Chapter 5

Particles Small Compared with the Wavelength

If we were interested only in scattering and absorption by spheres, we would need go no further than the Mie theory. There is, strictly speaking, no need for approximations because we have the exact theory in hand. Given enough time, a suitable computer program will generate cross sections and scattering matrix elements for an arbitrary sphere. But physics is—or should be—more than just a semi-infinite strip of computer output: we need not denude vast tracts of forest in order to obtain some insight into scattering and absorption by small particles. In fact, great reams of calculations often serve only to obscure from view the basic physics, which can be quite simple. Therefore, it is worthwhile to consider approximate expressions, which are valid in certain limiting cases, in the hope that we may acquire some insight. Aside from the immediate applicability of these expressions to back-of-the-envelope calculations without worrying about convergence of series, misbehavior of Bessel functions, and significant digits, they point the way toward approximate methods to be used to tackle problems for which there is no exact theory.

5.1 SPHERE SMALL COMPARED WITH THE WAVELENGTH

The power series expansions of the spherical Bessel functions are (Antosiewicz, 1964)

$$j_n(\rho) = \frac{\rho^n}{1 \cdot 3 \cdot 5 \cdots (2n+1)}\left[1 - \frac{\frac{1}{2}\rho^2}{1!(2n+3)} + \frac{\left(\frac{1}{2}\rho^2\right)^2}{2!(2n+3)(2n+5)} - \cdots\right], \quad (5.1)$$

$$y_n(\rho) = -\frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{\rho^{n+1}}\left[1 - \frac{\frac{1}{2}\rho^2}{1!(1-2n)} + \frac{\left(\frac{1}{2}\rho^2\right)^2}{2!(1-2n)(3-2n)} - \cdots\right]. \quad (5.2)$$

Let us expand the various functions in the scattering coefficients a_n and b_n in power series and retain only the first few terms. From (5.1) and (5.2) we have

$$
\begin{aligned}
\psi_1(\rho) &\simeq \frac{\rho^2}{3} - \frac{\rho^4}{30}, & \psi_1'(\rho) &\simeq \frac{2\rho}{3} - \frac{2\rho^3}{15},\\
\xi_1(\rho) &\simeq -\frac{i}{\rho} - \frac{i\rho}{2} + \frac{\rho^2}{3}, & \xi_1'(\rho) &\simeq \frac{i}{\rho^2} - \frac{i}{2} + \frac{2\rho}{3},\\
\psi_2(\rho) &\simeq \frac{\rho^3}{15}, & \psi_2'(\rho) &\simeq \frac{\rho^2}{5},\\
\xi_2(\rho) &\simeq -\frac{i3}{\rho^2}, & \xi_2'(\rho) &\simeq \frac{i6}{\rho^3}.
\end{aligned}
\tag{5.3}
$$

We have retained a sufficient number of terms in the expansions (5.3) to ensure that the scattering coefficients are accurate to terms of order x^6. The first four coefficients so obtained are

$$
\begin{aligned}
a_1 &= -\frac{i2x^3}{3}\frac{m^2-1}{m^2+2} - \frac{i2x^5}{5}\frac{(m^2-2)(m^2-1)}{(m^2+2)^2}\\
&\quad + \frac{4x^6}{9}\left(\frac{m^2-1}{m^2+2}\right)^2 + O(x^7),\\
b_1 &= -\frac{ix^5}{45}(m^2-1) + O(x^7),\\
a_2 &= -\frac{ix^5}{15}\frac{m^2-1}{2m^2+3} + O(x^7),\\
b_2 &= O(x^7),
\end{aligned}
$$

where we have taken the permeability of the sphere to be equal to that of the surrounding medium. The expansions for higher-order scattering coefficients involve terms of order x^7 and higher. If $|m|x \ll 1$, then $|b_1| \ll |a_1|$; with this assumption the amplitude scattering matrix elements to terms of order x^3 are

$$
S_1 = \tfrac{3}{2}a_1, \qquad S_2 = \tfrac{3}{2}a_1\cos\theta,
$$

$$
a_1 = -\frac{i2x^3}{3}\frac{m^2-1}{m^2+2}. \tag{5.4}
$$

The corresponding scattering matrix, accurate to terms of order x^6, is

$$\frac{9|a_1|^2}{4k^2r^2}\begin{pmatrix} \frac{1}{2}(1+\cos^2\theta) & \frac{1}{2}(\cos^2\theta - 1) & 0 & 0 \\ \frac{1}{2}(\cos^2\theta - 1) & \frac{1}{2}(1+\cos^2\theta) & 0 & 0 \\ 0 & 0 & \cos\theta & 0 \\ 0 & 0 & 0 & \cos\theta \end{pmatrix}. \tag{5.5}$$

If the incident light is unpolarized with irradiance I_i, the scattered irradiance I_s is

$$I_s = \frac{8\pi^4 N a^6}{\lambda^4 r^2}\left|\frac{m^2-1}{m^2+2}\right|^2 (1+\cos^2\theta) I_i. \tag{5.6}$$

Thus, if the quantity $|(m^2-1)/(m^2+2)|^2$ is weakly dependent on wavelength (this is *not* always true), the irradiance scattered by a sphere small compared with the wavelength or, indeed, *any* sufficiently small particle regardless of its shape, is proportional to $1/\lambda^4$. Such scattering is often referred to as Rayleigh scattering, and we are quite content to adopt this term in all that follows. However, there are those who object to associating Rayleigh's name with small particles if they absorb as well as scatter light: it seems that Rayleigh did not explicitly consider absorbing particles. Nevertheless, we shall attach the name "Rayleigh" to small-particle scattering for convenience even though the term may lack strict historical accuracy. We have not followed the historical path to the $1/\lambda^4$ scattering law but, rather, have considered the limiting case of the Mie theory. However, Rayleigh's (1871) original derivation was simplicity itself, and it is worth reproducing here to show how much can be obtained from such a small expenditure of effort.

> Having disposed of the polarization, let us now consider how the intensity of the scattered light varies from one part of the spectrum to another, still supposing that all the particles are many times smaller than the wavelength even of violet light. The whole question admits of analytical treatment; but before entering upon that, it may be worthwhile to show how the principal result may be anticipated from a consideration of the *dimensions* of the quantities concerned.
>
> The object is to compare the intensities of the incident and scattered rays; for these will clearly be proportional. The number (i) expressing the ratio of the two amplitudes is a function of the following quantities: T, the volume of the disturbing particle; r, the distance of the point under consideration from it; λ, the wavelength; b, the velocity of propagation of light; D and D', the original and altered densities [the density parameter of the ether, which was still in vogue in Rayleigh's day, corresponds to the dielectric function (Twersky, 1964)]: of which the first three depend only on space, the fourth on space and time, while the fifth and sixth introduce the consideration of mass. Other elements of the problem there are none, except mere numbers and angles, which do not depend

on the fundamental measurements of space, time, and mass. Since the ratio i, whose expression we seek, is of no dimension in mass, it follows at once that D and D' only occur under the form $D : D'$, which is a simple number and may therefore be omitted. It remains to find how i varies with T, r, λ, and b.

Now of these quantities, b is the only one depending on time; and therefore, as i is of no dimensions in time, b cannot occur in its expression. We are left, then, with T, r, and λ; and from what we know of the dynamics of the question, we may be sure that i varies directly as T and inversely as r, and must therefore be proportional to $T \div \lambda^2 r$, T being of three dimensions in space. In passing from one part of the spectrum to another λ is the only quantity which varies, and we have the important law:

When light is scattered by particles which are very small compared with any of the wavelengths, the ratio of the amplitudes of the vibrations of the scattered and incident light varies inversely as the square of the wavelength and the intensity of the lights themselves as the inverse fourth power.

Equation (5.6) applies to incident unpolarized light; it is important to remember that the angular distribution of the scattered light depends on the polarization of the incident light:

$$i_{\parallel} = \frac{9|a_1|^2}{4k^2r^2}\cos^2\theta$$ *Incident light polarized parallel to the scattering plane.*

$$i_{\perp} = \frac{9|a_1|^2}{4k^2r^2}$$ *Incident light polarized perpendicular to the scattering plane.*

$$i = \tfrac{1}{2}(i_{\parallel} + i_{\perp})$$ *Unpolarized incident light.*

The angular distribution of the scattered light (normalized to the forward direction) for incident light polarized parallel and perpendicular to the scattering plane and unpolarized is shown in Fig. 5.1; both linear and polar plots are given.

