# INHERENT OPTICAL PROPERTIES OF NON-SPHERICAL MARINE-LIKE PARTICLES — FROM THEORY TO OBSERVATION

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**Abstract** *In situ* measurements of inherent optical properties (IOPs) of aquatic particles show great promise in studies of particle dynamics. Successful application of such methods requires an understanding of the optical properties of particles. Most models of IOPs of marine particles assume that particles are spheres, yet most of the particles that contribute significantly to the IOPs are non-spherical. Only a few studies have examined optical properties of non-spherical aquatic particles. The state-of-the-art knowledge regarding IOPs of non-spherical particles is reviewed here and exact and approximate solutions are applied to model IOPs of marine-like particles. A comparison of model results for monodispersions of randomly oriented spheroids to results obtained for equal-volume spheres shows a strong dependence of the biases in the IOPs on particle size and shape, with the greater deviation occurring for particles much larger than the wavelength. Similarly, biases in the IOPs of polydispersions of spheroids are greater, and can be higher than a factor of two, when populations of particles are enriched with large particles. These results suggest that shape plays a significant role in determining the IOPs of marine particles, encouraging further laboratory and modelling studies on the effects of particle shape on their optical properties.

## Introduction

Recent advances in optical sensor technology have opened new opportunities to study biogeochemical processes in aquatic environments at spatial and temporal scales that were not possible before. Optical sensors are capable of sampling at frequencies that match the sub-metre and sub-second sampling scales of physical variables such as temperature and salinity and can be used in a variety of ocean-observing platforms including moorings, drifter buoys, and autonomous vehicles. *In situ* measurements of inherent optical properties (IOPs) such as absorption, scattering, attenuation and fluorescence reveal information on the presence, concentration and composition of particulate and dissolved material in the ocean. Variables such as organic carbon, chlorophyll-*a*, dissolved organic material, nitrate and total suspended matter, among others, are now estimated routinely from IOPs (e.g., Twardowski et al. 2005). Retrieval of seawater constituents from *in situ* (bulk) IOP measurements is not a straightforward problem — aquatic systems are complex mixtures of particulate and dissolved material, of which each component has specific absorption, scattering and fluorescence characteristics. *In situ* IOP measurements provide a measure of the sum of the different properties of all individual components present in the water column. Interpretation of optical data and its

successful application to studies of biogeochemical processes thus requires an understanding of the relationships between the different biogeochemical constituents, their optical characteristics and their contribution to bulk optical properties.

Suspended organic and inorganic particles play an important role in mediating biogeochemical processes and significantly affect IOPs of aquatic environments, as can be attested from images taken from air- and space-borne platforms of the colour of lakes and oceans where phytoplankton blooms and suspended sediment have a strong impact (e.g., Pozdnyakov & Grassl 2003). Interactions of suspended particles with light largely depend on the physical characteristics of the particles, such as size, shape, composition and internal structure (e.g., presence of vacuoles). Optical characteristics of marine particles have been studied since the early 1940s (summarised by Jerlov 1968) and, with an increased pace, since the 1970s (e.g., Morel 1973, Jerlov 1976). In the past decade, development of commercial *in situ* optical sensors and the launch of several successful ocean-colour missions have accelerated the efforts to understand optical characteristics of marine particles, in particular the backscattering coefficient because of its direct application to remote sensing (e.g., Boss et al. 2004). These efforts, which have focused on both the theory and measurement of IOPs of particles, are summarised in books, book chapters and review articles on this topic (Shifrin 1988, Stramski & Kiefer 1991, Kirk 1994, Mobley 1994, Stramski et al. 2004, Jonasz & Fournier 2007, and others).

Although considerable effort has been given to the subject of marine particles and their IOPs, there is still a gap between theory and the reality of measurement. Such a gap is attributed to both instrumental limitations (e.g., Jerlov 1976, Roesler & Boss 2007) and simplifying assumptions used in theoretical and empirical models (e.g., Stramski et al. 2001). The majority of theoretical investigations on the IOPs of marine particles assume that particles are homogeneous spheres. Optical properties of homogeneous spheres are well characterised (see Mie theory in, e.g., Kerker 1969, van de Hulst 1981) and there is good agreement between theory and measurement for such particles. Mie theory has been used to model IOPs of aquatic particles (e.g., Stramski et al. 2001) and in retrieving optical properties of oceanic particles (e.g., Bricaud & Morel 1986, Boss et al. 2001, Twardowski et al. 2001) with varying degrees of success. For example, while phytoplankton and bacteria dominate total scattering in the open ocean, based on Mie theory calculations for homogeneous spheres, they account for only a small fraction (<20%) of the measured backscattering (referred to as the 'missing backscattering enigma', Stramski et al. 2004). Uncertainties in the backscattering efficiencies of phytoplankton cells due to shape effects, however, are not well constrained and may account for a portion of this 'missing' backscattering.

A sphere is not likely to be a good representative of the shape of the 'average' aquatic particle for two main reasons: (1) the majority of marine particles are not spherical, and (2) of all the convex shapes a sphere is rather an extreme shape: for a given particle volume it has the smallest surface-area-to-volume ratio. Only a limited number of studies have examined the IOPs of non-spherical marine particles and results indicate a strong dependence of optical properties, in particular scattering, on shape (Aas 1984, Voss & Fry 1984, Jonasz 1987b, Volten et al. 1998, Gordon & Du 2001, Herring 2002, MacCallum et al. 2004, Quirantes & Bernard 2004, 2006, Gordon 2006). Unfortunately, with the exception of two, non-peer-reviewed publications (Aas 1984, Herring 2002) and a short book chapter (Jonasz 1991), there is no published methodical evaluation of shape effects on IOPs in the context of marine particles.

The goal of this review is to provide a systematic evaluation of the effects of particle shape on the IOPs of marine particles, bringing together knowledge gained in ocean optics and other relevant fields. While it is recognised that marine particles (in particular, living cells) are not necessarily homogeneous, the focus in this article, for the sake of simplicity and due to limitations in available analytical and numerical solutions, is on the significance of the deviation from sphericity by homogeneous particles. A survey of theoretical and experimental studies on the IOPs of



**Figure 1** Illustration of spheroids of different aspect ratios, s/t; oblate spheroids (s/t < 1) and prolate spheroids (s/t < 1). A sphere is a spheroid with an aspect ratio of one.

non-spherical homogeneous particles addressing the wide range of particle sizes and indices of refraction relevant to aquatic systems is presented here. Exact analytical solutions are available for a limited number of shapes and physical characteristics (e.g., cylinders and concentric spheres larger than the wavelength and with an index of refraction similar to the medium, Aas 1984), but advances in computational power have enabled the growth of numerical and approximate techniques that permit calculations for a wider range of particle shapes and sizes (Mishchenko et al. 2000 and references therein). It is not realistic to develop a model for all possible shapes of marine particles but in order to cover the range of observed shapes, from elongated to squat geometries, a simple and smooth family of shapes — spheroids — is used here to model particles. Spheroids are ellipsoids with two equal equatorial axes and a third axis being the axis of rotation. The ratio of the axis of rotation, s, to an equatorial axis, t, is the aspect ratio, s/t, of a spheroid (Figure 1). The family of spheroids include oblate spheroids (s/t < 1; disc-like bodies), prolate spheroids (s/t > 1; cigar-shaped bodies), and spheres (s/t = 1). Spheroids provide a good approximation to the shape of phytoplankton and other planktonic organisms that often dominate the IOP signal. Furthermore, by choosing spheroids of varying aspect ratios as a model, solutions for elongated and squat shapes can easily be compared with solutions for spheres and the biases associated with optical models that are based on spheres can be quantified. This review focuses on marine particles because the vast majority of studies on IOPs of aquatic particles have been done in the marine context. However, the results presented here apply to particles in any other aquatic environment.

## Bulk inherent optical properties (IOPs)

## Definitions

Inherent optical properties (IOPs) refer to the optical properties of the aquatic medium and its dissolved and particulate constituents that are independent of ambient illumination. To set the stage for an IOP model of non-spherical particles, a brief description of the parameters that define the IOPs of particles is given here. For a more extensive elaboration on IOPs, the reader is referred to Jerlov (1976), van de Hulst (1981), Bohren & Huffman (1983) and Mobley (1994). Most of the notation used in this review follows closely that used by the ocean optics community (e.g., Mobley

1994). A summary of the notation along with their definitions and units of measure is provided in the Appendix (see p. 37).

Light interacting with a suspension of particles can either be transmitted (remain unaffected) or attenuated due to absorption (transformed into other forms of energy, e.g., chemical energy in the case of photosynthesis) and due to scattering (redirected). Neglecting fluorescence, the two fundamental IOPs are the absorption coefficient,  $a(\lambda)$ , and the volume scattering function (VSF),  $\beta(\theta,\lambda)$ , where  $\lambda$  is the incident wavelength and  $\theta$  is the scattering angle. All other IOPs discussed here can be derived from these two IOPs. Other IOPs not discussed in the current review include the polarisation characteristics of scattering and fluorescence. While all quantities are wavelength dependent, the notation is henceforth ignored for compactness.

The absorption coefficient, *a*, describes the rate of loss of light propagating as a plane wave due to absorption. According to the Beer-Lambert-Bouguer law (e.g., Kerker 1969, Shifrin 1988), the loss of light in a purely absorbing medium follows (Equation 11.1 in Bohren & Huffman 1983):

$$E(R) = E(0)e^{-aR} [W m^{-2} nm^{-1}], \qquad (1)$$

where E(R) is the incident irradiance at a distance R from the light source with irradiance E(0) [W m<sup>-2</sup> nm<sup>-1</sup>]. The light source and detector are assumed to be small compared with the path length and the light is plane parallel and well collimated. The absorption coefficient, *a*, is thus computed from

$$a = -\left(\frac{1}{R}\right) \ln\left[\frac{E(R)}{E(0)}\right] [\mathrm{m}^{-1}].$$
<sup>(2)</sup>

This equation reveals that the loss of light due to absorption is a function of the path length and that the decay along that path is exponential. In a scattering *and* absorbing medium, such as natural waters, the measurement of absorption requires the collection of *all* the scattered light (e.g., using a reflecting sphere or tube).

