Applicability of Effective-Medium Theories to Problems of Scattering and Absorption by Nonhomogeneous Atmospheric Particles

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ABSTRACT

Effective-medium theories yield effective dielectric functions (or, equivalently, refractive indices) of composite media. Such theories have been formulated that go beyond the Maxwell-Garnett and Bruggeman theories, which are restricted to media composed of grains much smaller than the wavelength. These extended effective-medium theories do not, however, yield effective dielectric functions that can be used for the same purposes for which we unhesitatingly use the dielectric functions of substances such as pure water and pure ice (e.g., reflection and transmission by smooth interfaces; absorption and scattering by particles). Extended dielectric functions can lead to unphysical results; for example, absorption in composite media with nonabsorbing components. Moreover, if the grains in composite media are large enough to give rise to magnetic dipole and higher-order multipole radiation, then the effective permeability of the composite medium cannot be taken to be that of free space even if the grains are nonmagnetic.

Recently, extended effective-medium theories have been applied to the problem of determining the effective dielectric function of ice in which soot grains are embedded in order to explain a factor of 2 discrepancy between measurements of the albedo of soot-contaminated snow and calculations based on a snow albedo model. Setting aside questions about the applicability of these theories, reasonable alternative explanations for the discrepancy exist: (i) Soot is not an invariable substance; measured refractive indices of carbonaceous materials vary appreciably, especially the imaginary part (about a factor of 5). (ii) Absorption by a small soot particle depends on its shape, varying by as much as a factor of 2. (iii) Absorption by a soot particle may be enhanced by porosity; for a fixed particle volume, the enhancement is roughly proportional to the porosity. To predict exactly how much a given amount of soot reduces the visible albedo of snow requires, therefore, more detailed information about the soot than is likely to be readily obtainable.

1. Introduction

Some particles in the atmosphere are nonhomogeneous, which leads to questions about how one calculates absorption and scattering by them. One example is determining radar backscattering cross sections of melting snowflakes and spongy-ice hailstones (Bohren and Battan, 1980, 1982; Battan and Bohren, 1982, Chýlek et al., 1984a). In recent papers by Chýlek et al. (1983, 1984b) the particles considered are inhomogeneous by virtue of embedded soot grains. Since interest in nonhomogeneous atmospheric particles seems to be on the rise, the time has come for a critical look at effective-medium theories. This is particularly important because, as will be shown, serious errors can occur when effective-medium concepts are used uncritically outside their limited domain of validity.

An example of an effective-medium theory is one that gives the dependence of the effective dielectric function of a two-component mixture on the dielectric functions of the components and their volume fractions. Such theories have a long history (Landauer, 1978) predating the publication of Maxwell's *A Treatise on Electricity and Magnetism*. Subsequently, effective-medium theories (or mixing rules) have been turned out steadily, some with solid theoretical foundations, others based on no more than empirical fits to limited sets of data. There is now a bewildering array of them in the scientific literature, although sometimes the differences among them are more apparent than real (e.g., see Bohren and Battan, 1980). Two of these, the Maxwell-Garnett (1904) and the Bruggeman (1935) theories, have had the widest use.

According to both the Maxwell-Garnett and the Bruggeman theories, the effective, or average, dielectric function ϵ_{av} of a two-component mixture depends on only the dielectric functions of its components and their volume fractions:

$$\epsilon_{av} = F(\epsilon, \epsilon_m, f),$$

where f and $1-f$ are the volume fractions of the components with dielectric functions ϵ and ϵ_m. In the Bruggeman theory F is symmetric with respect to interchange of the components, whereas in the Maxwell-Garnett theory it is not:

$$F(\epsilon, \epsilon_m, f) = F(\epsilon_m, \epsilon, 1-f), \quad \text{Bruggeman}$$

$$F(\epsilon, \epsilon_m, f) \neq F(\epsilon_m, \epsilon, 1-f), \quad \text{Maxwell-Garnett.}$$