If the incident light is 100% polarized, the scattered light will be similarly polarized. However, because light of two different polarization states is scattered differently, the scattered light will be partially polarized if the incident light is unpolarized. From (4.78) we have

$$P = \frac{1 - \cos^2\theta}{1 + \cos^2\theta},$$

where the degree of polarization of the scattered light, given incident unpolarized light, is $|P|$ (Fig. 5.2). P is always positive; therefore, the scattered light is partially polarized *perpendicular* to the scattering plane. If a sufficiently small sphere is illuminated by unpolarized light, the scattered light is 100%

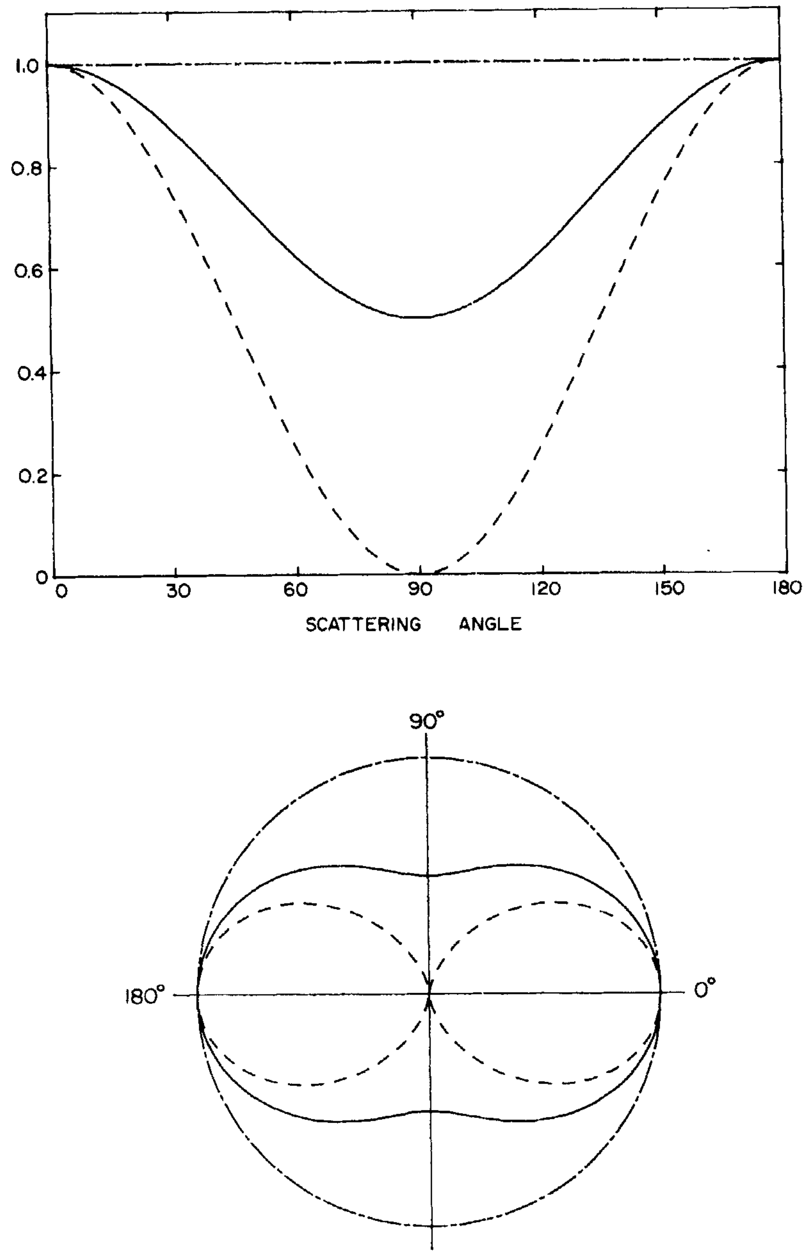

Figure 5.1 Angular distribution (normalized) of the light scattered by a sphere small compared with the wavelength: incident light polarized parallel (– – – –) and perpendicular (—-—) to the scattering plane; (——) unpolarized incident light.

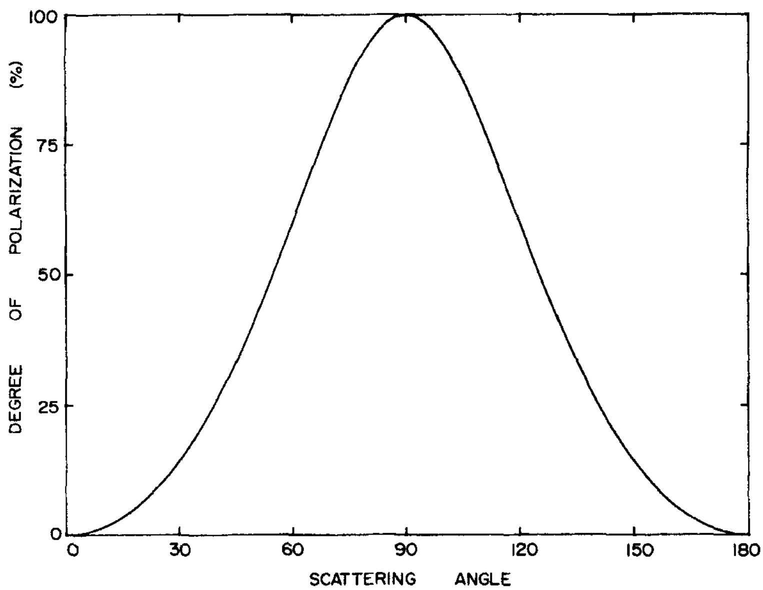

Figure 5.2 Degree of polarization of light scattered by a sphere small compared with the wavelength for incident unpolarized light.

polarized at a scattering angle of 90°. This is analogous to complete polarization upon reflection of unpolarized light incident on a plane interface at the Brewster angle (Section 2.7).

Note that P is independent of particle size, as are the functional forms of $i_{\parallel}(\theta)$ and $i_{\perp}(\theta)$; the *absolute* scattered irradiance depends on size (the volume squared), but it is difficult to measure absolute irradiances. Therefore, the radius of small spheres cannot readily be determined from scattering measurements; in this sense, all small spheres are equal.

The extinction, scattering, and radar backscattering efficiencies are (to terms of order x^4)

$$Q_{\text{ext}} = 4x\,\text{Im}\left\{\frac{m^2-1}{m^2+2}\left[1+\frac{x^2}{15}\left(\frac{m^2-1}{m^2+2}\right)\frac{m^4+27m^2+38}{2m^2+3}\right]\right\}$$
$$+\frac{8}{3}x^4\,\text{Re}\left\{\left(\frac{m^2-1}{m^2+2}\right)^2\right\}, \tag{5.7}$$

$$Q_{\text{sca}} = \frac{8}{3}x^4\left|\frac{m^2-1}{m^2+2}\right|^2, \tag{5.8}$$

$$Q_b = 4x^4\left|\frac{m^2-1}{m^2+2}\right|^2, \tag{5.9}$$

and the absorption efficiency Q_{abs} is $Q_{ext} - Q_{sca}$. If $|m|x \ll 1$, the coefficient (in brackets) of $(m^2 - 1)/(m^2 + 2)$ in the first term of (5.7) is approximately unity; with this restriction, the absorption efficiency is

$$Q_{abs} = 4x\,\mathrm{Im}\left\{\frac{m^2-1}{m^2+2}\right\}\left[1 - \frac{4x^3}{3}\mathrm{Im}\left\{\frac{m^2-1}{m^2+2}\right\}^2\right]. \tag{5.10}$$

Therefore, if $(4x^3/3)\mathrm{Im}\{(m^2 - 1)/(m^2 + 2)\} \ll 1$, a condition that will be satisfied for sufficiently small x, the absorption efficiency is approximately

$$Q_{abs} = 4x\,\mathrm{Im}\left\{\frac{m^2 - 1}{m^2 + 2}\right\}. \tag{5.11}$$

To the extent that (5.11) is a good approximation, the absorption cross section $C_{abs} = \pi a^2 Q_{abs}$ is proportional to the *volume* of the particle.

Equations (5.8), (5.11), and the scattering matrix (5.5) are widely—and wildly—quoted in the literature. However, some care must be exercised if they are to be used in calculations. Kerker et al. (1978) have investigated the validity of Rayleigh theory by calculating the scattered irradiance $i_{\parallel}(0°)$ according to the exact and approximate theories for size parameters between 0.01 and 0.11 and a range of real and imaginary parts of m. Their results clearly show that, for given x, the accuracy of the Rayleigh theory decreases as $|m|$ is increased.

If $(m^2 - 1)/(m^2 + 2)$ is a weak function of wavelength over some interval (this is not true, for example, for *metallic* particles), then for sufficiently small particles

$$Q_{abs} \propto \frac{1}{\lambda}, \qquad Q_{sca} \propto \frac{1}{\lambda^4}.$$

If extinction is dominated by absorption, the extinction spectrum will vary as $1/\lambda$; if extinction is dominated by scattering, the extinction spectrum will vary as $1/\lambda^4$. In either case, and in intermediate cases as well, shorter wavelengths are extinguished more than longer wavelengths; that is, there is *reddening* of the spectrum of incident light upon transmission through a collection of sufficiently small spheres the optical properties of which (n and k) are not strongly dependent on wavelength over the region of interest.

5.2 THE ELECTROSTATICS APPROXIMATION

The absorption and scattering efficiencies of a small ($x \ll 1$, $|m|x \ll 1$) sphere may be written

$$Q_{abs} = 4x\,\mathrm{Im}\frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}, \qquad Q_{sca} = \frac{8}{3}x^4\left|\frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}\right|^2, \tag{5.12}$$

where ε_1 and ε_m are the permittivities of the sphere and the surrounding medium, respectively. The quantity $(\varepsilon_1 - \varepsilon_m)/(\varepsilon_1 + 2\varepsilon_m)$ appears in the problem of a sphere embedded in a uniform *static* electric field. This suggests a connection between electrostatics and scattering by particles small compared with the wavelength; in this section we examine the reasons for this connection.