The volume scattering function (VSF),  $\beta(\Psi)$ , describes the angular distribution of light scattered by a suspension of particles toward the direction  $\Psi$  [rad]. It is defined as the radiant intensity,  $dI(\Omega)$ [W sr<sup>-1</sup> nm<sup>-1</sup>] ( $\Omega$  [sr] being the solid angle), emanating at an angle  $\Psi$  from an infinitesimal volume element dV [m<sup>3</sup>] for a given incident irradiant intensity, E(0):

$$\beta(\Psi) = \frac{1}{E(0)} \frac{dI(\Omega)}{dV} [m^{-1} \text{sr}^{-1}].$$
(3)

It is often assumed that scattering is azimuthally symmetric so that  $\beta(\Psi) = \beta(\theta)$ , where  $\theta$  [rad] is the angle between the initial direction of light propagation and that to which the light is scattered irrespective of azimuth. The assumption of azimuthal symmetry is valid for spherical particles or randomly oriented non-spherical particles. This assumption is most likely valid for the turbulent aquatic environment of interest here; it is assumed throughout this review and is further addressed in the following discussion.

A measure of the overall magnitude of the scattered light, without regard to its angular distribution, is given by the scattering coefficient, b, which is the integral of the VSF over all  $(4\pi[sr])$  angles:

$$b \equiv \int_{0}^{4\pi} \beta(\Psi) d\Omega = \int_{0}^{2\pi} \int_{0}^{\pi} \beta(\theta, \phi) \sin \theta d\theta d\phi = 2\pi \int_{0}^{\pi} \beta(\theta) \sin \theta d\theta \, [m^{-1}], \qquad (4)$$

where  $\varphi$  [rad] is the azimuth angle. Scattering is often described by the phase function,  $\beta(\theta)$ , which is the VSF normalised to the total scattering. It provides information on the shape of the VSF regardless of the intensity of the scattered light:

$$\tilde{\beta}(\theta) \equiv \frac{\beta(\theta)}{b} [\mathrm{sr}^{-1}].$$
(5)

Other parameters that define the scattered light include the backscattering coefficient,  $b_b$ , which is defined as the total light scattered in the hemisphere from which light has originated (i.e., scattered in the backward direction):

$$b_b \equiv \int_0^{2\pi} \beta(\Psi) d\Omega = 2\pi \int_{\frac{\pi}{2}}^{\pi} \beta(\theta) \sin \theta d\theta \, [m^{-1}], \qquad (6)$$

and the backscattering ratio, which is defined as

$$\tilde{b} \equiv \frac{b_b}{b} \text{ [dimensionless].}$$
(7)

Finally, the attenuation coefficient, *c*, describes the total rate of loss of a collimated, monochromatic light beam due to absorption and scattering:

$$c = a + b [m^{-1}],$$
 (8)

which is the coefficient of attenuation in the Beer-Lambert-Bouguer law (see Equation 1) in an absorbing and/or scattering medium (Bohren & Huffman 1983):

$$E(R) = E(0)e^{-cR} [W m^{-2} nm^{-1}].$$
(9)

When describing the interaction of light with individual particles it is convenient to express a quantity with dimensions of area known as the optical cross section. An optical cross section is the product of the geometric cross section of a particle and the ratio of the energy attenuated, absorbed, scattered or backscattered by that particle to the incident energy projected on an area that is equal to its cross-sectional area (denoted by  $C_c$ ,  $C_a$ ,  $C_b$  and  $C_{b_b}$ , respectively). For a non-spherical particle, the cross-sectional area perpendicular to the light beam, G [m<sup>2</sup>], depends on its orientation. In the case when particles are randomly oriented, as assumed here, it has been found that for convex particles (such as spheroids) the average cross-sectional area perpendicular to the beam of light (here denoted as  $\langle G \rangle$ ) is one-fourth of the surface area of the particle (Cauchy 1832).

In analogy to the IOPs (Equation 8), the attenuation cross section is equal to the sum of the absorption and scattering cross sections:

$$C_c = C_a + C_b [\mathrm{m}^2]. \tag{10}$$

Many theoretical texts on optics focus on optical efficiency factors,  $Q_{c,a,b,b_b}$ , in their treatment of light interaction with particles (e.g., van de Hulst 1981). Optical efficiency factors are the ratios of the optical cross sections to the particle cross-sectional area; their appeal is in that efficiency factors of compact particles are bounded (i.e., their values rarely exceed three) and their values for particles much larger than the wavelength are constant and independent of composition (see below). For non-spherical particles efficiency factors for attenuation, absorption, scattering and backscattering, respectively, are defined as (e.g., Mishchenko et al. 2002):

$$Q_{c,a,b,b_b} \equiv \frac{C_{c,a,b,b_b}}{\langle G \rangle} \text{ [dimensionless].}$$
(11)

Other useful optical parameters are the volume-normalised cross sections defined as:

$$\alpha_{c,a,b,b_b} \equiv \frac{C_{c,a,b,b_b}}{V} \, [\mathrm{m}^{-1}] \,, \tag{12}$$

where  $V[m^{-3}]$  is the particle volume; they provide insight into what size particle most effectively affects light per unit volume (or per unit mass, see Bohren & Huffman 1983, and Figure 6 in Boss et al. 2001).

To relate IOPs to optical cross sections, efficiency factors and volume-normalised cross sections, information on particle concentration (and size distribution, see below) is required. For example, for N identical particles within a unit volume, the relations are given by:

$$c,a,b,b_b = NC_{c,a,b,b_b} = N\langle G \rangle Q_{c,a,b,b_b} = NV\alpha_{c,a,b,b_b} [m^{-1}].$$
(13)

## Characteristics of particles affecting their optical properties

Three physical characteristics of homogeneous particles determine their optical properties: the complex index of refraction relative to the medium in which the particle is immersed, the size of the particle with respect to the wavelength of the incident light and the shape of the particle. For non-spherical particles, specifying the orientation of the particle in relation to the light beam is an additional requirement. To continue to set the stage for an optical model for non-spherical particles, the physical characteristics of marine particles are discussed in this section and the values that are used to parameterise them in the current study are provided.

## Index of refraction

The complex index of refraction comprises real, *n*, and imaginary, *k*, parts:

$$m = n + ik \,[\text{dimensionless}]\,. \tag{14}$$

The real part is proportional to the ratio of the speed of light within a reference medium to that within the particle. It is convenient to choose the reference medium to be that in which the particle is immersed, in which case the proportionality constant is one. The imaginary part of the index of refraction (referred to as the absorption index, e.g., Kirk 1994) represents the absorption of light

as it propagates through the particle. It is proportional to the absorption by the intra-particle material,  $\alpha^*[nm^{-1}]$ :

$$k = \frac{\alpha^* \lambda}{4\pi} \text{[dimensionless]}.$$
 (15)

These definitions are independent of particle shape.

For purposes of biogeochemical and optical studies it is often convenient to group aquatic particles into organic and inorganic pools. Organic particles comprise living (viruses, bacteria, phytoplankton and zooplankton) and non-living material (faecal pellets, detritus; although these are likely to harbour bacteria). Inorganic particles consist of lithogenous minerals (quartz, clay and other minerals) and minerals associated with biogenic activity (calcite, aragonite and siliceous particles). Particles in each of these two main groups share similar characteristics with respect to their indices of refraction. Living organic particles often have a large water content (Aas 1996), making them less refractive than inorganic particles. The real part of the index of refraction of aquatic particles ranges from 1.02 to 1.2; the lower range is associated with organic particles while the upper range is associated with highly refractive inorganic materials (Jerlov 1968, Morel 1973, Carder et al. 1974, Aas 1996, Twardowski et al. 2001). The imaginary part of the index of refraction spans from nearly zero to 0.01, with the latter associated with strongly absorbing bands due to pigments (e.g., Morel & Bricaud 1981, Bricaud & Morel 1986). This review aims to primarily illustrate the effects of shape as it applies to two 'representative' particle types: phytoplankton with m = 1.05 + i0.01 and inorganic particles with m = 1.17 + i0.0001 (Stramski et al. 2001). Varying the real and imaginary parts of the index of refraction among the values of the two illustrative particles chosen here showed similar dependence on changes in index of refraction to those observed in spheres (van de Hulst 1981, Herring 2002) and was not found to provide additional insight into the effects of shape on IOPs.

## Size

Size is a fundamental property of particles that determines sedimentation rates, mass transfer to and from the particle (e.g., nutrient fluxes and dissolution), encounter rates between particles and, most relevant to this review, their optical properties. Foremost, the ratio of particle size to wavelength determines the resonance characteristics of the VSF (its oscillatory pattern as a function of scattering angle) and the size for which maximum scattering per volume will occur (i.e., maximum  $\alpha_b$ ). In addition, in general, the larger an absorbing particle is, the less efficient it becomes in absorbing light per unit volume (i.e., the volume-normalised absorption efficiency,  $\alpha_a$ , decreases with increasing size), often referred to as the package effect or self-shading (see Duysens 1956).