The Maxwell-Garnett theory applies to mixtures (sometimes said to have a separated grain structure) containing distinguishable inclusions, or grains, with dielectric function ϵ embedded in an otherwise homogeneous matrix with dielectric function ϵ_m, whereas the Bruggeman theory applies to mixtures (sometimes said to have an aggregated structure) in which such a distinction is not possible (for diagrams showing the differences between these two kinds of mixtures see Niklasson et al., 1981 or Bohren and Battan, 1982). If the two components are dielectrically similar, then both theories—indeed, any theory—yield the same result: that the dielectric function of the mixture is just the volume-weighted average of the dielectric functions of its components:

$$\epsilon_{av} \approx f\epsilon + (1 - f)\epsilon_m, \quad |(\epsilon - \epsilon_m)/\epsilon_m| \ll 1.$$

Both theories have in common that ϵ_{av} does not depend explicitly on the *size* of the grains. This is because only the electric dipole term, which is proportional to grain volume, is retained in the series expansion of the amplitude of the electric field scattered by a single grain. Thus only volume fractions (grain volume per unit volume of the medium) appear in these theories. Recently, however, there have been attempts to extend the Maxwell-Garnett and Bruggeman theories by retaining additional terms (Stroud and Pan, 1978; Niklasson et al., 1981). If used with full awareness of their range of validity such extended effective-medium theories may have a limited usefulness in interpreting some measurements, but by no means all. If used uncritically, however, errors are inevitable.

We may define an *unrestricted* effective-medium theory as one that yields effective dielectric functions with the same range of validity as those of media that are usually taken to be homogeneous (e.g., pure water). Thus, an unrestricted effective dielectric function may be used without hesitation to calculate reflection and transmission by composite slabs regardless of the direction of the incident light and its state of polarization. Moreover, it may be used to calculate absorption and scattering (at all angles) by particles that are themselves composite. I shall show that extended effective-medium theories are not unrestricted as they do not yield dielectric functions that can be used for all of the same purposes that we use the dielectric functions of pure substances such as water and ice.

2. The validity of effective-medium theories when magnetic dipole terms are not negligible

To show that there are limits to the applicability of effective dielectric functions, consider a composite slab consisting of a *dilute* suspension of identical particles embedded in an otherwise homogeneous medium. It is possible to calculate transmission by such a slab when it is normally illuminated. Then one can ask the following question: Does there exist an effective refractive index that, when substituted into the expression for slab transmission derived from macroscopic electromagnetic theory, yields the correct result? This question was raised by van de Hulst (1957, p. 33), and later by Bohren and Huffman (1983, p. 77), whose notation is followed here. Transmission by a dilute suspension of particles is formally equivalent to transmission by a homogeneous medium with an effective refractive index for transmission N_{av}

$$N_{av} = N\left\{1 + i\frac{2\pi}{k^3}\mathcal{N}(\mathbf{X}\cdot\hat{\mathbf{e}}_x)_{\theta=0}\right\}, \tag{1}$$

where N is the refractive index of the medium in which the particles are embedded, k is the wavenumber, and $\mathcal{N}$ is the number density of particles. For a unit incident field, assumed to be polarized along the x-direction, the vector scattering amplitude $\mathbf{X}$ is the field scattered by a particle at distances large compared with the wavelength. The quantity $(\mathbf{X}\cdot\hat{\mathbf{e}}_x)_{\theta=0}$ is the x-component of the vector-scattering amplitude in the forward direction ($\theta = 0$). For spherical particles much smaller than the wavelength, (1) is identical with both the Maxwell-Garnett and Bruggeman theories if $f \ll 1$. Although van de Hulst (1957, p. 33) issued a warning against "incorrect use of this refractive index," it has not always been heeded. He knew that reflection by the composite slab was not necessarily given by the refractive index (1); he did not state the conditions under which the effective refractive indices are the same for reflection and transmission, although this is implicit in his statement that reflection "should be computed by means of the scattering function for $\theta = \pi$."