Consider a homogeneous, isotropic sphere that is placed in an arbitrary medium in which there exists a uniform static electric field $\mathbf{E}_0 = E_0\hat{\mathbf{e}}_z$ (Fig. 5.3). If the permittivities of the sphere and medium are different, a charge will be induced on the surface of the sphere. Therefore, the initially uniform field will be distorted by the introduction of the sphere. The electric fields inside and outside the sphere, $\mathbf{E}_1$ and $\mathbf{E}_2$, respectively, are derivable from scalar potentials $\Phi_1(r, \theta)$ and $\Phi_2(r, \theta)$

$$\mathbf{E}_1 = -\nabla\Phi_1, \qquad \mathbf{E}_2 = -\nabla\Phi_2,$$

where

$$\nabla^2\Phi_1 = 0 \quad (r < a), \qquad \nabla^2\Phi_2 = 0 \quad (r > a).$$

Because of the symmetry of the problem, the potentials are independent of the azimuthal angle ϕ. At the boundary between sphere and medium the potentials must satisfy

$$\Phi_1 = \Phi_2, \qquad \varepsilon_1\frac{\partial\Phi_1}{\partial r} = \varepsilon_m\frac{\partial\Phi_2}{\partial r} \quad (r = a).$$

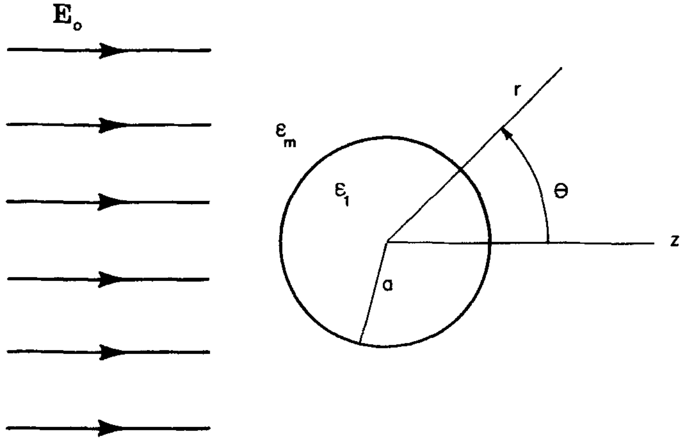

Figure 5.3 Sphere in a uniform static electric field.

In addition, we require that

$$\lim_{r \to \infty} \Phi_2 = -E_0 r \cos\theta = -E_0 z;$$

that is, at large distances from the sphere, the electric field is the unperturbed applied field. It is not difficult to show that the functions

$$\Phi_1 = -\frac{3\varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} E_0 r \cos\theta,$$

$$\Phi_2 = -E_0 r \cos\theta + a^3 E_0 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} \frac{\cos\theta}{r^2}, \tag{5.13}$$

satisfy the partial differential equations and boundary conditions above.

Consider now two point charges q and $-q$ which are separated by a distance d (Fig. 5.4). This configuration of charges is called a *dipole* with *dipole moment* $\mathbf{p} = p\mathbf{e}_z$, where $p = qd$. If the charges are embedded in a uniform unbounded medium with permittivity ε_m, the potential Φ of the dipole at any point P is

$$\Phi = \frac{q}{4\pi\varepsilon_m}\left(\frac{1}{r_+} - \frac{1}{r_-}\right),$$

$$r_+ = r\left(1 - \frac{\mathbf{r}\cdot\hat{\mathbf{e}}_z}{r^2}d + \frac{d^2}{4r^2}\right)^{1/2}, \qquad r_- = r\left(1 + \frac{\mathbf{r}\cdot\hat{\mathbf{e}}_z}{r^2}d + \frac{d^2}{4r^2}\right)^{1/2}.$$

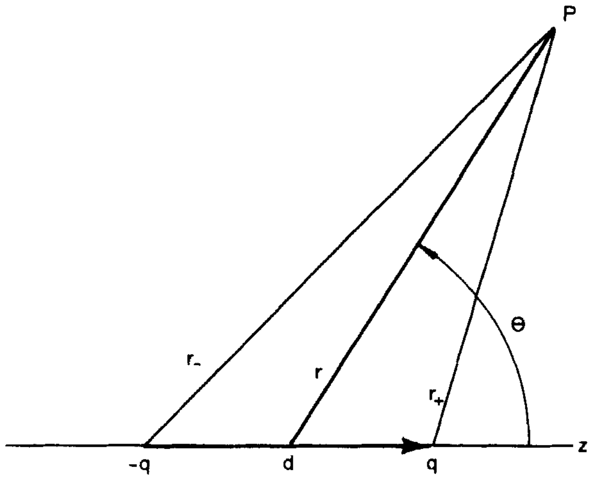

Figure 5.4 Electric dipole.

If we let d approach zero in such a way that the product qd remains constant, we obtain the potential of an *ideal dipole*

$$\Phi = \frac{\mathbf{p} \cdot \mathbf{r}}{4\pi\varepsilon_m r^3} = \frac{p \cos\theta}{4\pi\varepsilon_m r^2}. \tag{5.14}$$

Let us return now to the problem of a sphere in a uniform field. We note from (5.13) and (5.14) that the field outside the sphere is the superposition of the applied field and the field of an ideal dipole at the origin with dipole moment

$$\mathbf{p} = 4\pi\varepsilon_m a^3 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} \mathbf{E}_0.$$

Thus, the applied field *induces* a dipole moment proportional to the field. The ease with which the sphere is polarized may be specified by the *polarizability* α defined by

$$\mathbf{p} = \varepsilon_m \alpha \mathbf{E}_0,$$

$$\alpha = 4\pi a^3 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}. \tag{5.15}$$

Our analysis has been restricted to the response of a sphere to an applied uniform static electric field. But we are interested in scattering problems where the applied (incident) field is a plane wave that varies in space and time. We showed that a sphere in an electrostatic field is equivalent to an ideal dipole; therefore, let us assume that for purposes of calculations we may replace the sphere by an ideal dipole with dipole moment $\varepsilon_m \alpha \mathbf{E}_0$ even when the applied field is a plane wave. However, the permittivities in (5.15) are those appropriate to the frequency of the incident wave rather than the static field values.

The dipole moment $\mathbf{p} = \varepsilon_m \alpha E_0 e^{-i\omega t}\hat{\mathbf{e}}_x$ of an ideal dipole, located at $z = 0$ and illuminated by an x-polarized plane wave $E_0 \exp(ikz - i\omega t)\hat{\mathbf{e}}_x$, oscillates with the frequency of the applied field; therefore, the dipole radiates (i.e., scatters) an electric field $\mathbf{E}_s$ (Stratton, 1941, p. 435)

$$\mathbf{E}_s = \frac{e^{ikr}}{-ikr} \frac{ik^3}{4\pi\varepsilon_m} \hat{\mathbf{e}}_r \times (\hat{\mathbf{e}}_r \times \mathbf{p}), \qquad (kr \gg 1) \tag{5.16}$$

where we have omitted the time-dependent factor $e^{-i\omega t}$. After some manipulation (5.16) can be put in the form (3.21):

$$\mathbf{E}_s = \frac{e^{ik(r-z)}}{-ikr} \mathbf{X} E, \qquad E = E_0 e^{ikz},$$

$$\mathbf{X} = \frac{ik^3}{4\pi} \alpha \hat{\mathbf{e}}_r \times (\hat{\mathbf{e}}_r \times \hat{\mathbf{e}}_x). \tag{5.17}$$

Therefore, from (3.22) and (4.22) we have the scattering amplitudes

$$S_1 = \frac{-ik^3\alpha}{4\pi}, \qquad S_2 = \frac{-ik^3\alpha}{4\pi}\cos\theta,$$

which are equivalent to (5.4). The cross sections for extinction and scattering are obtained from (3.24) and (3.26):

$$C_{\text{ext}} = k\,\text{Im}\{\alpha\} = \pi a^2 4x\,\text{Im}\left\{\frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}\right\}. \tag{5.18}$$

$$C_{\text{sca}} = \frac{k^4}{6\pi}|\alpha|^2 = \pi a^2 \frac{8}{3} x^4 \left|\frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}\right|^2. \tag{5.19}$$

Equations (5.18) and (5.19) are similar to (5.12) with one exception: (5.18) is accurate only if scattering is small compared with absorption. In place of (5.18) we should therefore write

$$C_{\text{abs}} = k\,\text{Im}\{\alpha\}.$$

Thus, replacing a sphere small compared with the wavelength by an ideal dipole has been justified—we obtain correct expressions for the scattering matrix elements and cross sections. However, let us briefly examine why this is so just to be sure that it is not a happy accident. At any instant the amplitude of the wave illuminating the sphere is $E_0\exp(ikz)$; therefore, if $x = ka \ll 1$, then $\exp(-ika) \simeq \exp(ika) \simeq 1$, and the field to which the sphere is exposed is approximately uniform over the region occupied by the sphere. Note also from (5.13) that the field inside the sphere is uniform in the electrostatic case. However, we would not expect the field in the sphere to be uniform when the external field is a plane wave unless $2\pi k_1 a/\lambda \ll 1$, where k_1 is the imaginary part of the particle's refractive index. The field changes over a characteristic time of order $\tau = 1/\omega$, where ω is the angular frequency of the incident field. The time τ^* required for a signal to propagate across the sphere is of order an_1/c, where n_1 is the real part of the particle's refractive index and c is the speed of light *in vacuo* [we have assumed that the group velocity coincides with the signal velocity and that the group velocity and phase velocity are approximately equal (see Stratton, 1941, pp. 333–340); these conditions will be satisfied at wavelengths not too close to strong absorption bands]. Thus, when the incident field changes, every point of the sphere will simultaneously get the message provided that $\tau^* \ll \tau$ or, equivalently, $2\pi n_1 a/\lambda \ll 1$. The two inequalities involving the real and imaginary parts of the refractive index may be combined into a single inequality: $|m|x \ll 1$.