In both marine and freshwater environments particles relevant to optics span at least eight orders of magnitude in size, ranging from sub-micron particles (colloids and viruses) to centimetresize aggregates and zooplankton (Figure 2). Numerically, small particles are much more abundant than larger particles. A partitioning of particles into logarithmic size bins shows that each bin includes approximately the same volume of particulate material (Sheldon et al. 1972). This observation is consistent with a Junge-like (power-law) particulate size distribution (PSD), where the differential particle number concentration is inversely proportional to the fourth power of size (Junge 1963, Morel 1973; see p. 22).

Several other distribution functions have been used to represent size distributions of particles in the ocean, which include the log-normal distribution (Jonasz 1983, Shifrin 1988, Jonasz & Fournier 1996), the Weibull distribution (Carder et al. 1971), the gamma distribution (Shifrin 1988)



**Figure 2** Representative sizes of different constituents in sea-water, after Stramski et al (2004). Optical regions referred to in the text are denoted at the top axis (shading represents approximate boundaries between these regions). These boundaries vary with refractive index for a given particle size.

and sums of log-normal distributions (Risoviç 1993). Here, the focus is on particles ranging in diameter from 0.2 to 200  $\mu$ m (diameter here is given by that of an equal-volume sphere). The lower bound is associated with a common operational cutoff between dissolved and particulate material — often set by a filter with that pore size — and the upper bound chosen arbitrarily to represent the upper bound of particles that can still be assumed to be distributed as a continuum in operational measurements (Siegel 1998). Two particulate size distributions are adopted (as in Twardowski et al. 2001) for the illustrative optical model used in this study: the power-law distribution and that described by Risoviç (1993).

### Shape

Several measures have been used to characterise the shape of particles in nature; some focus on the overall shape while others concentrate on specific features such as roundness and compactness. An elementary measure of particle shape is the aspect ratio, which is the ratio of the principal axes of a particle. It describes the elongation or flatness of a particle and hence the deviation from a spherical shape (a sphere having an aspect ratio of one). Shape effects on optical properties are examined here by modelling the IOPs of spheroids of varying aspect ratios.

Aquatic particles vary greatly in their shape; most notable is the striking diversity in cell shapes among phytoplankton. Hillebrand et al. (1999) provides a comprehensive survey of geometric models for phytoplankton species from 10 taxa. Two relevant results arise from their analysis: (1) the sphere is not a common shape among microphytoplankton taxa and (2) despite the apparent high diversity of cell geometries, the diverse morphologies represent variations on a smaller subset of geometric forms, primarily ellipsoids, spheroids and cylinders. Picoplankton, which are not included in the analysis of Hillebrand et al. (1999), tend to be more spherical in shape, although rod-like morphologies are also common.

The authors are not aware of any published paper that provides the range of values of aspect ratios of phytoplankton cells in natural assemblages. To demonstrate the deviation from a spherical shape among phytoplankton, field data on cell dimensions of different taxonomic groups (nanoand microphytoplankton) were used to calculate aspect ratios of phytoplankton (Figure 3; data available from the California State Department of Water Resources). Aspect ratios of phytoplankton span a wide range, varying between 0.4 and 72 (Figure 3). Diatom chains, which are not included in the analysis, can have even higher aspect ratios. The frequency distribution of the aspect ratios shows that elongated shapes are a more common form compared with spheres or squat shapes (Figure 3).

Inorganic aquatic particles are very often non-spherical; clay mineral particles have plate-like crystalline structures with sizes on the order of  $D = 0.5 \,\mu\text{m}$  and have aspect ratios varying between 0.05 and 0.3 (Jonasz 1987b, Bickmore et al. 2002). In nature, clays tend to aggregate and form larger particles with reduced aspect ratios. It is not possible to generalise their shapes except to say that they are extremely variable and do not look like spheres. Larger sedimentary particles such as sand and silt have aspect ratios ranging between 0.04 and 11 (derived from Komar & Reimers 1978, Baba & Komar 1981). Consistent with these observations, spheroids with aspect ratios between 0.1 and 46 are used in the analysis of IOPs of non-spherical particles presented here (98% of the cells that constitute the data in Figure 3 are within this range). Finer-scale structures that may be found in each particle do not dominate scattering, in general, as much as the effect of the



**Figure 3** Frequency distribution of aspect ratios of phytoplankton. Data are provided by the California State Department of Water Resources and the U.S. Bureau of Reclamation and are available on the Bay-Delta and Tributaries (BDAT) project website at http://baydelta.water.ca.gov/. A subset of the data was randomly selected for the analysis here and includes data collected during the period 2002–2003 from a variety of aquatic habitats: from freshwater in the Sacramento-San Joaquin Delta to estuarine environments in the Suisun and San Pablo Bays (California, USA). The data include phytoplankton from five different classes, including Bacillario-phyceae (diatoms), Chlorophyceae, Cryptophyceae, Dynophyceae, and Cyanophyceae (N = 8059 cells). Phytoplankton analyses (identification, counts, and measurements of cell dimensions) were conducted at the Bryte Chemical Laboratory (California Department of Water Resources). Further information on the methods used can be found at http://iep.water.ca.gov/emp/Metadata/Phytoplankton/. The aspect ratio is calculated as the ratio between the rotational and equatorial axes of a cell based on the three-dimensional shape associated with each species as provided in Hillebrand et al. (1999). The reader is cautioned on the fact that the phytoplankton data do not include picophytoplankton (i.e., cells smaller than 2  $\mu$ m) that tend to be more spherical in shape.

'gross' shape of the particle (Gordon 2006). Furthermore, Gordon (2006) found that, in theory, the total scattering of any curved shape (that is not rotationally symmetric) will behave similarly for a given particle thickness and cross-sectional area. However, when a particle exhibits sharp edges, smooth shapes are not able to reproduce the sharp spikes observed in the forward scattering (Macke & Mishchenko 1996).

To allow comparisons between spheroids and spheres, particle size is used as a reference. The definition of size is often ambiguous when dealing with non-spherical particles; here the size of a spheroid is defined as the diameter of an equal-volume sphere ( $D = 2\sqrt[3]{st^2}$ ). This was chosen for two main reasons: (1) popular particle sizers such as the Coulter counter are sensitive to particle volume and (2) mass, which is most often the property of interest in studies of particles, is proportional to particle volume. Size and shape, however, may not be independent attributes for aquatic particles. There appears to be a tendency for particles in ocean samples to deviate from a spherical shape as particle size increases (Jonasz 1987b). This trend has been observed for particles in both coastal (Baltic Sea) and offshore areas (Kadyshevich 1977, Jonasz 1987a). Shape effects on IOPs are examined here for two types of particulate populations: monodispersions (comprising particles with one size and one shape) and polydispersions (comprising particles with varying sizes and shapes) and are quantified by defining a bias,  $\gamma_{c,a,b,b_b}$ , which is the ratio of the IOPs (attenuation, absorption, scattering and backscattering, respectively) of spheroids to that of spheres with the same particle volume distribution.

#### Orientation

In this review particles are assumed to be randomly oriented. IOPs of non-spherical particles, however, are strongly dependent on particle orientation (e.g., Latimer et al. 1978, Asano 1979) but data on the orientation of particles found in the natural marine environment are practically non-existent. There are certain cases for which the assumption of random orientation may not apply because of methodological issues or because environmental conditions cause particles to align in a preferred orientation. Non-random orientation associated with methodology will be encountered when: (1) the instrument used to measure an IOP causes particles to orient themselves relative to the probing light beam (e.g., the flow cytometer in which particles are aligned one at a time within the flow chamber) and (2) when the existence of particles of a given sub-population (e.g., big diatom chains) is rare enough in the sample volume such that not all orientations are realised in a given measurement. In the latter case, averaging over many samples is necessary to randomise orientations.

In the natural environment, shear flows can result in the alignment of particles with respect to the flow (e.g., Karp-Boss & Jumars 1998). When the environment is quiescent enough, large aggregates are oriented by the force of gravity as can be seen in photographs of *in situ* long stringers and teardrop-shape flocs (e.g., Syvitski et al. 1995).

The following optical characteristics can be used to assess whether or not an ensemble of particles is randomly oriented (Mishchenko et al. 2002): (1) the attenuation, scattering and absorption coefficients are independent of polarisation and instrument orientation; (2) the polarised scattering matrix is block diagonal; and (3) the emitted blackbody radiation is unpolarised. Note that care should be applied so that the measurement procedures have minimal effect on the orientation of the particles investigated.

Given that the orientation of aquatic particles is currently unconstrained we proceed in this review by assuming random orientation. Future studies, however, may find orientation effects to be important under certain conditions as was found in atmospheric studies due, for example, to orientation of particles under gravity (e.g., Aydin 2000).

## **Optical regimes**

A century and a half of theoretical studies on the interaction of light and particles has taught us that this interaction is strongly dependent on several parameters. First among them is the size parameter, x, which is defined as the ratio of the particle size to the wavelength:

$$x = \pi \frac{D}{\lambda} \text{ [dimensionless]}, \tag{16}$$

where D is the particle size and  $\lambda$  is the wavelength of light within the medium (both with the same units), in this case water.

An additional important parameter is the ratio of the speed of light within the particle to that in the medium (it is the reciprocal of the real part of the index of refraction of the particle to that of water, *n*). Marine particles are mostly considered to be 'soft'; their index of refraction is close to that of water, that is,  $|m-1| \approx n-1 \ll 1$ .

