends to be concentrated around the forward direction. Therefore, the larger the particle, the more difficult it is to exclude scattered light from the detector.

From (3.13) and (3.27) we have

$$U_{\text{ext}} = \iint_D \tfrac{1}{2}\,\text{Re}\{\mathbf{E}_i \times \mathbf{H}_s^* + \mathbf{E}_s \times \mathbf{H}_i^*\}\cdot\hat{\mathbf{e}}_r\,dA. \tag{3.35}$$

It is obvious from the form of the integrand in (3.35) that it is a manifestation of interference between the incident and forward scattered light. Conservation of energy then requires that the light removed from the incident beam by interference is accounted for by scattering in all directions and absorption in the particle.

We derived C_{ext} by two different methods. The first, integrating the Poynting vector over an imaginary sphere around the particle, emphasized the conservation of energy aspect of extinction: extinction = scattering + absorption. The second, focusing attention on what is measured in a hypothetical extinction experiment, emphasized the interference aspect of extinction: extinction = interference between incident and forward scattered light.

Up to this point we have considered only extinction by a single particle. However, the vast majority of extinction measurements involve collections of very many particles. Let us now consider such a collection, which is confined to a finite volume, the *scattering volume*. The total Poynting vector is

$$\mathbf{S} = \tfrac{1}{2}\operatorname{Re}\left\{\mathbf{E}_i \times \mathbf{H}_i^* + \sum_j (\mathbf{E}_i \times \mathbf{H}_{sj}^* + \mathbf{E}_{sj} \times \mathbf{H}_i^*) + \sum_j \sum_k \mathbf{E}_{sj} \times \mathbf{H}_{sk}^*\right\},$$

where $(\mathbf{E}_{sj}, \mathbf{H}_{sj})$ is the electromagnetic field scattered by the jth particle. As before, we construct an imaginary sphere centered on an arbitrary point taken as origin in the scattering volume, the dimensions of which are small compared with the sphere radius r. The electric field scattered by the jth particle is

$$\mathbf{E}_{sj} \sim \frac{e^{ik(r-z)}}{-ikr}\mathbf{X}_j e^{i\delta_j} E,$$

where the incident field is taken to be x-polarized. The phase δ_j is approximately $(r \gg \xi_j)$

$$\delta_j \simeq k\left[(\hat{\mathbf{e}}_z - \hat{\mathbf{e}}_r)\cdot\boldsymbol{\xi}_j + \frac{\xi_j^2}{2r}\right],$$

where $\boldsymbol{\xi}_j$ is the position vector of the jth particle relative to the origin and $\hat{\mathbf{e}}_r = \mathbf{r}/r$ is the scattering direction. If we integrate $\mathbf{S}$ over the surface of the sphere, we obtain

$$C_{\text{ext}} = \frac{W_{\text{ext}}}{I_i} = \sum_j C_{\text{ext},\,j},$$

$$C_{\text{ext},\,j} = C_{\text{abs},\,j} + C_{\text{sca},\,j},$$

provided that $\delta_j(\theta = 0^0) = k\xi_j^2/2r \ll 1$ and that

$$\sum_j \int_A \frac{|\mathbf{X}_j|^2}{k^2 r^2}\,dA \gg \left|\sum_{\substack{j \\ j\neq k}}\sum_{k} \int_A \frac{\mathbf{X}_j\cdot\mathbf{X}_k^*}{k^2 r^2} e^{i(\delta_j - \delta_k)}\,dA\right|, \tag{3.36}$$

(i.e., the scattering is *incoherent*); $C_{\text{ext},\,j}$, $C_{\text{abs},\,j}$, and $C_{\text{sca},\,j}$ are the single-particle cross sections. It is difficult to give precise criteria under which (3.36) is satisfied. It is necessary, however, that the separations between the particles be uncorrelated during the time required to make a measurement.

If, in a measurement of extinction and scattering by a collection of small particles, a converging lens is placed in front of a detector which lies in the focal plane of the lens, r becomes effectively infinite. Therefore, under conditions that are likely to be frequently met in practice, the cross sections of a collection of particles are additive.