Equations (5.12) were obtained from the exact theory in the limit $x \ll 1$ and $|m|x \ll 1$; these same equations can be obtained by treating the sphere as an ideal dipole with moment given by electrostatics theory. In the preceding paragraph, we gave a physical justification for this correspondence. However, the shape of the particle was not relevant in our considerations; for an arbitrary particle we need merely interpret a as a characteristic length. Therefore, it is now a straightforward, although possibly laborious task to calculate matrix elements and cross sections for other particles in the electrostatics approximation: we merely use electrostatics (potential theory) to calculate the polarizability of the particle. Thus, we have the means to obtain approximate solutions to a limited class of scattering problems which do not possess exact solutions.

Although magnetic particles are infrequently encountered, particularly at visible wavelengths, it is worth noting that our analysis would have to be modified somewhat if we wished to consider such particles. We have assumed that the secondary radiation is *electric dipole radiation*; but if μ_1 and μ_2 are appreciably different there will also be *magnetic dipole radiation*. The magnetic dipole moment can be calculated from magnetostatic theory and the resulting field radiated by the magnetic dipole added to that radiated by the electric dipole (see Stratton, 1941, p. 437, for a discussion of magnetic dipole radiation).

5.3 ELLIPSOID IN THE ELECTROSTATICS APPROXIMATION

The most general smooth particle—one without edges or corners—of regular shape is an ellipsoid with semiaxes $a > b > c$ (Fig. 5.5), the surface of which is specified by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1.$$

The natural coordinates, albeit unfamiliar and not without their disagreeable features, for formulating the problem of determining the dipole moment of an ellipsoidal particle induced by a uniform electrostatic field are the *ellipsoidal coordinates* (ξ, η, ζ) defined by

$$\frac{x^2}{a^2+\xi} + \frac{y^2}{b^2+\xi} + \frac{z^2}{c^2+\xi} = 1, \qquad -c^2 < \xi < \infty$$

$$\frac{x^2}{a^2+\eta} + \frac{y^2}{b^2+\eta} + \frac{z^2}{c^2+\eta} = 1, \qquad -b^2 < \eta < -c^2$$

$$\frac{x^2}{a^2+\zeta} + \frac{y^2}{b^2+\zeta} + \frac{z^2}{c^2+\zeta} = 1, \qquad -a^2 < \zeta < -b^2.$$

The surfaces ξ = constant are confocal ellipsoids, and the particular ellipsoid $\xi = 0$ coincides with the boundary of the particle. The surfaces η = constant

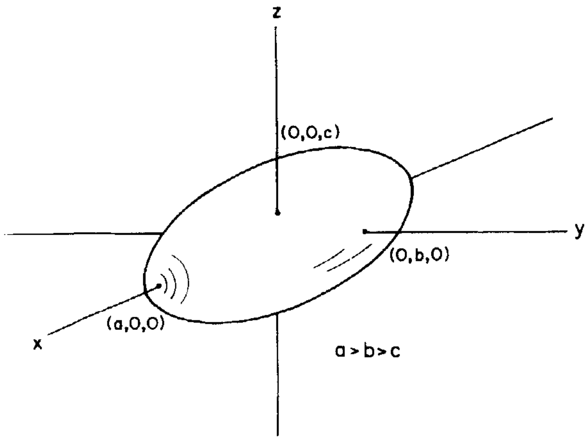

Figure 5.5 Ellipsoidal particle.

are hyperboloids of one sheet, and the surfaces ζ = constant are hyperboloids of two sheets. To any point (x, y, z) there corresponds one set of ellipsoidal coordinates (ξ, η, ζ); the converse, however, is not true. The coordinates (ξ, η, ζ) determine *eight* points symmetrically located in each of the octants into which space is partitioned by the xyz coordinate axes:

$$x^2 = \frac{(a^2+\xi)(a^2+\eta)(a^2+\zeta)}{(b^2-a^2)(c^2-a^2)},$$

$$y^2 = \frac{(b^2+\xi)(b^2+\eta)(b^2+\zeta)}{(a^2-b^2)(c^2-b^2)},$$

$$z^2 = \frac{(c^2+\xi)(c^2+\eta)(c^2+\zeta)}{(a^2-c^2)(b^2-c^2)}.$$

This ambiguity may be removed by introducing the Weierstrassian elliptic function (Jones, 1964, p. 32). Fortunately, such a drastic step is not necessary in the problem at hand, a homogeneous ellipsoid in a uniform electrostatic field aligned along the z axis. In this instance the potential Φ has the symmetry properties

$$\Phi(x, y, z) = \Phi(-x, y, z) = \Phi(x, -y, z) = \Phi(-x, -y, z),$$

$$\Phi(x, y, -z) = \Phi(-x, y, -z) = \Phi(x, -y, -z) = \Phi(-x, -y, -z), \tag{5.20}$$

where x, y, z are positive. Thus, we need only consider the potential in two octants: one with positive z and one with negative z. The potential and its derivative with respect to z are also required to be continuous on the plane $z = 0$.

Let us consider the octant in which x, y, z are positive. We denote by Φ_1 the potential inside the particle; outside the particle the potential Φ_2 may be written as the superposition of the potential Φ_0 of the external field

$$\Phi_0 = -E_0 \left[\frac{(c^2+\xi)(c^2+\eta)(c^2+\zeta)}{(a^2-c^2)(b^2-c^2)} \right]^{1/2}, \tag{5.21}$$

and the perturbing potential Φ_p caused by the particle. At sufficiently large distances from the particle the perturbing potential is negligible. We note that when $\xi \gg a^2$, then $\xi \simeq r^2$; therefore, we require that

$$\lim_{\xi \to \infty} \Phi_p = 0. \tag{5.22}$$

On the boundary of the particle the potentials are required to be continuous:

$$\Phi_1(0,\eta,\zeta) = \Phi_0(0,\eta,\zeta) + \Phi_p(0,\eta,\zeta). \tag{5.23}$$

Laplace's equation in ellipsoidal coordinates is

$$\nabla^2\Phi = (\eta-\zeta)f(\xi)\frac{\partial}{\partial\xi}\left\{ f(\xi)\frac{\partial\Phi}{\partial\xi} \right\} + (\zeta-\xi)f(\eta)\frac{\partial}{\partial\eta}\left\{ f(\eta)\frac{\partial\Phi}{\partial\eta} \right\}$$
$$+ (\xi-\eta)f(\zeta)\frac{\partial}{\partial\zeta}\left\{ f(\zeta)\frac{\partial\Phi}{\partial\zeta} \right\} = 0, \tag{5.24}$$

where $f(q) = \{(q+a^2)(q+b^2)(q+c^2)\}^{1/2}$. At this point we could seek a complete set of solutions to (5.24) and expand the potentials in an infinite series of ellipsoidal harmonics. We can save ourselves an enormous amount of labor, however, by recognizing that, as in the case of scattering by a sphere, the form of these expansions is dictated by the form of the incident (external) field and the necessity of satisfying the boundary condition (5.23). Thus, because of (5.21), we postulate that the potentials Φ_1 and Φ_p are of the form

$$\Phi(\xi,\eta,\zeta) = F(\xi)\{(c^2+\eta)(c^2+\zeta)\}^{1/2},$$

where it follows from (5.24) that $F(\xi)$ satisfies the ordinary differential equation

$$f(\xi)\frac{d}{d\xi}\left\{ f(\xi)\frac{dF}{d\xi} \right\} - \left(\frac{a^2+b^2}{4} + \frac{\xi}{2} \right)F(\xi) = 0. \tag{5.25}$$

The solution

$$F_1(\xi) = (c^2+\xi)^{1/2}, \tag{5.26}$$

which can be verified by substitution in (5.25), follows from the fact that (5.21) satisfies Laplace's equation. A second linearly independent solution to (5.25) may be obtained by integration of (5.26) (see, e.g., Sokolnikoff and Redheffer, 1958, pp. 76–77):

$$F_2(\xi) = F_1(\xi)\int_\xi^\infty \frac{dq}{F_1^2(q)f(q)}, \tag{5.27}$$

with the property $\lim_{\xi\to\infty} F_2(\xi) = 0$. The function F_1 is not compatible with the requirement (5.22); therefore, the perturbing potential of the particle is

$$\Phi_p(\xi, \eta, \zeta) = C_2 F_2(\xi)\{(c^2+\eta)(c^2+\zeta)\}^{1/2}, \tag{5.28}$$

where C_2 is a constant. If the potential inside the particle is to be finite at the origin, we must have

$$\Phi_1(\xi, \eta, \zeta) = C_1 F_1(\xi)\{(c^2+\eta)(c^2+\zeta)\}^{1/2}, \tag{5.29}$$

where C_1 is a constant. Thus, the field inside the particle is uniform and parallel to the applied field. The boundary condition (5.23) yields one equation in the constants C_1 and C_2:

$$C_2\int_0^\infty \frac{dq}{(c^2+q)f(q)} - C_1 = \frac{E_0}{\{(a^2-c^2)(b^2-c^2)\}^{1/2}},$$

and the requirement that the normal component of **D** be continuous at the boundary between particle and medium

$$\varepsilon_1\frac{\partial\Phi_1}{\partial\xi} = \varepsilon_m\frac{\partial\Phi_0}{\partial\xi} + \varepsilon_m\frac{\partial\Phi_p}{\partial\xi} \qquad (\xi = 0),$$

yields a second equation

$$\varepsilon_m C_2\left[\int_0^\infty \frac{dq}{(c^2+q)f(q)} - \frac{2}{abc}\right] - \varepsilon_1 C_1 = \frac{\varepsilon_m E_0}{\{(a^2-c^2)(b^2-c^2)\}^{1/2}}.$$

Therefore, the potentials inside and outside the particle are

$$\Phi_1 = \frac{\Phi_0}{1 + \dfrac{L_3(\varepsilon_1-\varepsilon_m)}{\varepsilon_m}}, \tag{5.30}$$

$$\Phi_p = \Phi_0\frac{\dfrac{abc}{2}\dfrac{\varepsilon_m-\varepsilon_1}{\varepsilon_m}\displaystyle\int_\xi^\infty \frac{dq}{(c^2+q)f(q)}}{1 + \dfrac{L_3(\varepsilon_1-\varepsilon_m)}{\varepsilon_m}}, \tag{5.31}$$

where

$$L_3 = \frac{abc}{2} \int_0^{\infty} \frac{dq}{(c^2 + q) f(q)}.$$

Although we considered only the octant with positive x, y, and z, it follows from the form of (5.30) and (5.31) that they are the potentials in the neighboring octant with z negative. Moreover, the eightfold degeneracy of the ellipsoidal coordinates implies that the conditions (5.20) are satisfied. Thus, (5.30) and (5.31) give the potential at all points in space; this fortunate result is a consequence of the fact that the particle has the same symmetry as the ellipsoidal coordinates. For particles with less symmetry we would have to attack the problem octant by octant.