Finally, another important parameter is the phase shift parameter,  $\rho$ , which describes the shift in phase between the wave travelling within the particle and the wave travelling in the medium surrounding it and is a function of both the size parameter and the index of refraction of that particle:

$$\rho = 2x(n-1) [\text{dimensionless}].$$
(17)

These parameters are useful to delineate optical regimes for which analytical approximations that apply to soft particles have been developed (see below). The material in this section borrows heavily from Bohren & Huffman (1983), Mishchenko et al. (2002) and Kokhanovsky (2003), where more details can be found. Many of the approximations discussed in these references are applicable to randomly oriented non-spherical particles (as in the case of marine particles) and help establish an intuition for their optical characteristics when compared with spheres. The characteristics of particles (size and index of refraction) most emphasised in Bohren & Huffman (1983), Mishchenko et al. (2002) and Kokhanovsky (2003), however, are significantly different from those of marine particles.

## Particles much smaller than the wavelength

## The Rayleigh region (RAY) ( $x \ll 1$ , $\rho \ll 1$ , $D \ll \lambda$ )

In this optical region shape does not contribute to the optical properties of particles; for a given wavelength, the IOPs are only dependent on particle volume and its index of refraction (e.g., Kerker 1969, Bohren & Huffman 1983, Kokhanovsky 2003):

$$\tilde{\beta}(\theta) = \frac{3\left[1 + \cos^2(\theta)\right]}{4} \text{ [dimensionless],}$$
(18)

$$C_{c} = \frac{k^{2}V^{2}\left|m^{2}-1\right|^{2}}{6\pi} [m^{2}], \qquad (19)$$

$$C_a = \frac{4\pi kV}{\lambda} \,[\mathrm{m}^2],\tag{20}$$

$$C_b = C_c - C_a \,[\mathrm{m}^2],$$
 (21)

$$C_{b_b} = \frac{C_b}{2} \,[\mathrm{m}^2],\tag{22}$$

where  $k = 2\pi/\lambda$  [nm<sup>-1</sup>] is the wave number. Since the IOPs are a function of only particle volume, incident wavelength and index of refraction (Equations 18–22), there is no difference between the IOPs of non-spherical particles and equal-volume spheres. In the marine environment, small organic and inorganic dissolved molecules fall within this regime.

## Particles of size much larger than the wavelength

### The geometric optics (GO) region $(x \gg 1, \rho \gg 100, D \gg \lambda)$

In this optical region scattering is dominated by diffraction although refraction effects introduce a necessary correction for intermediate values of the size parameter (known as 'edge effects', e.g., Kokhanovsky & Zege 1997). An analytical solution has been derived for the attenuation cross section of absorbing particles of random shape in this region (e.g., Kokhanovsky & Zege 1997) and is given by:

$$C_c = 2\left(1 + x^{-\frac{2}{3}}\right) \langle G \rangle [\text{m}^2].$$
<sup>(23)</sup>

The absorption cross section,  $C_a$ , can also be derived analytically. In general, it is a complex function of both parts of the index of refraction and x (e.g., Kokhanovsky & Zege 1997). For sizes where  $kx \gg 1$ , it simplifies to  $C_a = \langle G \rangle$ .

Within the GO region, these analytical solutions imply that the attenuation, absorption, and scattering (but not the VSF) of a randomly oriented non-spherical particle will be the same as that of a sphere of the same cross-sectional area, that is, it will approach the geometric optics limit (Kerker 1969):

$$\lim_{\rho \to \infty} \gamma_{c,a,b} = \frac{\langle G \rangle}{G} \ge 1.$$
(24)

Given that the average cross-sectional area of a sphere is always the smallest of any convex shape of the same volume, an equal-volume sphere will always underestimate the IOPs of particles much larger than the wavelength. The VSF in this regime for known shapes (including spheroids) can be obtained from ray tracing computations (see below). Particles that fall in this region in the marine environment include large diatom chains, large heterotrophs (e.g., *Noctiluca* sp.), meso-and macrozooplankton and macrosize aggregates, including faecal pellets.

## Particles of size comparable to or larger than the wavelength

*The Rayleigh-Gans-Debye (RGD)* (x < 1,  $\rho < 1$ ,  $D \approx \lambda$ ) and the van de Hulst (VDH) (x > 1,  $1 < \rho < 100$ ,  $D > \lambda$ ) regions

The RGD and VDH optical regions are of particular interest because many optically relevant marine particles (e.g., phytoplankton and sediments) fall within them. However, no simple closed-form analytical solution exists for randomly oriented non-spherical particles in these regions (Aas 1984).

Scattering by soft particles in the RGD and VDH regions is dominated by diffraction although contributions from reflection and refraction need to be taken into account. Absorption is assumed to be independent of the real part of the index of refraction, although more recent approximations have included *n* effects on absorption (Kokhanovsky & Zege 1997). Simple analytical solutions for  $C_c$ ,  $C_a$  and  $C_b$  have been derived for spheres and for some simple shapes by van de Hulst (1981) and Aas (1984). Shepelevich et al. (2001), following Paramonov (1994a,b), derive  $C_c$ ,  $C_a$  and  $C_b$ for randomly oriented monodispersed spheroids from a polydispersed population of spheres having the same volume and cross-sectional area. A similar approach is used here to examine the IOPs of non-spherical marine-like particles but, rather than follow Shepelevich et al. (2001) who used the approximation given by van de Hulst (1981) to obtain the optical values for spheres, values for spheres are derived here directly from Mie theory.

Size ranges of aquatic constituents and optical regions are provided in Figure 2 for the particular wavelength ( $\lambda = 676$  nm) and the specific refractive indices (n = 1.05, 1.17) used in this review. Results for other visible wavelengths are not expected to be very different and can be deduced from the results presented here by changing the diameter while keeping *x* constant. Similarly, the indices of refraction used here span the range of those of marine particles thus bounding the likely results for all relevant marine particles. The sizes associated with the different optical size regions are provided in Table 1.

## IOPs of monodispersions of randomly oriented spheroids

## Exact and approximate methods

Since the 1908 paper by Mie there is now an exact solution (in the form of a series expansion) providing the optical properties of a homogeneous sphere of any size and index of refraction relevant to aquatic optics. Unfortunately, there is no equivalent converging solution for non-spherical particles for all relevant sizes. Asano & Yamamoto (1975) obtained an exact series solution for scattering by spheroids of arbitrary orientation but their solution did not converge for size parameters >30. Obtaining optical properties of non-spherical particles for the wide range of sizes exhibited by marine particles requires the use of several methods, each valid within a specific optical region. The appropriate application of each of these approaches depends on the combination of sizes, shapes and refractive indices of the particles of interest. For small particles the T-matrix method (Waterman 1971, cf. Mishchenko et al. 2000), which is an exact solution to Maxwell's equations for light scattering, applies. This method is limited to particles with a phase shift parameter that is smaller than approximately 10 (it covers particles with phase shift parameters as large as those in the RGD region, see Table 1). As particles deviate from a spherical shape the phase shift parameter for which this method is valid decreases. For larger particles, a variety of methods that provide approximate solutions for optical properties have been used (see Mishchenko et al. 2002 for a review of the state of the art).

**Table 1** Size ranges roughly corresponding to the size regions defined for two different refractive indices given  $\lambda = 676$  nm

Size region	<i>n</i> = 1.05	<i>n</i> = 1.17	Equivalent p
RAY	$D \ll 0.2 \ \mu m$	$D \ll 0.2 \ \mu m$	$\rho \ll 0.1$
RGD	$D < 5 \ \mu m$	$D < 2 \ \mu m$	ρ < 3
VDH	$5 < D < 200 \; \mu\mathrm{m}$	$2 < D < 65 \ \mu \mathrm{m}$	$3 < \rho < 100$
GO	$D \gg 200 \ \mu m$	$D \gg 65 \ \mu m$	$\rho \gg 100$

One such approximation is the Paramonov (1994b) method for obtaining the attenuation, absorption and scattering of optically soft spheroids (Shepelevich et al. 2001). In this approach, a polydispersion of spheres with the same volume and average cross section (given an appropriate size distribution) is used to provide the attenuation, absorption and scattering coefficients of a monodispersion of randomly oriented spheroids. A comparison of absorption and attenuation efficiencies obtained by this method with T-matrix results (for the largest sizes possible) reveals that the differences are <0.2% for  $Q_a$  and <3% for  $Q_c$  when m = 1.05 + i0.01 (i.e., an organic-like particle). When m = 1.17 + i0.0001 (i.e., an inorganic-like particle), differences between the two methods are <4% for  $Q_a$  and <5% for  $Q_c$ .

Another method is the ray tracing technique (the implementation by Macke et al. 1995 is used here), which provides solutions for the IOPs in the geometric optics region (good for soft particles with a phase shift parameter greater than  $\rho = 400 (n - 1)$  (based on Mishchenko et al. 2002) and applies to particles such as large zooplankton and aggregates; Table 1 and Figure 2). Using this approach, the phase function,  $\tilde{\beta}(\theta)$ , for which there is no solution in the relevant intermediate sizes, can be approximated. In addition, it provides both the VSF,  $\beta(\theta)$ , and the backscattering coefficient,  $b_b$ , for this size range. This method agrees well with the Paramonov method described above,with a difference of 3% for  $Q_c$ , 5% for  $Q_a$  and 0.2% for  $Q_b$ , for m = 1.05 + i0.01; and of 3% for  $Q_c$ , 40% for  $Q_a$  and 3% for  $Q_b$ , for m = 1.17 + i0.0001, thus increasing the confidence in the former approach as well. The relatively larger difference in the absorption efficiency is due to the fact that the absorption index is too small to bring even the largest particles considered here to approach the geometric optics limit, that is, the condition  $kx \gg 1$  is not satisfied. The ray tracing method is therefore used here only for computing the VSF in the GO limit while the Paramonov approach is used to obtain c, a and b at that limit.