A more detailed discussion of the conditions under which the two refractive indices are the same was given by Bohren and Huffman (1983, p. 78), who showed that a *sufficient* condition is that the scattering amplitudes be the same in the forward and the backward directions:

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

For convenience, we shall henceforth take the particles in the composite slab to be identical spheres. In this instance, the vector-scattering amplitudes are

$$\mathbf{X}_{\theta=0} = S_1(0)\hat{\mathbf{e}}_x, \quad \mathbf{X}_{\theta=180} = S_1(180)\hat{\mathbf{e}}_x,$$

where the scalar amplitude S_1 is an infinite series in the scattering coefficients a_n and b_n (e.g., see van de Hulst, 1957; Kerker, 1969).

If this infinite series is terminated after the first terms we obtain

$$S_1(0) = \frac{3}{2}(a_1 + b_1), \quad S_1(180) = \frac{3}{2}(a_1 - b_1).$$

Thus, if b_1 is not negligible compared with a_1, then *different* refractive indices appear to be needed for reflection and transmission. This was recognized by Niklasson et al. (1981), who stated without proof that "when more than the first term is included . . . the same effective medium formulation does not apply to both the transmittance and the reflectance determinations on a nonhomogeneous medium."

The previous analysis contains the implicit assumption (which is almost always made) that the dielectric function (relative permittivity) is the only quantity of interest. In composite media, however, this is not necessarily so. This was pointed out to me by William Doyle, to whom I am grateful for making available his unpublished work. I shall rely heavily on this work in the following paragraphs.

In general, the refractive index N of *any* medium is determined by *both* the dielectric function and the relative permeability μ:

$$N = \sqrt{\epsilon\mu}. \tag{2}$$

Moreover, other quantities depend on both ϵ and μ, the reflection coefficient $\tilde{r}$ at normal incidence, for example:

$$\tilde{r} = \frac{\sqrt{\mu} - \sqrt{\epsilon}}{\sqrt{\mu} + \sqrt{\epsilon}}. \tag{3}$$

It is almost always assumed that $\mu = 1$, that is, the medium is nonmagnetic, an excellent approximation for homogeneous media at visible wavelengths. Indeed, this assumption has been made so often that it is rarely mentioned any more. And yet it is an assumption that is incorrect, in general, for composite media, which was recognized as long ago as 1909 by Gans and Happel. It might be expected that a composite medium is nonmagnetic if its components are, but this is not correct.

Let us again consider a slab composed of a dilute suspension of identical spheres, but this time we make no assumptions about the permeability. Derivations from a microscopic point of view of the electric fields reflected and transmitted by this slab are given by Bohren and Huffman (1983, pp. 77–79). These expressions can then be compared with those obtained from macroscopic electromagnetic theory. The result is that the effective dielectric function and permeability (relative to the medium in which the slab is embedded, which we may take to be air for convenience) satisfy

$$(\epsilon_{av}\mu_{av})^{1/2} = 1 + \frac{i2\pi}{k^3}\mathcal{N}S_1(0), \tag{4}$$

$$\sqrt{\epsilon_{av}} - \sqrt{\mu_{av}} = \frac{i2\pi}{k^3}\mathcal{N}S_1(180). \tag{5}$$

Equation (4) is merely a restatement of (1) and (2). What is new is that μ_{av} is not equal to 1. The extent to which it differs from 1, and why, can be shown more explicitly by rewriting (4) and (5) in the form

$$(\epsilon_{av}\mu_{av})^{1/2} = 1 + A + B, \tag{6}$$

$$\sqrt{\epsilon_{av}} - \sqrt{\mu_{av}} = A - B, \tag{7}$$

where

$$A = \frac{i2\pi}{k^3}\mathcal{N}\left\{\frac{3}{2}a_1 + \frac{5}{6}b_2 + \frac{7}{12}a_3 + \cdots\right\},$$

$$B = \frac{i2\pi}{k^3}\mathcal{N}\left\{\frac{3}{2}b_1 + \frac{5}{6}a_2 + \frac{7}{12}b_3 + \cdots\right\}.$$

It follows from the assumption of a dilute suspension that to good approximation the solutions to (6) and (7) are

$$\sqrt{\epsilon_{av}} = 1 + A,$$

$$\sqrt{\mu_{av}} = 1 + B.$$

To the extent that the coefficients b_1, a_2, etc. are not negligible, therefore, μ_{av} cannot be equal to 1 and ϵ_{av} different from 1. The previous conclusion, namely that two different refractive indices are needed to yield transmission and reflection by a composite slab, was incorrect. Although there is only *one* refractive index, transmission and reflection are functions of *two* independent variables ϵ_{av} and μ_{av}, rather than merely their product.