At distances r from the origin which are much greater than the largest semiaxis a, the integral in (5.31) is approximately

$$\int_{\xi}^{\infty} \frac{dq}{(c^2 + q) f(q)} \simeq \int_{\xi}^{\infty} \frac{dq}{q^{5/2}} = \frac{2}{3} \xi^{-3/2} \qquad (\xi \simeq r^2 \gg a^2)$$

and therefore the potential Φ_p is given asymptotically by

$$\Phi_p \sim \frac{E_0 \cos\theta}{r^2} \frac{\dfrac{abc}{3} \dfrac{\varepsilon_1 - \varepsilon_m}{\varepsilon_m}}{1 + \dfrac{L_3(\varepsilon_1 - \varepsilon_m)}{\varepsilon_m}}, \qquad (r \gg a),$$

which, from (5.14), we recognize as the potential of a dipole with moment

$$\mathbf{p} = 4\pi\varepsilon_m abc \frac{\varepsilon_1 - \varepsilon_m}{3\varepsilon_m + 3L_3(\varepsilon_1 - \varepsilon_m)} \mathbf{E}_0.$$

Therefore, the polarizability α_3 of an ellipsoid in a field parallel to one of its principal axes is

$$\alpha_3 = 4\pi abc \frac{\varepsilon_1 - \varepsilon_m}{3\varepsilon_m + 3L_3(\varepsilon_1 - \varepsilon_m)}. \tag{5.32}$$

We chose the applied field to be parallel to the z axis; however, this axis has no special property to distinguish it from the other principal axes. Therefore, the polarizabilities α_1 and α_2 when the applied field is parallel to the x and y axes, respectively, are

$$\alpha_1 = 4\pi abc \frac{\varepsilon_1 - \varepsilon_m}{3\varepsilon_m + 3L_1(\varepsilon_1 - \varepsilon_m)},$$

$$\alpha_2 = 4\pi abc \frac{\varepsilon_1 - \varepsilon_m}{3\varepsilon_m + 3L_2(\varepsilon_1 - \varepsilon_m)},$$

where

$$L_1 = \frac{abc}{2}\int_0^\infty \frac{dq}{(a^2+q)f(q)},$$

$$L_2 = \frac{abc}{2}\int_0^\infty \frac{dq}{(b^2+q)f(q)}.$$

To check these results, we note that a sphere is a special ellipsoid with $a = b = c$; therefore,

$$L_1 = L_2 = L_3 = \frac{a^3}{2}\int_0^\infty \frac{dq}{(a^2+q)^{5/2}} = \frac{1}{3},$$

and the polarizabilities reduce to that of a sphere (5.15) as required.

Only two of the three *geometrical factors* L_1, L_2, L_3 are independent because of the relation

$$L_1 + L_2 + L_3 = -abc\int_0^\infty \frac{d}{dq}\frac{1}{f(q)}\,dq = 1.$$

Moreover, they satisfy the inequalities $L_1 \leqslant L_2 \leqslant L_3$.

A special class of ellipsoids are the *spheroids*, which have two axes of equal length; therefore, only one of the geometrical factors is independent. The *prolate* (cigar-shaped) spheroids, for which $b = c$ and $L_2 = L_3$, are generated by rotating an ellipse about its *major* axis; the *oblate* (pancake-shaped) spheroids, for which $b = a$ and $L_1 = L_2$, are generated by rotating an ellipse about its *minor* axis. For spheroids, we have the following analytical expressions for L_1 as a function of the *eccentricity* e:

Prolate spheroid ($b = c$):

$$L_1 = \frac{1-e^2}{e^2}\left(-1 + \frac{1}{2e}\ln\frac{1+e}{1-e}\right) \qquad e^2 = 1 - \frac{b^2}{a^2}, \tag{5.33}$$

Oblate spheroid ($a = b$):

$$L_1 = \frac{g(e)}{2e^2}\left[\frac{\pi}{2} - \tan^{-1}g(e)\right] - \frac{g^2(e)}{2},$$

$$g(e) = \left(\frac{1-e^2}{e^2}\right)^{1/2}, \qquad e^2 = 1 - \frac{c^2}{a^2}. \tag{5.34}$$

The functions (5.33) and (5.34) are shown in Fig. 5.6. The shape of the oblate spheroid ranges from a *disk* ($e = 1$) to a *sphere* ($e = 0$); that of the prolate spheroid ranges from a *needle* ($e = 1$) to a sphere.

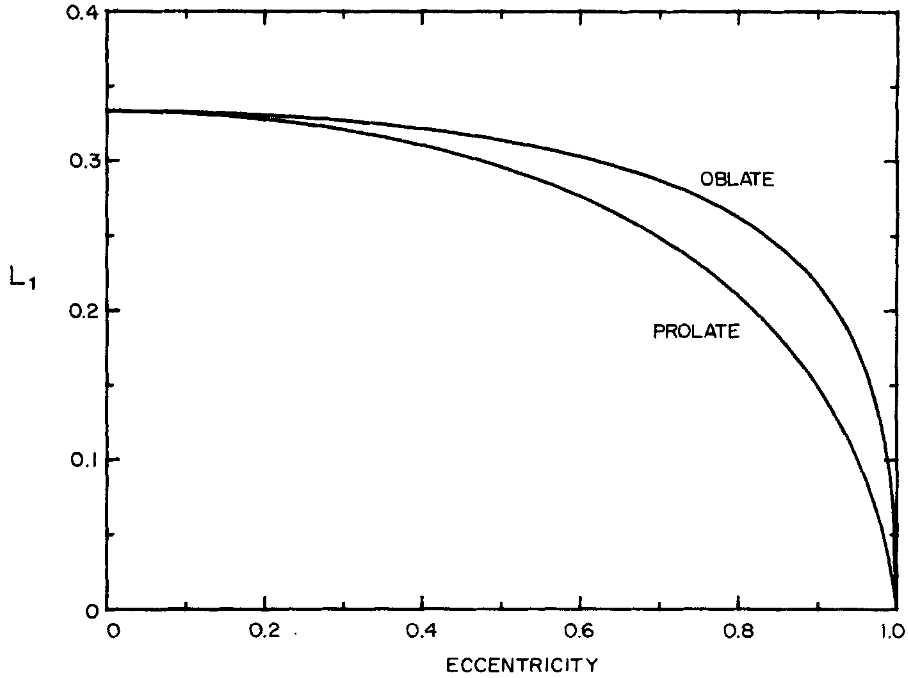

Figure 5.6 Geometrical factors for a spheroid.

The geometrical factors L_j are related to the *depolarization factors* $\bar{L}_j$ defined by

$$E_{1x} = E_{0x} - \bar{L}_1 P_{1x}, \qquad E_{1y} = E_{0y} - \bar{L}_2 P_{1y}, \qquad E_{1z} = E_{0z} - \bar{L}_3 P_{1z},$$

where $\mathbf{E}_1$ and $\mathbf{P}_1$ are the electric field and polarization induced in the particle by the applied field $\mathbf{E}_0$. The depolarization factors as defined above are meaningful quantities only for material particles (as opposed to *voids*, in which $\mathbf{P}_1 = 0$). The depolarization and geometrical factors are related by

$$\bar{L}_j = \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 - \varepsilon_0} \frac{L_j}{\varepsilon_m}.$$

Only when the particle is in free space ($\varepsilon_m = \varepsilon_0$) are its depolarization factors independent of composition; in this instance $\bar{L}_j = L_j/\varepsilon_0$. The induced field in an ellipsoidal particle is uniform but not necessarily parallel to an arbitrary applied field except in the special case of a sphere.

We do not restrict ourselves to material particles; ellipsoidal voids in an otherwise homogeneous medium scatter light in no way significantly different from that of "real" particles. Therefore, we shall avoid using the term depolarization factor, a concept that is meaningless for voids. Moreover, the word "*de*polarization" implies that the field inside the particle is *less* than the applied field; such is by no means always true. We shall encounter in later chapters examples where the internal field is *greater*, sometimes very much greater, than the applied field.