3.4.1 Extinction by a Slab of Particles

As a final example of extinction by a collection of particles let us consider a semi-infinite region $0 \leq z \leq h$, $-\infty < x < \infty$, $-\infty < y < \infty$, throughout which particles are more or less uniformly distributed (Fig. 3.8). The field $\mathbf{E}_t$ at the point P is the sum of the incident field $\mathbf{E}_i = E_0 e^{ikz}\hat{\mathbf{e}}_x$ and the fields scattered by the particles:

$$\mathbf{E}_t = \mathbf{E}_i + \sum_j \mathbf{E}_{sj}, \tag{3.37}$$

where the contribution to $\mathbf{E}_t$ from the particle with coordinates (x_j, y_j, z_j) is

$$\mathbf{E}_{sj} = \frac{e^{ikR_j}}{-ikR_j}\mathbf{X}_j(\hat{\mathbf{e}}_j)E_0 e^{ikz_j}, \qquad R_j = |\mathbf{R}_j|,$$

$$\hat{\mathbf{e}}_j = \frac{\mathbf{R}_j}{R_j}, \qquad \mathbf{R}_j = -x_j\hat{\mathbf{e}}_x - y_j\hat{\mathbf{e}}_y + (d - z_j)\hat{\mathbf{e}}_z.$$

We may assume without appreciable loss of generality that the particles are identical ($\mathbf{X}_j = \mathbf{X}$). A more important assumption is that $\mathcal{N}$, the number of particles per unit volume, is sufficiently large such that the summation in (3.37) may be replaced by integration:

$$\sum_j \to \int\int\int \mathcal{N}\, dx\, dy\, dz.$$

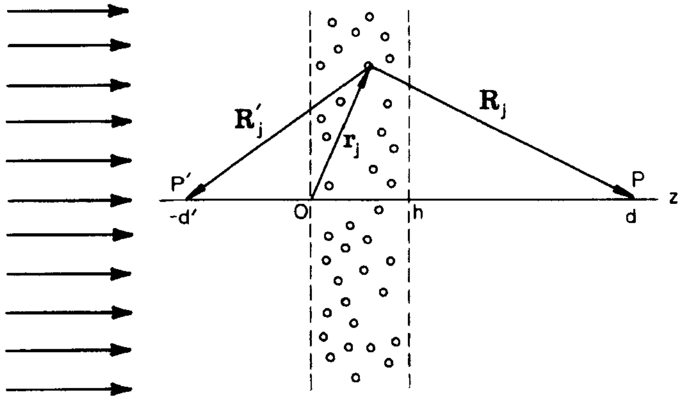

Figure 3.8 Extinction by a slab of particles.

With this assumption, the discrete variables x_j, y_j, z_j are replaced by the continuous variables x, y, z, and

$$\sum_j \mathbf{E}_{sj} \simeq E_0 \int_0^h dz \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{e^{i\mathrm{k}(R+z)}}{-i\mathrm{k}R} \mathbf{X}(\hat{\mathbf{e}}) \mathfrak{N} \, dx \, dy, \tag{3.38}$$

where $R = \sqrt{x^2 + y^2 + (d-z)^2}$ and $\hat{\mathbf{e}} = \mathbf{R}/R$. The integral over x and y in (3.38) can be evaluated in a straightforward manner by the method of stationary phase; although the limits of this integral are infinite, its value is independent of the lateral extent of the slab provided that it is large compared with $\sqrt{4\pi d/\mathrm{k}}$. After performing the necessary integrations we obtain

$$\mathbf{E}_t = E_0 e^{i\mathrm{k}d} \left\{ \left[1 - \frac{2\pi\mathfrak{N}}{\mathrm{k}^2} (\mathbf{X} \cdot \hat{\mathbf{e}}_x)_{\theta=0} h \right] \hat{\mathbf{e}}_x - \frac{2\pi\mathfrak{N}}{\mathrm{k}^2} (\mathbf{X} \cdot \hat{\mathbf{e}}_y)_{\theta=0} h \hat{\mathbf{e}}_y \right\}.$$

Although the incident light is x-polarized, the transmitted light has a y component if $(\mathbf{X} \cdot \hat{\mathbf{e}}_y)_{\theta=0} \neq 0$; that is, the direction of vibration of the incident beam is, in general, *rotated* on transmission through the slab. If we assume that there is no rotation and, moreover, if $|2\pi\mathfrak{N}\mathrm{k}^{-2}h(\mathbf{X} \cdot \hat{\mathbf{e}}_x)_{\theta=0}| \ll 1$, we may write

$$\mathbf{E}_t = \mathbf{E}_i \exp\left[-\frac{2\pi\mathfrak{N}h}{\mathrm{k}^2} (\mathbf{X} \cdot \hat{\mathbf{e}}_x)_{\theta=0} \right]. \tag{3.39}$$