Two other approaches were evaluated: (1) an analytical approximation method developed by Fournier & Evans (1991) to obtain the attenuation efficiency of randomly oriented spheroids (this approach works extremely well for a wide range of particles) and (2) an analytical approximation method developed by Kirk (1976) to obtain the absorption cross section of randomly oriented spheroids. The agreement between these two methods and the T-matrix method was not as good as the agreement with the Paramonov method and therefore these two methods are not used here.

The data used in this review can be found at http://misclab.umeoce.maine.edu/research/research10\_ data.php. Numerical codes used in this review can be found at http://misclab.umeoce.maine.edu/ software.php.

## Results: IOPs of a monodispersion

Application of the methods described above to a wide range of particle sizes and aspect ratios (across all optical regions) reveals the potential biases associated with the use of spheres as models to obtain optical properties of monodispersed non-spherical particles (which may apply, for example, to single species blooms and laboratory studies of phytoplankton cultures).

#### The volume scattering function

The VSFs of monodispersed, non-spherical particles do not have the resonance structure (expressed as oscillations in the VSF as a function of scattering angle) observed for monodispersed spheres, much like polydispersions of spheres (Chýlek et al. 1976; see also Figure 4 in Mishchenko et al.

**Figure 4** (see facing page) (See also Colour Figure 4 in the insert following page 344.) The volume scattering function for spheres,  $\beta_{\odot}(\theta)$  (A, D), and for equal-volume spheroids,  $\beta_{\odot}(\theta)$  with aspect ratio s/t = 2 (B, E). The ratio between the two (i.e., the bias denoted as  $\gamma_{\beta(\theta)}$  is presented in panels C and F. The primary *y*-axis for each plot represents variation in particle size,  $D[\mu m]$ , while the secondary *y*-axis represents variation in the phase shift parameter,  $\rho$  (scale found on C and F). Results are for two different types of particles: phytoplankton-like particles with m = 1.05 + i0.01 (A, B, C) and inorganic-like particles with m = 1.17 + i0.0001 (D, E, F). Values for spheroids have been obtained using the T-matrix method for  $D \le 10 \ \mu m$  and by the ray tracing method for  $D \ge 40 \ \mu m$ . No solution is available for  $10 < D < 40 \ \mu m$  (white regions in B, C, E and F).





2002). Because the VSF is smoother for spheroids (Figure 4B,E, see also Colour Figure 4 in the insert following p. 344), the anomalous diffraction peaks inherent in spheres determine the pattern of the biases (Figure 4C,F). Internal transmission and refraction cause the number of peaks in the VSF for spheres to increase with particle size; however, the magnitudes are dampened and so is the general trend in the bias.

For both large non-spherical organic-like and inorganic-like particles, forward scattering is stronger compared with that of equal-volume spheres (Figure 4). In the backward and side-scattering directions, however, there are differences in the biases in the VSF between the two types of particles; for organic-like particles, the largest biases are in the backward direction and are associated with small particles (in particular, particles on the order of the wavelength of light, e.g.,  $D \approx 0.5 \,\mu\text{m}$ ; Figure 4C). For inorganic-like particles the largest differences are in the side-scattering direction and are associated with large particles (Figure 4F).

### Attenuation, absorption and scattering: efficiency factors and biases

Efficiency factors for attenuation,  $Q_c$ , as a function of particle size, show a similar trend of variation for spheres and spheroids (Figures 5 and 6), approaching an asymptotic value of two when the GO limit is reached (Figure 6A,B). The size, D, however, at which  $Q_c$  reaches its maximal value increases with increased departure from a spherical shape (Figure 6A,B).

In general, a sphere will overestimate the attenuation ( $\gamma_c < 1$ ) of an equal-volume spheroid (up to 50% for the most extreme shapes) but will underestimate the attenuation ( $\gamma_c > 1$ ) of an equal-volume spheroid for particles larger than the wavelength (Figures 7A,C and 8A,B). Scattering dominates attenuation; the efficiency factors and biases for scattering are very similar to those of attenuation (Figures 6E,F, 8E,F, 9A,C and 10A,C).

The trend in the change of the efficiency factors for absorption,  $Q_a$ , as a function of particle size is similar for spheres and spheroids, approaching an asymptotic value of one at the GO limit (Figures 5B,D and 6C,D). The absorption efficiency factor of spheroids, however, is always lower than or equal to that of an equal-volume sphere, regardless of particle size and aspect ratio (Figure 6C,D). Absorption efficiency factors of inorganic-like particles are low (Figure 6D) and the biases in absorption between spheres and spheroids are small (Figure 8D). Biases in absorption are also small for small organic-like particles ( $\gamma_a \approx 1$ ; Figure 8C), but increase with increasing particle size and deviation from sphericity. For large organic-like particles, absorption by a spheroid is always larger than that of a sphere of the same volume (Figures 7B and 8C). That is because the absorbing material in a randomly oriented spheroid is less packaged compared with that in a sphere, exposing more absorbing material to the incident light. However,  $Q_a$  is smaller for a randomly oriented spheroid (Figures 5B,D and 6C,D), as it is derived from  $C_a$  by dividing by the average cross-sectional area, which is always smaller for spheres.

The backscattering bias can be very large (by a factor of 16, Figure 10B), especially in the RGD region and for particles much larger than the wavelength (Figures 8G,H and 10B,D). For the largest particles, the backscattering does not reach the asymptotic value of the other IOPs, at least in the range of sizes examined here. By applying an unrealistically large absorption value, however, the backscattering bias does approach the same asymptotic value as total scattering (by using the T-matrix method, Herring 2002).

The volume-normalised cross sections for attenuation and scattering,  $\alpha_c$  and  $\alpha_b$ , respectively, illustrate that the size contributing most to attenuation and scattering (per unit volume or per unit mass) is larger for spheroids than for equal-volume spheres (Figure 11A,B,E,F; consistent with the findings by Jonasz (1987a) that there is as much as a 300% difference between spheres and spheroids in the volume-normalised attenuation cross section). In general, the magnitude of the volume-normalised cross sections for attenuation and scattering decreases with departure from sphericity, suggesting





**Figure 5** Efficiency factors for attenuation,  $Q_c$  (A, C), and absorption,  $Q_a$  (B, D), for spheroids as a function of size, D [µm] (primary *x*-axis, bottom), with corresponding phase shift parameter,  $\rho$  (secondary *x*-axis, top), and aspect ratio, *s/t*. Results were derived using the T-matrix method for small particles (area within the white line to the left of each plot), and the Paramonov (1994b) method for intermediate and larger particles (rest of the plot), for two different types of particles: phytoplankton-like particles with refractive index m = 1.05 + i0.01 (A, B) and inorganic-like particles with m = 1.17 + i0.0001 (C, D).

that spheres interact (resonate) better, per unit volume, with the impinging radiation compared with other shapes. Similar to attenuation and scattering, model results for the volume-normalised cross section for backscattering,  $\alpha_{b_b}$ , show that the size contributing most to backscattering is larger for spheroids than for equal-volume spheres (Figure 11G,H). Unfortunately, the lack of solutions for intermediate regions limits the ability here to discuss  $\alpha_{b_b}$  any further.

The volume-normalised absorption cross section,  $\alpha_a$ , is higher for all strongly absorbing spheroids with low indices of refraction, consistent with the idea that in a randomly oriented monodispersion of homogeneous spheroids more material can interact with the incident light than in a monodispersion of spheres of the same volume, which is better 'packaged' or 'self-shaded' (Figure 11C,D). This is not the case for weakly absorbing particles that are smaller than a few microns — probably due to scattering within the particle that increases the average path length of a light ray — hence increasing the probability of absorption. This effect is slightly larger for spheres given that they are more effective scatterers (Figure 11D).



**Figure 6** Efficiency factors for attenuation,  $Q_c$  (A, B), absorption,  $Q_a$  (C, D), scattering,  $Q_b$  (E, F), and backscattering,  $Q_{bb}$  (G, H), for spheroids as a function of size, D [µm] (primary *x*-axis, bottom), with corresponding phase shift parameter,  $\rho$  (secondary *x*-axis, top), and aspect ratio, *s/t*. Results were derived using the T-matrix method for small particle sizes and the Paramonov (1994b) method for intermediate sizes, while the ray tracing method was used to obtain  $Q_{bb}$  for large sizes. Results are presented for two different types of particles: a phytoplankton-like particle with refractive index m = 1.05 + i0.01 (A, C, E, G) and an inorganic-like particle with m = 1.17 + i0.0001 (B, D, F, H). The lines represent aspect ratios (legend is shown in D): oblate spheroids with *s/t* = 0.5 (grey solid line) and *s/t* = 0.1 (grey dashed line), prolate spheroids with *s/t* = 2 (dark solid line) and *s/t* = 10 (dark dashed line), and spheres with *s/t* = 1 (solid line with dots).



**Figure 7** Bias in attenuation,  $\gamma_c$  (A, C), and absorption,  $\gamma_a$  (B, D). Results were derived as in Figure 5. Thick grey lines indicate where  $\gamma = 1$ .

The smallest particles (in the Rayleigh limit) have the highest backscattering ratios,  $\tilde{b} \approx 0.5$  (Figure 12A,C). For particles in the RGD region, the backscattering ratio of non-spherical particles is largely underestimated by spheres ( $\gamma_{\tilde{b}} > 1$ ; Figure 12B,D). The backscattering ratio is lowest in the transition from the RGD to the VDH regions reaching a constant value for spheres in the mid-VDH region;  $\tilde{b} \approx 0.0005$  for organic-like particles and  $\tilde{b} \approx 0.0042$  for inorganic-like particles. For large inorganic-like particles, a spherical particle overestimates the backscattering ratio of non-spherical particles (Figure 12D), though generalisations do not seem possible. The available results for spheroids, however, are not sufficient to predict how the backscattering ratio of non-spheres will behave in the intermediate region.