It might seem at first glance that arriving at the dipole moment $\mathbf{p}$ of an ellipsoidal particle via the asymptotic form of the potential Φ_p is a needlessly complicated procedure and that $\mathbf{p}$ is simply $v\mathbf{P}_1$, where v is the particle volume. However, this correspondence breaks down for a void, in which $\mathbf{P}_1 = 0$, but which nonetheless has a nonzero dipole moment. Because the medium is, in general, polarizable, $v\mathbf{P}_1$ is not equal to $\mathbf{p}$ even for a material particle except when it is in free space. In many applications of light scattering and absorption by small particles—in planetary atmospheres and interstellar space, for example—this condition is indeed satisfied. Laboratory experiments, however, are frequently carried out with particles suspended in some kind of medium such as water. It is for this reason that we have taken some care to ensure that the expressions for the polarizability of an ellipsoidal particle are completely general.

5.4 COATED ELLIPSOID

Although the necessary labor is increased, no new concepts are required to extend the results above for a homogeneous ellipsoid to a coated ellipsoid. We denote by ε_1 the permittivity of the inner or core ellipsoid with semiaxes a_1, b_1, c_1; ε_2 is the permittivity of the outer ellipsoid with semiaxes a_2, b_2, c_2. This coated ellipsoidal particle is in a medium with permittivity ε_m. As in the preceding section, we introduce ellipsoidal coordinates ξ, η, ζ:

$$\frac{x^2}{a_1^2+\xi} + \frac{y^2}{b_1^2+\xi} + \frac{z^2}{c_1^2+\xi} = 1, \qquad -c_1^2 < \xi < \infty,$$

with similar expressions for η and ζ. Therefore, $\xi = 0$ is the equation of the surface of the inner ellipsoid and $\xi = t$ is that of the surface of the outer ellipsoid, where $a_1^2 + t = a_2^2$, $b_1^2 + t = b_2^2$, $c_1^2 + t = c_2^2$.

The potential of the applied field, which we take to be parallel to the z axis, is

$$\Phi_0 = -E_0 z = -E_0 F_1(\xi) G(\eta, \zeta),$$

$$F_1(\xi) = \left(c_1^2 + \xi\right)^{1/2}, \qquad G(\eta,\zeta) = \left[\frac{\left(c_1^2+\eta\right)\left(c_1^2+\zeta\right)}{\left(a_1^2-c_1^2\right)\left(b_1^2-c_1^2\right)}\right]^{1/2}.$$

The potentials Φ_1 and Φ_2 in the inner and outer ellipsoids, respectively, are

$$\Phi_1 = C_1 F_1(\xi) G(\eta, \zeta), \qquad -c_1^2 < \xi < 0,$$

$$\Phi_2 = \left[C_2 F_1(\xi) + C_3 F_2(\xi)\right] G(\eta, \zeta), \qquad 0 < \xi < t,$$

$$F_2(\xi) = F_1(\xi) \int_\xi^\infty \frac{dq}{\left(c_1^2 + q\right) f_1(q)},$$

$$f_1(q) = \left[\left(a_1^2 + q\right)\left(b_1^2 + q\right)\left(c_1^2 + q\right)\right]^{1/2}.$$

The potential Φ_3 in the surrounding medium is the sum of Φ_0 and the perturbing potential Φ_p of the particle:

$$\Phi_p = C_4 F_2(\xi) G(\eta, \zeta).$$

The requirement that Φ and $\varepsilon \partial\Phi/\partial\xi$ be continuous at boundaries gives us four linear equations in the unknown constants C_1, C_2, C_3, C_4, the solution to which yields the polarizability

$$\alpha_3 = \frac{v\left(\left(\varepsilon_2 - \varepsilon_m\right)\left[\varepsilon_2 + \left(\varepsilon_1 - \varepsilon_2\right)\left(L_3^{(1)} - f L_3^{(2)}\right)\right] + f \varepsilon_2\left(\varepsilon_1 - \varepsilon_2\right)\right)}{\left(\left[\varepsilon_2 + \left(\varepsilon_1 - \varepsilon_2\right)\left(L_3^{(1)} - f L_3^{(2)}\right)\right]\left[\varepsilon_m + \left(\varepsilon_2 - \varepsilon_m\right) L_3^{(2)}\right] + f L_3^{(2)} \varepsilon_2\left(\varepsilon_1 - \varepsilon_2\right)\right)}, \tag{5.35}$$

where $v = 4\pi a_2 b_2 c_2/3$ is the volume of the particle, $f = a_1 b_1 c_1 / a_2 b_2 c_2$ is the fraction of the total particle volume occupied by the inner ellipsoid, and $L_3^{(1)}$ and $L_3^{(2)}$ are the geometrical factors for the inner and outer ellipsoids:

$$L_3^{(k)} = \frac{a_k b_k c_k}{2} \int_0^\infty \frac{dq}{\left(c_k^2 + q\right) f_k(q)} \qquad (k = 1, 2).$$

When $\varepsilon_1 = \varepsilon_2$, (5.35) is equivalent to (5.32), as required. Similar expressions for the polarizabilities are obtained when the field is applied along the x and y axes.

A special case is the *coated sphere* ($L_j^{(1)} = L_j^{(2)} = \frac{1}{3}$), for which $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$:

$$\alpha = 4\pi a_2^3 \frac{\left(\varepsilon_2 - \varepsilon_m\right)\left(\varepsilon_1 + 2\varepsilon_2\right) + f\left(\varepsilon_1 - \varepsilon_2\right)\left(\varepsilon_m + 2\varepsilon_2\right)}{\left(\varepsilon_2 + 2\varepsilon_m\right)\left(\varepsilon_1 + 2\varepsilon_2\right) + f\left(2\varepsilon_2 - 2\varepsilon_m\right)\left(\varepsilon_1 - \varepsilon_2\right)}. \tag{5.36}$$

We note that (5.36) implies that a homogeneous spherical particle will be *invisible* (i.e., $\alpha = 0$) if it is coated with a material such that the numerator in

(5.36) vanishes:

$$f\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} - \frac{\varepsilon_m - \varepsilon_2}{\varepsilon_m + 2\varepsilon_2} = 0.$$

5.5 THE POLARIZABILITY TENSOR

In the preceding sections the applied field was taken to be parallel to the *principal axes* of the ellipsoid. When the applied field $\mathbf{E}_0$ is arbitrarily directed, the induced dipole moment follows readily from superposition:

$$\mathbf{p} = \varepsilon_m\left(\alpha_1 E_{0x}\hat{\mathbf{e}}_x + \alpha_2 E_{0y}\hat{\mathbf{e}}_y + \alpha_3 E_{0z}\hat{\mathbf{e}}_z\right), \tag{5.37}$$

where E_{0x}, E_{0y}, E_{0z} are the components of $\mathbf{E}_0$ *relative to the principal axes of the ellipsoid.* In scattering problems, the coordinate axes are usually chosen to be fixed *relative to the incident beam.* Let $x'y'z'$ be such a coordinate system, where the direction of propagation is parallel to the z' axis. If the incident light is x'-polarized, we have from the optical theorem

$$C_{\text{abs},\,x'} = \frac{k\,\mathrm{Im}\{p_{x'}\}}{\varepsilon_m E_{0x'}}. \tag{5.38}$$

To evaluate (5.38) we need the components of $\mathbf{p}$ relative to the primed axes. Equation (5.37) can be written in matrix form

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \varepsilon_m \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{pmatrix} \begin{pmatrix} E_{0x} \\ E_{0y} \\ E_{0z} \end{pmatrix}. \tag{5.39}$$

In the interests of economy we shall write column vectors and matrices according to the following notational scheme:

$$[b] = \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix}, \qquad \bar{U} = \begin{pmatrix} u_{11} & u_{12} & u_{13} \\ u_{21} & u_{22} & u_{23} \\ u_{31} & u_{32} & u_{33} \end{pmatrix}.$$

With this notation, (5.39) is compactly written

$$[p] = \varepsilon_m \bar{\alpha}[E_0]. \tag{5.40}$$

The components of any vector $\mathbf{F}$ transform according to

$$[F] = \bar{A}[F'], \tag{5.41}$$

where $a_{11} = \hat{\mathbf{e}}_x \cdot \hat{\mathbf{e}}_{x'}$, $a_{12} = \hat{\mathbf{e}}_x \cdot \hat{\mathbf{e}}_{y'}$, and so on. Therefore, from (5.40) and the transformation (5.41), we have

$$[p'] = \varepsilon_m \bar{\alpha}' [E_0'], \tag{5.42}$$

$$\bar{\alpha}' = \bar{A}^T \bar{\alpha} \bar{A}, \tag{5.43}$$

where the inverse of the matrix $\bar{A}$ is its transpose $\bar{A}^T$ because of the orthogonality of the coordinate axes. Thus, the polarizability of an ellipsoid is a *Cartesian tensor*; if its components are given relative to principal axes, then its components relative to rotated coordinate axes can be determined from (5.43). The absorption cross section for incident x'-polarized light follows in a straightforward manner:

$$C_{\text{abs}, x'} = \mathrm{k}\,\mathrm{Im}\{\alpha_1 a_{11}^2 + \alpha_2 a_{21}^2 + \alpha_3 a_{31}^2\},$$

where $a_{11}^2 + a_{21}^2 + a_{31}^2 = 1$. Similarly, if the incident light is y'-polarized,

$$C_{\text{abs}, y'} = \mathrm{k}\,\mathrm{Im}\{\alpha_1 a_{12}^2 + \alpha_2 a_{22}^2 + \alpha_3 a_{32}^2\},$$

where $a_{12}^2 + a_{22}^2 + a_{32}^2 = 1$.