The transmission coefficient of a *homogeneous* slab of thickness h and refractive index $\tilde{N}$, which is embedded in a homogeneous medium with refractive index N, where $\tilde{N} \simeq N$, is given by (2.73):

$$\tilde{t}_{\text{slab}} \simeq e^{i(\tilde{\mathrm{k}} - \mathrm{k})h}, \tag{3.40}$$

where $\tilde{\mathrm{k}} = 2\pi\tilde{N}/\lambda$. If we compare (3.39) and (3.40), we note that the slab of particles is equivalent, at least as far as transmission is concerned, to the homogeneous slab if

$$\frac{\tilde{N}}{N} = 1 + i\frac{2\pi\mathfrak{N}}{\mathrm{k}^3} (\mathbf{X} \cdot \hat{\mathbf{e}}_x)_{\theta=0}. \tag{3.41}$$

Therefore, within limits, we may interpret $\tilde{N}$ in (3.41) as the effective refractive index of the slab of particles. This leads naturally to the question: To what extent is $\tilde{N}$ similar to the refractive index of a homogeneous medium? For example, under what conditions, if any, will substitution of $\tilde{N}$ into the expression for the reflection coefficient of a homogeneous slab yield physically correct results? We can answer the latter and more specific of these two questions by calculating the field $\mathbf{E}_r$ at the point P' (Fig. 3.8), which is the sum of the individual fields scattered by the particles:

$$\mathbf{E}_r = \sum_j \frac{e^{ikR'_j}}{-ikR'_j} \mathbf{X}_j(\hat{\mathbf{e}}_j) E_0 e^{ikz_j}, \tag{3.42}$$

where $R'_j = -[x_j\hat{\mathbf{e}}_x + y_j\hat{\mathbf{e}}_y + (d - z_j)\hat{\mathbf{e}}_z]$. Again, we assume identical particles, and the summation (3.42) is approximated by an integral, which can be evaluated by the method of stationary phase:

$$\mathbf{E}_r = -E_0 e^{-ikd'}(1 - e^{i2kh}) \frac{i\pi\mathcal{N}}{k^3} \mathbf{X}_{\theta=180}. \tag{3.43}$$

The reflection coefficient for a homogeneous slab with refractive index $\tilde{N} \simeq N$ is, from (2.72),

$$\tilde{r}_{\text{slab}} \simeq \frac{N - \tilde{N}}{2N}\left(1 - e^{i2\tilde{k}h}\right). \tag{3.44}$$

Thus, if we assume that $(\mathbf{X}\cdot\hat{\mathbf{e}}_y)_{\theta=180} = 0$, then (3.41) substituted into (3.44) is consistent with (3.43) provided that

$$\mathbf{X}_{\theta=0} = \mathbf{X}_{\theta=180}. \tag{3.45}$$

As we shall see in later chapters, (3.45) is satisfied for particles small compared with the wavelength. For a collection of such particles, therefore, the concept of an effective refractive index is meaningful at least as far as transmission and reflection are concerned. However, even if the particles are small compared with the wavelength, $\tilde{N}$ should not be interpreted too literally as a refractive index on the same footing as the refractive index of a homogeneous medium. For example, attenuation in a strictly homogeneous medium is the result of absorption, which is accounted for quantitatively by the imaginary part of the refractive index. In a particulate medium, however, attenuation may be wholly or in part the result of scattering. Even if the particles are nonabsorbing, the imaginary part of the effective refractive index (3.41) can be nonzero.

From (3.39) and the optical theorem (3.24) it follows that the irradiance is attenuated according to $I_t = I_i \exp(-\alpha_{\text{ext}} h)$ as the incident beam traverses the slab of particles, where the *attenuation coefficient* α_{ext} is

$$\alpha_{\text{ext}} = \mathcal{N}C_{\text{ext}} = \mathcal{N}C_{\text{abs}} + \mathcal{N}C_{\text{sca}}. \tag{3.46}$$

Although we assumed identical particles, this was done to avoid a cluttered notation, and it is not a restriction on the validity of our analysis; the results above are readily generalized to a mixture of different particles. For example, the attenuation coefficient of such a mixture is

$$\alpha_{\text{ext}} = \sum_j \mathcal{N}_j C_{\text{ext},j},$$

where $\mathcal{N}_j$ is the number of particles of type j per unit volume and $C_{\text{ext},j}$ is the corresponding extinction cross section.