## **Optical properties of polydispersions**

## Obtaining the IOPs of polydispersions of particles

When modelling natural waters, it is impractical to account for the contribution of each individual particle because bulk IOPs are the sums of the IOPs of an assembly of particles varying in size, composition and shape. In order to model the optical properties of natural populations, assumptions regarding their size distribution as well as their optical properties need to be made. An advantage



**Figure 8** Biases for attenuation,  $\gamma_c$  (A, B), absorption,  $\gamma_a$  (C, D), scattering,  $\gamma_b$  (E, F), and backscattering,  $\gamma_{bb}$  (G, H), for spheroids as a function of size, D [µm] (primary *x*-axis, bottom), with corresponding phase shift parameter,  $\rho$  (secondary *x*-axis, top). Each line represents a different aspect ratio, *s/t* (legend is shown in panel D). Results were derived as in Figure 6 for two different types of particles: a phytoplankton-like particle with refractive index m = 1.05 + i0.01 (A, C, E, G) and an inorganic-like particle with m = 1.17 + i0.0001 (B, D, F, H).



**Figure 9** Efficiency factors for scattering,  $Q_b$  (A, C), and backscattering,  $Q_{b_b}$  (B, D), for spheroids as a function of size, D [µm] (primary *x*-axis, bottom), with corresponding phase shift parameter,  $\rho$  (secondary *x*-axis, top), and aspect ratio, *s/t*. Results were derived as described in Figure 5. Only the T-matrix and ray tracing methods were used for  $Q_{b_b}$ , however, as no other approximation is currently available for intermediate sizes.

of modelling polydispersions is that the results provide more realistic values of IOPs that better mimic natural populations by eliminating the extreme characteristics of monodispersions that are averaged out and smoothed in the IOPs for polydispersions.

Particles are distributed according to a particulate size distribution (PSD) that describes how their number concentration varies with size. Most often the PSD, f(D) [# m<sup>-3</sup> µm<sup>-1</sup>], is given in its differential form in number of particles per unit volume per *unit* bin length, such that the number concentration, *N*, between two size classes,  $D_1$  and  $D_2$ , is computed as:

$$N(\Delta D = D_2 - D_1) = \int_{D_1}^{D_2} f(D) dD \, [\# \, \mathrm{m}^{-3}].$$
(25)

For a population of particles with varied composition, the IOPs are computed from the PSD as:

$$c, a, b, b_b = \int_{D_{\min}}^{D_{\max}} C_{c, a, b, b_b} (D) f(D) dD [m^{-1}],$$
(26)



**Figure 10** Bias in scattering,  $\gamma_b$  (A, C), and backscattering,  $\gamma_{b_b}$  (B, D). Results were derived as in Figure 9. Thick grey lines indicate where  $\gamma = 1$ .

For the analysis conducted here two common PSDs previously used in other studies of IOPs are employed:

1. The power-law PSD (also referred to as the Junge-like PSD) is given by:

$$f(D) = \begin{cases} 0, & \text{if } D < D_{\min} \text{ or } D > D_{\max}; \\ n_0 \left[ \frac{D}{D_0} \right]^{-\xi}, & \text{if } D_{\min} \le D \le D_{\max} \end{cases}$$
 (27)

where  $D_0$  [µm] is a reference diameter and  $n_0$  [# m<sup>-3</sup>µm<sup>-1</sup>] is the differential number concentration at the reference diameter.  $\xi$  is the slope of the differential PSD (values in aquatic environments are within the range 2.5 <  $\xi$  < 5.0; Morel 1973, Jonasz 1983, Stramski & Kiefer 1991). When  $\xi$  = 4.0 the PSD is known as the Junge PSD for which an equal volume of particulate material is distributed in logarithmically increasing size bins. The smaller the value of the power-law slope,  $\xi$ , the smaller is the relative contribution of small particles to the PSD. In the analysis presented here,  $\xi$  is allowed to vary



**Figure 11** Volume-normalised cross sections for attenuation,  $\alpha_c$  (A, B), absorption,  $\alpha_a$  (C, D), scattering,  $\alpha_b$  (E, F), and backscattering,  $\alpha_{bb}$  (G, H), for spheroids as a function of size, *D* [µm] (primary *x*-axis, bottom), with corresponding phase shift parameter,  $\rho$  (secondary *x*-axis, top). Each line represents a different aspect ratio, *s/t* (legend is shown in panel G). Results were derived as in Figure 6 for two different types of particles: a phytoplankton-like particle with refractive index *m* = 1.05 + *i*0.01 (A, C, E, G) and an inorganic-like particle with *m* = 1.17 + *i*0.0001 (B, D, F, H).



**Figure 12** Backscattering ratios,  $\tilde{b} = \frac{b_b}{b}$  (A, C), and biases in the backscattering ratio,  $\gamma_{\tilde{b}_b}$  (B, D), as a function of particle size, D [µm] (primary *x*-axis, bottom), with corresponding phase shift parameter,  $\rho$  (secondary *x*-axis, top). Results are derived as in Figure 9 for two different types of particles: a phytoplankton-like particle with m = 1.05 + i0.01 (A, B) and an inorganic-like particle with m = 1.17 + i0.0001 (C, D). Each line represents a different aspect ratio, *s/t* (legend is shown in panel A).

(representing the variations in the natural environment) to examine how changes in the relative concentration of small to large particles affects biases between spherical and non-spherical populations of particles.

2. A more elaborate PSD based on generalised gamma functions was introduced by Risoviç (1993):

$$f(D) = \begin{cases} 0, & \text{if } D < D_{\min} \text{ or } D > D_{\max}; \\ n_{S} \left[ \frac{D}{D_{0}} \right]^{\mu_{S}} \exp(-\tau_{S} D^{\nu_{S}}) + n_{L} \left[ \frac{D}{D_{0}} \right]^{\mu_{L}} \exp(-\tau_{L} D^{\nu_{L}}), & \text{if } D_{\min} \le D \le D_{\max} \end{cases}$$

$$(28)$$

where  $n_s$  and  $n_L$  are the number concentrations of small and large particles [# m<sup>-3</sup> µm<sup>-1</sup>], respectively, and  $D_0$  [µm] is the reference diameter. The other parameters,  $\mu_{S,L}$ ,  $\tau_{S,L}$  and  $\upsilon_{S,L}$ , help to generalise the gamma functions that express the distributions of the small and large particles, respectively, and are site-specific with values provided by Risoviç (1993) (parametric values of a 'typical' water body are  $\mu_s = 2$ ,  $\tau_s = 52 \ \mu m^{-1}$ ,  $\upsilon_s = 0.157$ ; and  $\mu_L = 2$ ,  $\tau_L = 17 \ \mu m^{-1}$  and  $\upsilon_L = 0.226$ ). In the analysis that follows, the ratio of the number of small to large particles,  $n_s : n_L$ , is likewise varied, as with the power-law distribution earlier, to examine how changes in the relative concentration of small to large particles affects the bias between spherical and non-spherical particles. The smaller the value of  $n_s : n_L$ , the smaller is the relative contribution of small particles to the PSD.

Two types of comparisons between the IOPs of a polydispersion of spheroids are performed here:

- 1. A constant aspect ratio is assumed for the whole population and only the slope of the PSD ( $\xi$  or  $n_s : n_l$ ) is allowed to vary.
- 2. The slope of the PSD and the aspect ratio are varied as a function of size following the observations of Jonasz (1987b) who, utilising scanning electron microscopy, derived the following shape distribution:

$$\frac{\langle G \rangle}{G} = 1.28 D^{0.22} . \tag{29}$$

The implication of Equation 29 is that the smaller the particles are the more sphere-like they become. Jonasz (1987b) also found that the larger particles resembled elongated cylinders with aspect ratios >1. The geometric cross section of an elongated cylinder, however, is very similar to that of a prolate spheroid and so prolate spheroids are used here to model larger particles. Thus, the deviation from sphericity of a particle can be expressed in terms of its aspect ratio, s/t, and diameter of its equal-volume sphere, D, and Equation 29 becomes:

$$\frac{1}{2} \left[ \left(\frac{s}{t}\right)^{-\frac{2}{3}} + \frac{\left(\frac{s}{t}\right)^{\frac{1}{3}} \sin^{-1} \sqrt{1 - \left(\frac{s}{t}\right)^{-2}}}{\sqrt{1 - \left(\frac{s}{t}\right)^{-2}}} \right] = 1.28 D^{0.22}.$$
(30)

Given a size D, this equation is solved to obtain s/t, which is used in the population model with aspect ratios varying as a function of size (see also Figures 2 and 3 in Jonasz 1987b).

## Results for polydispersions

In the following section, the modelled IOPs (c, a and b) of polydispersions of spheroids are presented. Due to the inability to obtain the VSF of spheroids throughout the size range of interest, results regarding either the VSF or the backscattering coefficient,  $b_b$ , are not presented here.

For polydispersions of spheroids, shape effects depend on the relative contributions of small and large particles to the population and the degree to which particles deviate from a spherical shape (as indicated by the aspect ratio). In both the power-law and Risoviç (1993) PSD simulations, with constant and varying aspect ratios, the biases of all the IOPs increase with increasing proportion of large particles in the population (i.e., as  $\xi \rightarrow 3$  or as  $n_s : n_L \rightarrow 10^{12}$ , Figures 13 and 14). This is a direct consequence of the nearly monotonic change in the bias as a function of size for a monodispersion (Figure 8). As expected from the results for monodispersions of spheroids, the biases in attenuation and scattering increase as the aspect ratio departs from one, the absorption bias also increases with departure from sphericity and with increasing absorption index. In most cases the biases are >1 (i.e., a spherical model will underestimate a population of spheroids), being



**Figure 13** The bias in attenuation,  $\gamma_c$  (A, B), absorption,  $\gamma_a$  (C, D), scattering,  $\gamma_b$  (E, F), and backscattering,  $\gamma_{b_b}$  (G, H), for a power-law polydispersion of spheroids relative to a power-law polydispersion of spheres with the same volume as a function of the power-law exponent,  $\xi$ . Each line represents a different aspect ratio, *s/t* (legend below the plot). The grey line with dots (legend: 'x') denotes the polydispersions of spheroids where the shape co-varies with size following Jonasz (1983; see text). The dotted vertical lines are used to compare equivalent size distributions in Figure 14.