If the vector scattering amplitude

$$\mathbf{X} = \frac{i\mathrm{k}^3}{4\pi\varepsilon_m} \frac{\hat{\mathbf{e}}_r \times (\hat{\mathbf{e}}_r \times \mathbf{p})}{E_{0x'}}$$

for a dipole illuminated by x'-polarized light is substituted in (3.26), we obtain the scattering cross section

$$C_{\text{sca}, x'} = \frac{\mathrm{k}^4}{6\pi}\left(|\alpha_1|^2 a_{11}^2 + |\alpha_2|^2 a_{21}^2 + |\alpha_3|^2 a_{31}^2\right),$$

where we have used $\bar{A}^T \bar{A} = \bar{A}\bar{A}^T = \bar{I}$, the identity matrix. A similar expression holds for the scattering cross section when the incident light is y'-polarized.

5.5.1 Randomly Oriented Ellipsoids

In most experiments and observations we are confronted with a collection of very many particles; unless special pains are taken to align the particles, or in the absence of a known alignment mechanism, we may reasonably assume that they are randomly oriented. Under these conditions the quantities of interest are the average cross sections $\langle C_{\text{abs}} \rangle$ and $\langle C_{\text{sca}} \rangle$, which are independent of the polarization of the incident light provided that the particles are not intrinsically optically active. Let $p(\hat{\Omega})\, d\Omega$ be the probability that one of the axes fixed relative to a particle, the x axis, say, lies within a solid angle $d\Omega$ around the direction $\hat{\boldsymbol{\Omega}}$. If the particles are randomly oriented, $p(\hat{\boldsymbol{\Omega}}) = 1/4\pi$ and we have

$$\langle a_{11}^2 \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \cos^2\beta \sin\beta \, d\beta \, d\nu = \frac{1}{3},$$

where $a_{11} = \hat{\mathbf{e}}_x \cdot \hat{\mathbf{e}}_x' = \cos\beta$ and $\hat{\boldsymbol{\Omega}}(\beta, \nu)$ is the direction of the x axis relative to the primed coordinate system. Similarly, we have $\langle a_{21}^2 \rangle = \langle a_{31}^2 \rangle = \frac{1}{3}$, and therefore

$$\langle C_{\text{abs}} \rangle = \mathrm{k}\,\mathrm{Im}\{\tfrac{1}{3}\alpha_1 + \tfrac{1}{3}\alpha_2 + \tfrac{1}{3}\alpha_3\}, \tag{5.44}$$

$$\langle C_{\text{sca}} \rangle = \frac{\mathrm{k}^4}{6\pi}\left(\tfrac{1}{3}|\alpha_1|^2 + \tfrac{1}{3}|\alpha_2|^2 + \tfrac{1}{3}|\alpha_3|^2\right). \tag{5.45}$$

5.6 ANISOTROPIC SPHERE

We noted in the preceding section that the polarizability of an ellipsoid is anisotropic: the dipole moment induced by an applied uniform field is not, in general, parallel to that field. This anisotropy originates in the *shape* anisotropy of the ellipsoid. However, ellipsoids are not the only particles with an anisotropic polarizability; in fact, all the expressions above for cross sections are valid regardless of the origin of the anisotropy provided that there exists a coordinate system in which the polarizability tensor is diagonal.

Up to this point we have restricted consideration to materials for which the dielectric function is a scalar. However, except for amorphous materials and crystals with cubic symmetry, the dielectric function is a tensor; therefore, the constitutive relation connecting **D** and **E** is

$$\begin{pmatrix} D_x \\ D_y \\ D_z \end{pmatrix} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}. \tag{5.46}$$

Let us consider a sphere composed of a material described by the constitutive relation (5.46). We assume that the principal axes of the real and imaginary parts of the permittivity tensor coincide; this condition is not necessarily satisfied except for crystals with at least orthorhombic symmetry (Born and Wolf, 1965, p. 708). If we take as coordinate axes the principal axes of the permittivity tensor, the constitutive relation (5.46) in the sphere is

$$D_{1x} = \varepsilon_{1,1} E_{1x}, \qquad D_{1y} = \varepsilon_{1,2} E_{1y}, \qquad D_{1z} = \varepsilon_{1,3} E_{1z}.$$

As before, the potential in the surrounding medium, which is taken to be isotropic, is the sum of the potentials of the applied field and the perturbing field, both of which satisfy Laplace's equation. In the sphere we have

$$\mathbf{E}_1 = -\nabla\Phi_1, \qquad \nabla \cdot \mathbf{D}_1 = 0.$$

If the applied field is parallel to one of the principal axes, the z axis, say, we might be tempted to guess, on the basis of previous experience, that the field in the sphere is uniform and parallel to the z axis:

$$\Phi_1 = C_1 z = C_1 r\cos\theta \qquad (r < a);$$

therefore, the divergence of $\mathbf{D}_1$ vanishes as required. We can show by direct substitution that

$$\Phi_2 = -E_0 r\cos\theta + C_2\frac{\cos\theta}{r^2} \qquad (r > a)$$

is a solution to Laplace's equation and, moreover, that Φ and D_r, the radial component of $\mathbf{D}$, are continuous if

$$C_1 = -\frac{\varepsilon_m}{\varepsilon_{1,3} + 2\varepsilon_m}E_0, \qquad C_2 = a^3\frac{\varepsilon_{1,3} - \varepsilon_m}{\varepsilon_{1,3} + 2\varepsilon_m}E_0.$$

Therefore, the polarizability when the field is applied along the z axis is

$$\alpha_3 = 4\pi a^3\frac{\varepsilon_{1,3} - \varepsilon_m}{\varepsilon_{1,3} + 2\varepsilon_m}.$$

Similar expressions are obtained for the polarizabilities when the field is applied along the other two principal axes.

It is interesting to compare and contrast an isotropic ellipsoid and an anisotropic sphere; the polarizability of both particles is a tensor, the principal values of which are

$$\alpha_j^e = 4\pi abc\frac{\varepsilon_1 - \varepsilon_m}{3\varepsilon_m + 3L_j(\varepsilon_1 - \varepsilon_m)} \qquad \textit{isotropic ellipsoid}$$

$$\alpha_j^s = 4\pi a^3\frac{\varepsilon_{1,j} - \varepsilon_m}{\varepsilon_{1,j} + 2\varepsilon_m} \qquad \textit{anisotropic sphere}$$

Although there are similarities between the two types of particle, they are not completely equivalent: given an anisotropic sphere in a particular medium, there does not exist, in general, an equal volume ellipsoid with the same polarizability. That this is so is evident from the fact that *six* parameters, the real and imaginary parts of the $\varepsilon_{1,j}$, determine the polarizability tensor of the sphere, whereas only *four* parameters, the real and imaginary parts of ε_1 together with two geometrical factors, determine the polarizability tensor of the ellipsoid. In the special case of a nonabsorbing sphere or when two principal values of the permittivity tensor are equal an isotropic ellipsoid can be found—on paper, at least—with the same polarizability tensor.

It is not difficult to generalize the results of this section to an anisotropic ellipsoid the axes of which coincide with the principal axes of its permittivity tensor. The principal values of the polarizability tensor of such a particle are

$$\alpha_j = 4\pi abc \frac{\varepsilon_{1,j} - \varepsilon_m}{3\varepsilon_m + 3L_j(\varepsilon_{1,j} - \varepsilon_m)}.$$

More general ellipsoidal particles in an anisotropic *medium*, where there is no restriction on the principal axes of either the real or imaginary parts of the permittivity tensors, have been treated by Jones (1945).

5.7 SCATTERING MATRIX

The proof is lengthy, but it follows from (5.16), (5.37), and (5.42) that the amplitude scattering matrix elements (3.12) for an anisotropic dipole are

$$\begin{aligned}
S_1 &= \frac{-ik^3}{4\pi}\left(\alpha_{11}\sin^2\phi - 2\alpha_{12}\sin\phi\cos\phi + \alpha_{22}\cos^2\phi\right),\\
S_2 &= \frac{-ik^3}{4\pi}\left[\cos\theta\left(\alpha_{11}\cos^2\phi + 2\alpha_{12}\sin\phi\cos\phi + \alpha_{22}\sin^2\phi\right)\right.\\
&\qquad \left. -\sin\theta\left(\alpha_{13}\cos\phi + \alpha_{23}\sin\phi\right)\right],\\
S_3 &= \frac{-ik^3}{4\pi}\left\{\cos\theta\left[\alpha_{11}\sin\phi\cos\phi + \alpha_{12}\left(\sin^2\phi - \cos^2\phi\right)\right.\right.\\
&\qquad \left.\left. -\alpha_{22}\sin\phi\cos\phi\right] - \sin\theta\left(\alpha_{13}\sin\phi - \alpha_{23}\cos\phi\right)\right\}, \qquad (5.47)\\
S_4 &= \frac{-ik^3}{4\pi}\left[\alpha_{11}\sin\phi\cos\phi + \alpha_{12}\left(\sin^2\phi - \cos^2\phi\right) - \alpha_{22}\sin\phi\cos\phi\right],
\end{aligned}$$

where

$$\alpha_{ij} = \alpha_{ji} = \sum_{k=1}^{3} \alpha_k a_{ki} a_{kj}$$

are the components of the polarizability tensor in the coordinate system fixed relative to the incident beam [see (5.43)].