Underlying (3.39), and hence exponential attenuation of irradiance in particulate media, is the requirement that $\alpha_{\text{ext}}h \ll 1$. This condition may be relaxed somewhat if the scattering contribution to total attenuation is small (i.e., $\mathcal{N}C_{\text{sca}}h \ll 1$). To justify this assertion fully would take us somewhat afield into the theory of radiative transfer. But we can give a brief heuristic argument as follows. An amount of light dI is removed from a beam propagating in the z direction through an infinitesimal distance between z and $z + dz$ in a slab of particles:

$$dI = -\alpha_{\text{ext}} I \, dz, \tag{3.47}$$

where I is the beam irradiance at z. However, light can get back into the beam by multiple scattering; that is, light scattered at other positions in the slab may ultimately contribute to the irradiance at z. Scattered light, in contradistinction to absorbed light, is not irretrievably lost from the system—it merely changes direction and is lost from a beam propagating in a particular direction—but contributes to other directions. Clearly, the greater the scattering cross section, number density of particles, and slab thickness h, the greater will be the multiple scattering contribution to the irradiance at z. Thus, if $\mathcal{N}C_{\text{sca}}h$ is sufficiently small, we may ignore multiple scattering and (3.47) can be integrated to yield $I_t = I_i \exp(-\alpha_{\text{ext}}h)$.

Sometimes it is of interest to compare attenuation of light by a given material in the bulk with that in the finely divided, or particulate, states. In order for the comparison to be fair, however, we have to consider equal masses or, equivalently, equal volumes of material in the two states. If $\mathcal{N}$ is the particle number density, $1/\mathcal{N}$ is the average volume allocated to a single particle, and the volume fraction f of particles in the collection is $\mathcal{N}v$, where v is the volume of a single particle. Thus, we can write the attenuation coefficient (3.46) as $\alpha_{\text{ext}} = fC_{\text{ext}}/v$. Imagine now that the particles are compressed into a homogeneous slab ($f = 1$) without, however, losing their individual identities and properties. We shall call the resulting attenuation coefficient, which is the extinction cross section per unit particle volume, the *volume attenuation coefficient* α_v:

$$\alpha_v = \frac{C_{\text{ext}}}{v}. \tag{3.48}$$

The *mass attenuation coefficient* α_m, defined as the extinction cross section per unit particle mass, is related to the volume attenuation coefficient by

$$\alpha_m = \frac{\alpha_v}{\rho},$$

where ρ is the density of the particle. If any quantity deserves to be called an extinction "efficiency," it is the extinction cross section per unit volume (or mass) rather than the extinction cross section per unit area. For it is the former quantity that tells us how effective a *fixed mass* of particles is in removing light from a beam. Suppose that we set on a chunk of material with a hammer and smash it to bits. What size should the bits be to most effectively extinguish light of a given wavelength? To answer this question, it is clear that we should plot C_{ext}/v as a function of size rather than, as is traditionally done, Q_{ext}. Sacrosanct though it may be, Q_{ext} conveys less physical information than C_{ext}/v, and we shall often present the latter rather than the former.

A set of measurements of I_t/I_i over some range of wavelengths for a homogeneous slab of material is called the *transmission*, or *absorption*, *spectrum* of the material. We may look on this spectrum as the fingerprints of the material. However, it is possible to smudge these fingerprints drastically. If, for example, we measure the transmission spectrum of a given homogeneous material and then divide it by some means into a collection of small particles, the transmission spectrum of the particulate medium will often bear little resemblance to that of the bulk parent material. The chemical composition is the same in both instances, but the state of aggregation has changed. An obvious source of difference between the two spectra is scattering: if fluctuations are ignored, the homogeneous slab does not scatter light, whereas the transmission spectrum of the particulate medium may be primarily the result of scattering. But the difference goes deeper than this: even if one could correct for scattering (e.g., by suitably collecting the scattered light), large differences might still exist. Thus, the gross optical properties (e.g., reflection and transmission) of a given material can and do differ appreciably depending on its state of aggregation. We shall encounter many examples of this in later chapters.

NOTES AND COMMENTS

Our derivation of (3.24) is similar to that of Jones (1955).