<1 only for attenuation and scattering by populations dominated by small particles (i.e., as  $\xi \rightarrow 4.5$  or as  $n_s : n_L \rightarrow 10^{17}$ , Figures 13 and 14) and for absorption when small cells dominate and the aspect ratio is significantly different from one (Figure 13D). Biases of the Risoviç (1993) PSD are similar to those of the power-law PSD (Figures 13 and 14). Changes in the bias as a function of the PSD parameter (Figures 13 and 14) are smooth due to the averaging over particles of many different sizes, as well as to random orientation. The more realistic case of a population varying in both size and shape exhibits, in general, a larger bias than populations with a constant shape (Figures 13 and 14) because for all the particles in this population the bias is one or larger while for those with constant shape the smallest particles very often have biases smaller than one.



**Figure 14** The biases in attenuation,  $\gamma_c$  (A, B), absorption,  $\gamma_a$  (C, D), and scattering,  $\gamma_b$  (E, F), for a Risoviç (1993) polydispersion of spheroids relative to a Risoviç polydispersion of spheres with the same volume as a function of the relative numbers of small to large particles,  $n_s : n_L$ . Each line represents a different aspect ratio, *s/t* (legend below the plot). The grey line with dots (legend: 'x') denotes the polydispersions of spheroids where the shape co-varies with size following Jonasz (1983; see text). The dotted vertical lines indicate the ratios where the size distributions having approximately a power-law slope of  $\xi = 3.5$  and  $\xi = 4.0$ , from left to right respectively, as shown on Figure 13.

The results here are consistent with those of Herring (2002) who investigated the attenuation bias of a population of particles with a power-law PSD with varying shape as well as varying refractive index (using the model of the dependence of the index of refraction on size by Zaneveld et al. 1974). Variations in the attenuation bias were slightly larger in the study by Herring (2002) than the results obtained here (Figure 13), varying from 2.2 to 1.1 as the power-law slope varied between  $3 \le \xi \le 5$ . Varying the imaginary part of the index of refraction between  $0.0015 \le k \le 0.01$  results in a difference of up to 10% in the attenuation bias, most pronounced for a steeper PSD (Herring 2002).

In general, for the populations of particles modelled here with particle sizes ranging from D = 0.2 to 200 µm, at least 50% of the contribution to *c*, *a* and *b* comes from particles smaller than D = 10 µm (Figure 15). However, the strongest contribution, as much as 65% (indicated by the steepness of the curves in the plots), comes from the contribution made by particles of intermediate sizes belonging to the VDH region. Because in this region the biases are large (Figure 8), models based on spherical particles will underestimate the IOPs (lines with dots in Figure 15).



**Figure 15** The normalised cumulative contribution to attenuation (*c*) (A, B), absorption (*a*) (C, D), and scattering (*b*) (E, F), for both the Risoviç ( $n_s : n_L = 10^{16}$ ) and power-law ( $\xi = 4$ ) polydispersions. Each line represents a different aspect ratio, *s/t* (legend below the plot). The uppermost curves in each panel represent populations with a power-law size distribution (compare with Figure 13) and the lowermost curves represent populations with a Risoviç size and shape distribution (compare with Figure 14). In all cases, the greater the deviation from sphericity (as indicated by the aspect ratio, *s/t*) the greater is the contribution by larger particles to the IOPs of the polydispersion.

The reader is cautioned that the shapes chosen here, the specific choices for size distribution (including the size range from  $D_{\min}$  to  $D_{\max}$ ), the index of refraction and the internal structure are all idealisations and may differ from natural environmental conditions. The general trends in the results, however, are expected to hold true for the natural environment as has been found in many past studies where idealised optical theory has been used to interpret and invert *in situ* observations. In addition, model results presented here provide an order of magnitude estimate for the likely bias resulting when spherical particles are used to model natural assemblages of particles. Two conclusions can be drawn from the results here and from Herring (2002): (1) biases in IOPs are expected to be greatest in populations enriched with large particles similar to those in coastal assemblies of phytoplankton and those in benthic environments and (2) these biases are likely to be smaller than a factor of three (the biases are likely to be <30% when a population is enriched with small particles as in the near-surface layer of an oligotrophic ocean).

## Observations on the effects of particle shape on IOPs

There are relatively few direct observations on the effects of shape on the IOPs of aquatic particles (e.g., Volten et al. 1998). Size determination and hence volume are often ambiguous. For example, when size fractionation is used (i.e., using filters or sieves of increasingly smaller pore sizes) information on only two of the three dimensions (possibly the largest) of the particles can be estimated. Similarly, when microscopy is used in sizing, it is difficult to estimate the third (usually smaller) dimension. Thus, there are uncertainties in both measurements and modelling of IOPs of non-spherical particles. Several studies provide evidence that aquatic particles in general, and non-spherical particles in particular, are not optically equivalent to spheres.

Kadyshevich (1977), Voss & Fry (1984) and Volten et al. (1998) measured the VSF and polarised scattering characteristics of oceanic samples and phytoplankton cultures, respectively, and found that the polarisation characteristics of scattering are not consistent with spherical particles. Hod-kinson (1963), Proctor & Barker (1974) and Proctor & Harris (1974) have found that the attenuation efficiency factor ( $Q_c$ ) as a function of size of sorted nonspherical particles did not exhibit the oscillatory behaviour seen for monodispersed spheres and, similar to spheres, attained an asymptotic value for large particles. This behaviour is similar to  $Q_c$  for a polydispersion of spheres. However, the asymptotic value found in those studies was not always two, probably a consequence of the variety of means by which the 'size' of the particles of interest has been determined in the various studies (Aas 1984).

An example of recent measurements of the near-forward VSF of natural particles from the Satluj River in India (Figure 16) exhibits two features that are similar to those suggested by the theoretical analysis presented in this review (Figure 4) and in previous theoretical papers (e.g., Kerker 1969). The resonance pattern in the VSF associated with a monodispersion of spheres disappears for even tightly sorted natural particles, in a similar manner as a polydispersion of spheres (Figure 16A,C). Associated with a larger cross-sectional area, non-spherical particles exhibit stronger (diffraction-dominated) forward-peaked VSFs (Figure 16A,C). These results are consistent with the theoretical results showing no resonance pattern in the VSF of monodispersed spheroids as a function of angle (Figure 4) and a scattering bias >1 for large particles compared with wavelength (Figure 8F) due to a higher VSF in the near-forward direction. Similar results have been recorded by MacCallum et al. (2004) for phytoplankton cultures where the best agreement in the near-forward VSF was found for spheres with a volume larger by a factor of 1.5.

When Mie-based size inversions are applied to non-spherical and complex particles such as phytoplankton, unexpected results are produced. For example, inversion of VSF measurements conducted on a culture of *Ceratium longipes* suggests a multi-modal population (Figure 17). The



**Figure 16** Measurements of near-forward scattering. A is a comparison of the shape of the near-forward scattering between sorted particles (Satluj River sediment; solid line) and glass spheres (line with dots) 75–90  $\mu$ m in size. An image of the particles used in the measurement of the sediment in A is presented in B. C is a comparison between sediment (solid line) and glass spheres (line with dots) 25–30  $\mu$ m in size. Note the narrowing of the scattering pattern and absence of a secondary maximum for the non-spherical natural particles (solid lines) compared to polydispersions of spheres sieved similarly (lines with dots). Scattering measurements were performed with the LISST-100 instrument (data courtesy of Briggs-Whitmire and Agrawal at Sequoia Scientific, Inc.).

peaks in the volume size distribution, however, are found to correspond to the outer boundary of the cell, the core part of the cell and the thickness of the appendages (Figure 17).

## Summary and future prospect

Together with size, composition and internal structure (not addressed here, however, the reader is referred to Kitchen et al. 1982, Quirantes & Bernard 2004, 2006), shape has important effects on IOPs. For a monodispersion of particles, the biases between spheroids and equal-volume spheres can be larger than a factor of three, while for more realistic polydispersions biases in attenuation, absorption and scattering are smaller than a factor of three. The size of the particles having the maximal IOP per unit volume is larger for spheroids than for spheres for all IOPs; this size increases with non-sphericity.

Many studies have attempted to solve the problem of optical properties of non-spherical particles by looking for a spherical equivalent. While for certain optical properties and size ranges a single sphere can provide an adequate model for a non-spherical particle, it has been found that other properties cannot be modelled with spheres; of these, the degree of polarisation and the VSF in the backward direction are inherently different for non-spherical geometries (Bohren & Singham 1991). In this survey, following Paramonov (1994b), a polydispersion of spheres with the same volume and cross-sectional area as a monodispersion of spheroids is used to model the attenuation, absorption and scattering for the size range in which no 'exact' solutions are available (the T-matrix approach or the ray tracing method). This approximation works well in that it merges into the T-matrix and ray tracing solutions with very little difference. This method, however, does not provide an accurate estimate for the VSF or the backscattering coefficient of non-spherical particles.