The scattering matrix elements S_{ij} corresponding to (5.47) can be obtained from (3.16). However, of possibly greater interest than the most general scattering matrix is that for a collection of identical, but randomly oriented, anisotropic dipoles; this scattering matrix is proportional to $\mathfrak{N}\langle S_{ij}\rangle$, where $\mathfrak{N}$ is the number of dipoles per unit volume and $\langle S_{ij}\rangle$ are the scattering matrix elements for a single anisotropic dipole averaged over all orientations. The $\langle S_{ij} \rangle$ are independent of the azimuthal angle ϕ; therefore, we can save ourselves a good bit of labor by choosing $\phi = 90°$ in (5.47) before computing the matrix elements (3.16) and performing the required averaging. A complete derivation of the average scattering matrix is less formidable than it might seem at first glance, but it is time consuming and best left to a long winter's evening. Most of the effort is bookkeeping; however, there are a few essential steps, which we outline in the following paragraphs.

The S_{ij} are of second degree in α_{kl} and hence of fourth degree in a_{mn}. Thus, we must calculate averages of the form $\langle a_{ij} a_{kl} a_{mn} a_{pq} \rangle$, many of which either vanish or are identical because of symmetry. If we assume that all orientations are equally probable, as in Section 5.5, then

$$\langle a_{11}^4 \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \cos^4\beta \sin\beta \, d\beta \, d\nu = \frac{1}{5}.$$

However, designating coordinate axes as x, y, z and so on, is arbitrary; therefore, the various averages must be invariant with respect to relabeling axes. Thus, it follows that $\langle a_{ij}^4 \rangle = \frac{1}{5}$ for all i and j. From the orthogonality of the transformation (5.41) we have

$$\sum_{k=1}^{3} a_{ki} a_{kj} = \sum_{k=1}^{3} a_{ik} a_{jk} = \delta_{ij}, \tag{5.48}$$

where δ_{ij}, the Kronecker delta, is 0 if $i \neq j$ and 1 otherwise. It follows from (5.48) that

$$\langle a_{11}^2 a_{21}^2 \rangle + \langle a_{11}^2 a_{31}^2 \rangle = \langle a_{11}^2 \rangle - \langle a_{11}^4 \rangle = \tfrac{2}{15}.$$

But again, by symmetry, $\langle a_{11}^2 a_{31}^2 \rangle = \langle a_{11}^2 a_{21}^2 \rangle = \langle a_{mj}^2 a_{nj}^2 \rangle = \langle a_{jm}^2 a_{jn}^2 \rangle = 1/15$, where j is not equal to both m and n. We also have $a_{11}a_{12} + a_{22}a_{21} + a_{31}a_{32} = 0$ from (5.48); therefore,

$$\langle a_{11}a_{12}a_{22}a_{21} \rangle + \langle a_{22}a_{21}a_{31}a_{32} \rangle = -\langle a_{22}^2 a_{21}^2 \rangle = -\tfrac{1}{15},$$

and by symmetry

$$\langle a_{11}a_{12}a_{22}a_{21} \rangle = \langle a_{22}a_{21}a_{31}a_{32} \rangle = -\tfrac{1}{30}.$$

Similarly, any average that can be obtained from $\langle a_{11}a_{12}a_{22}a_{21} \rangle = \langle (\hat{\mathbf{e}}_x \cdot \hat{\mathbf{e}}_{x'})(\hat{\mathbf{e}}_x \cdot \hat{\mathbf{e}}_{y'})(\hat{\mathbf{e}}_y \cdot \hat{\mathbf{e}}_{x'})(\hat{\mathbf{e}}_y \cdot \hat{\mathbf{e}}_{y'}) \rangle$ by relabeling axes is equal to $-\frac{1}{30}$. If we recall that $a_{12} = \hat{\mathbf{e}}_x \cdot \hat{\mathbf{e}}_{y'}$, $a_{13} = \hat{\mathbf{e}}_x \cdot \hat{\mathbf{e}}_{z'}$, and $\hat{\mathbf{e}}_x = \cos\beta \hat{\mathbf{e}}_{x'} + \sin\beta \cos\nu \hat{\mathbf{e}}_{y'} + \sin\beta \sin\nu \hat{\mathbf{e}}_{z'}$, then

$$\langle a_{12}^3 a_{13} \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \sin^4\beta \sin\beta \cos^3\nu \sin\nu \, d\beta \, d\nu = 0, \tag{5.49}$$

and similarly for all equivalent averages. From (5.48) and symmetry we have $\langle a_{12}a_{13}\rangle = \langle a_{23}a_{22}\rangle = \langle a_{33}a_{32}\rangle = 0$, from which, together with (5.49), it follows that $\langle a_{12}^2 a_{23}a_{22}\rangle = 0$. The only remaining averages are those of the form $\langle a_{11}a_{13}a_{21}a_{22}\rangle$, which can readily be shown to vanish. Thus, in the expressions for the average matrix elements $\langle S_{ij}\rangle$, the only nonvanishing terms quadratic in the α_{kl} are the following:

$$\begin{aligned}
\left\langle |\alpha_{11}|^2 \right\rangle &= \left\langle |\alpha_{22}|^2 \right\rangle = \tfrac{1}{5}\left(|\alpha_1|^2 + |\alpha_2|^2 + |\alpha_3|^2\right) \\
&\qquad + \tfrac{2}{15}\mathrm{Re}\{\alpha_1^*\alpha_2 + \alpha_1^*\alpha_3 + \alpha_2^*\alpha_3\}, \\
\left\langle |\alpha_{12}|^2 \right\rangle &= \left\langle |\alpha_{23}|^2 \right\rangle = \left\langle |\alpha_{13}|^2 \right\rangle \\
&= \tfrac{1}{15}\left(|\alpha_1|^2 + |\alpha_2|^2 + |\alpha_3|^2\right) - \tfrac{1}{15}\mathrm{Re}\{\alpha_1^*\alpha_2 + \alpha_2^*\alpha_3 + \alpha_1^*\alpha_3\}, \\
\langle \alpha_{11}\alpha_{22}^* \rangle &= \tfrac{1}{15}\left(|\alpha_1|^2 + |\alpha_2|^2 + |\alpha_3|^2\right) + \tfrac{4}{15}\mathrm{Re}\{\alpha_1^*\alpha_2 + \alpha_2^*\alpha_3 + \alpha_1^*\alpha_3\}.
\end{aligned} \tag{5.50}$$

All the essential ingredients for calculating the average scattering matrix for a randomly oriented anisotropic dipole are now at hand. From the relations (5.50), after a good bit of algebra, we obtain

$$\begin{pmatrix} I_s \\ Q_s \\ U_s \\ V_s \end{pmatrix} = \frac{1}{k^2 r^2} \begin{pmatrix} \langle S_{11}\rangle & \langle S_{12}\rangle & 0 & 0 \\ \langle S_{12}\rangle & \langle S_{22}\rangle & 0 & 0 \\ 0 & 0 & \langle S_{33}\rangle & 0 \\ 0 & 0 & 0 & \langle S_{44}\rangle \end{pmatrix} \begin{pmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{pmatrix},$$

$$\begin{aligned}
\langle S_{11}\rangle &= \frac{3k^2\langle C_{\mathrm{sca}}\rangle}{8\pi}\frac{1}{2}\left(\frac{6-M}{5} + \frac{2+3M}{5}\cos^2\theta\right), \\
\langle S_{12}\rangle &= \frac{3k^2\langle C_{\mathrm{sca}}\rangle}{8\pi}\frac{1}{2}(\cos^2\theta - 1)\frac{2+3M}{5}, \\
\langle S_{22}\rangle &= \frac{3k^2\langle C_{\mathrm{sca}}\rangle}{8\pi}\frac{1}{2}(\cos^2\theta + 1)\frac{2+3M}{5}, \\
\langle S_{33}\rangle &= \frac{3k^2\langle C_{\mathrm{sca}}\rangle}{8\pi}\frac{2+3M}{5}\cos\theta, \\
\langle S_{44}\rangle &= \frac{3k^2\langle C_{\mathrm{sca}}\rangle}{8\pi}M\cos\theta,
\end{aligned} \tag{5.51}$$

where the average scattering cross section $\langle C_{\mathrm{sca}}\rangle$ was derived in Section 5.5;

the ratio

$$M = \frac{\mathrm{Re}\{\alpha_1^*\alpha_2 + \alpha_1^*\alpha_3 + \alpha_2^*\alpha_3\}}{|\alpha_1|^2 + |\alpha_2|^2 + |\alpha_3|^2} \tag{5.52}$$

satisfies the inequality $-\frac{1}{2} \leqslant M \leqslant 1$. For an isotropic dipole the α_j are all equal, $M = 1$, and (5.51) reduces to (5.5).

If the incident light is unpolarized, the Stokes parameters of the scattered light are $I_s = \langle S_{11}\rangle$, $Q_s = \langle S_{12}\rangle$, $U_s = V_s = 0$. Thus, the scattered light is partially polarized of degree P:

$$P = \frac{-\langle S_{12}\rangle}{\langle S_{11}\rangle} = \frac{1 - \cos^2\theta}{\dfrac{6 - M}{2 + 3M} + \cos^2\theta}. \tag{5.53}$$

P is positive for all scattering angles θ and all allowed values of M; therefore, the scattered light is partially polarized perpendicular to the scattering plane. The maximum degree of polarization occurs at $\theta = 90°$:

$$P(90°) = \frac{2 + 3M}{6 - M} \tag{5.54}$$

and lies between $\frac{1}{13}$ and 1, depending on the value of M. Unlike scattering by an isotropic sphere small compared with the wavelength, light scattered by a collection of randomly oriented anisotropic dipoles is not 100% polarized at 90°. This anisotropy effect is, in part, responsible for the lack of complete polarization of scattered skylight viewed normally to the direction of the sun: the molecules responsible for the scattering are not spherically symmetrical.