For the smallest particles, such as viruses in aquatic environments, shape is not likely to affect the IOPs and hence these particles can be modelled as spheres. Particles with sizes comparable



Figure 17 Volume concentration (assuming spherical particles) inverted from VSF measurements of the dinoflagellate *Ceratium longipes* using the Sequoia Scientific LISST-100. The peaks in the size distribution correspond to different length scales associated with the individual cell.

with the wavelength (e.g., bacteria) have attenuation and scattering biases that are <1. This bias becomes greater than one as particle size increases (e.g., for microphytoplankton) until it reaches an asymptote: the ratio of the average cross-sectional area of the spheroid to that of an equal-volume sphere (Equation 24), which is always >1. For absorption, the bias generally increases with size until an asymptotic value is reached, as a randomly oriented spheroidal particle is less 'packaged' than a sphere.

Backscattering by non-spherical particles is still largely unexplored due to the lack of computational methods covering much of the range of interest (Figures 9B,D, 10B,D, and 12). The backscattering bias is, in general, >1 and can be greater by as much as a factor of seven (95% of the time in Figure 9B) for specific sizes of phytoplankton-like particles. For particles with a very large absorption coefficient (unrealistic for marine particles), an asymptotic value similar to the other IOPs is reached (Herring 2002), suggesting that in general, for particles larger than the wavelength, the backscattering should be more enhanced compared with that of equal-volume spheres. Despite the complexity observed, it seems sensible to conclude that the backscattering of spheroids is likely to be significantly larger than that of equal-volume spheres for the sizes relevant to phytoplankton (Figure 8G,H). In this respect, shape may be a factor contributing to the inability to account for the bulk backscattering coefficient in the ocean, when spheres are used as a model for natural particles (e.g., Stramski et al. 2004). Indeed, Morel et al. (2002) used a mixture of prolate and oblate spheroidal particles (using the T-matrix method) to generate the phase function

of small phytoplankton-like particles that was more realistic in the backward directions compared with that derived from spheres.

For polydispersions of particles with constant or varying shape as a function of size, the biases in attenuation, absorption and scattering have been found here to be bounded, reaching high values (270%) only for extreme shapes and size distribution parameters but generally being within about 50% of that of spheres (Figures 13 and 14). While not as large as for monodispersions, these biases are significant and most often >1, implying that populations of spherical particles perform poorly as an average, unbiased model.

Diffraction-based instruments provide an opportunity to measure particle size *in situ*. Given that measurements are made for angular scattering and that inversions from optical measurements to obtain particle size are based on Mie theory, shape may cause significant biases for the sizing of particles. A population of non-spherical particles will appear, on average, larger (and more dispersed) than a population of equal-volume spheres (Figure 11). In addition, such an inversion will 'create' populations at the tail ends of the size distribution due to the fact that the non-spherical particles have no resonance pattern in the near-forward scattering as a function of angle (in contrast to spheres, see Figures 4, 16 and 17; see also Heffels et al. 1996).

Shape is likely to have some effect on optical inversions that are based on Mie theory. In such inversions, IOPs are used to predict the physical characteristics of the underlying bulk particulate population. For example, the imaginary part of the index of refraction of phytoplankton has been found by inverting absorption data using measured size distributions and Mie theory (Bricaud & Morel 1986). Based on the results of this paper, the inverted k is likely to be an overestimate, with the bias increasing with increasing phytoplankton size and departure from sphericity. Similarly, an inversion of the backscattering ratio was used to obtain the real part of the index of refraction for populations of particles with a power-law size distribution, assuming spherical particles (Twardowski et al. 2001, Boss et al. 2004). Results of this work suggest that a spherical model is likely to underestimate the index of refraction as deviations from sphericity will enhance the backscattering ratio, thus increasing the bias of the inverted index of refraction. Shape effects, on the other hand, were not found to significantly change the spectral slope of the beam attenuation (Boss et al. 2001) and thus are not likely to significantly affect the inversion of this parameter to obtain information on the particulate size distribution. Given the inherent biases associated with using spheres as models for natural particles, it is sensible to predict that inversions that include nonspherical characteristics should provide an improvement compared to those based on Mie theory. This has been the case in several atmospheric studies (e.g., Dubovik et al. 2002, Zhao et al. 2003, Kocifaj & Horvath 2005).

Shape has important effects on the polarisation of light scattered by marine particles but is a topic which is beyond the focus of this review. Nevertheless, it is one of the future frontiers in ocean optics, as currently there is no *in situ* commercial instrumentation able to measure polarised scattering. The aquatic community has largely neglected polarisation when studying particulate suspensions (with a few exceptions, e.g., Quinby-Hunt et al. 2000 and references therein). Studies by Geller et al. (1985) and Hoovenier et al. (2003) suggest that there is promise in obtaining information regarding some aspects of particle shape (e.g., departure from sphericity) by analysing certain elements of the polarised scattering matrix. For example, theoretical shape indices have been derived based on both linear (Kokhanovsky & Jones 2002) and circular (Hu et al. 2003) polarisation measurements. In particular, the latter was found to be less sensitive to multiple scattering. Both were found to be most sensitive at scattering angles in the backward hemisphere. Polarimetry shows promise especially for extreme shapes and larger particles (Macke & Mishchenko 1996).

Both organic and inorganic aquatic particles are not randomly distributed among shapes but rather tend to span a limited and non-uniform range of aspect ratios, with spheres being relatively

rare. Given the limited amount of data available regarding shape distributions of natural particles, more measurements of shape parameters are needed; in particular, these are needed as input to improve inversion models that currently assume spherical particles. Laboratory experiments designed to measure the effects of shape on optical properties and their consistency with the predictions presented here and elsewhere are also required so that a more complete picture of the effect of shape on IOPs can be established.

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# APPENDIX: NOTATION

Notation used following Mobley (1994) closely. The actual units used are given in the text, however, only the dimensions are provided in this table for mass, M, length, L, and time, T, or angular measure as indicated.

Symbol	Definition	Dimension
a	Absorption coefficient	$L^{-1}$
b	Scattering coefficient	$L^{-1}$
$\tilde{b}$	Backscattering ratio	dimensionless
$b_b$	Backscattering coefficient	$L^{-1}$
$C_a$	Absorption cross section of a particle	$L^2$
$C_b$	Scattering cross section of a particle	$L^2$
$C_{b_h}$	Backscattering cross section of a particle	$L^2$
C <sub>c</sub>	Attenuation cross section of a particle	$L^2$
с	Attenuation coefficient	$L^{-1}$
D	Particle size represented by diameter of an equal-volume sphere	L
$D_0$	Reference diameter of size range	L
E(0)	Irradiance at the light source	$M L^{-1} T^{-3}$
E(R)	Irradiance at distance $R$ from the light source	$M L^{-1} T^{-3}$
f(D)	Particulate size distribution	$\# L^{-4}$
G	Geometrical cross-sectional area of a sphere	$L^2$
$\langle G \rangle$	Average geometrical cross-sectional area of a non-sphere	$L^2$
Ι	Radiant intensity	$M L^{-1} T^{-3} \mathrm{sr}^{-1}$
k	Imaginary part of the relative index of refraction	dimensionless
k	Wave number of the incident light	$L^{-1}$
т	Complex relative index of refraction	dimensionless
Ν	Number of particles per unit volume	# L <sup>-3</sup>
п	Real part of the relative index of refraction	dimensionless
$n_0$	Number concentration of particles at the reference diameter $D_0$	$\# L^{-4}$
n <sub>s</sub>	Number concentration of small particles	$\# L^{-4}$
$n_L$	Number concentration of large particles	$\# L^{-4}$
$Q_a$	Absorption efficiency factor of a particle	dimensionless
$Q_b$	Scattering efficiency factor of a particle	dimensionless
$Q_{b_h}$	Backscattering efficiency factor of a particle	dimensionless
$Q_c$	Attenuation efficiency factor of a particle	dimensionless
R	Arbitrary path length of light	L
S	Rotational axis of a spheroid	L
s/t	Aspect ratio of a spheroid	dimensionless
t	Equatorial axis of a spheroid	L
V	Particle volume	$L^3$
x	Size parameter	dimensionless
α*	Specific absorption coefficient of a particle	$L^{-1}$
$\alpha_a$	Volume-normalised absorption cross section	$L^{-1}$
$\alpha_b$	Volume-normalised scattering cross section	$L^{-1}$
$\alpha_{bb}$	Volume-normalised backscattering cross section	$L^{-1}$
$\alpha_c$	Volume-normalised attenuation cross section	$L^{-1}$
β(θ)	Volume scattering function (VSF)	$L^{-1}$ sr <sup>-1</sup>
$\tilde{\beta}(\theta)$	Volume scattering phase function	$sr^{-1}$
$\gamma_a$	Absorption bias	dimensionless
$\gamma_b$	Scattering bias	dimensionless

Symbol	Definition	Dimension
$\gamma_{b_b}$	Backscattering bias	dimensionless
$\gamma_c$	Attenuation bias	dimensionless
θ	Scattering angle	radians (rad)
λ	Wavelength of the incident light	L
$\mu_s$	Small-particle generalised gamma distribution parameter	dimensionless
$\mu_L$	Large-particle generalised gamma distribution parameter	dimensionless
ξ	Slope of the power-law size distribution	dimensionless
ρ	Phase shift parameter	dimensionless
$\tau_s$	Small-particle generalised gamma distribution parameter	$L^{-1}$
$\tau_L$	Large-particle generalised gamma distribution parameter	$L^{-1}$
$v_s$	Small-particle generalised gamma distribution parameter	dimensionless
$\upsilon_L$	Large-particle generalised gamma distribution parameter	dimensionless
φ	Azimuth angle	radians (rad)
Ψ	Angular direction into which light is scattered	radians (rad)
Ω	Solid angle into which light is scattered	steradians (sr)

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