Extended effective-medium theories are invoked when at the very least the coefficient b_1 is not negligible. When this is so, however, the expressions for transmission, reflection, and so on derived under the assumption of a relative permeability of 1 are no longer valid.

In general, the scattering coefficients for a particle (e.g., a sphere) depend on its permeability as well as on its refractive index. This is rarely mentioned, but it is nevertheless true (e.g., see Stratton, 1941, p. 565 for Mie coefficients where permeabilities are unrestricted). It is almost always implicitly assumed that spheres for which Mie calculations are done have permeabilities equal to that of free space. For homogeneous spheres this is usually a valid assumption, but not necessarily for heterogeneous spheres. That is, if it is believed that the Maxwell-Garnett or Bruggeman theories are inadequate and that an extended effective-medium theory is required, it necessarily follows that one must use the general expressions for the Mie coefficients with $\mu \neq 1$ as well.

Equations (4) and (5) were obtained under the assumption of diluteness, and the incident light was taken to be normally incident. With only two unknowns to be determined, ϵ_{av} and μ_{av}, from the two equations for transmission and reflection at normal incidence, a unique solution was possible. But it is not obvious that ϵ_{av} and μ_{av} so obtained are applicable if the light is not normally incident. Nor it is obvious that they are applicable to scattering and absorption by composite particles. All that can be said with confidence is that, subject to the restrictions underlying their derivation, (4) and (5) are applicable to transmission and reflection of normally incident light. We do not know if they can be used in any other equations of macroscopic electromagnetic theory. Indeed, (4) leads to results that are not in accord with this theory, which is shown in the following section.

3. Extended effective-medium theories predict absorption when none exists

In macroscopic electromagnetic theory, a nonzero imaginary part of refractive indices implies absorption. Equation (1) is an expression for the effective refractive index of a dilute suspension of identical particles, which we may take to be spheres. The imaginary part of the effective refractive index (1) may be written

$$\mathrm{Im}\{N_{\mathrm{av}}\} = f\frac{C_{\mathrm{ext}}}{v}\frac{\lambda}{4\pi}. \qquad (8)$$

The volume fraction f is the product of the number density of particles and the volume v of a single particle. For convenience we may take the particles to be nonabsorbing and embedded in a nonabsorbing medium. But the imaginary part of N_{av} is zero only if C_{ext} is zero, which it is not, even for nonabsorbing spheres. Suppose that the size parameter is 5 or greater; at visible wavelengths this corresponds to radii greater than about 0.5 μm. For such size parameters the extinction cross section is about twice the geometrical cross section. In this instance the imaginary part of the effective refractive index is of order f. Suppose that small glass spheres are suspended in water. At visible wavelengths both of these materials are weakly absorbing. Yet for a volume fraction of 10^{-4} and a radius of 0.5 μm, the imaginary part of the effective refractive index is of order 10^{-4}, about 10^4 times greater than the imaginary parts of the refractive indices of water and glass. According to (8), a cloud of such glass-contaminated droplets would be black to visible light, although nothing in it is very absorbing.

The preceding example was adduced to show just how far one can go astray by investing the term "effective refractive index" with more significance that it legitimately possesses. No doubt extended effective-medium theories have limited applicability to transmission and reflection by composite slabs. But they certainly cannot be used for calculating heating rates in composite media or absorption by composite particles. To explore further the limits of applicability of effective-medium theories, we now turn to the foundations of macroscopic electromagnetic theory.

4. From microscopic to macroscopic electromagnetic fields

The point of departure for scattering and absorption problems is the *macroscopic* Maxwell equations. These equations in turn are derived from the *microscopic* Maxwell equations. The transition from microscopic to macroscopic is not trivial; entire books have been written on this subject, beginning with Lorentz (1915) and continuing to modern times (Rosenfeld, 1951; deGroot, 1969; Robinson, 1973), as well as at least one lengthy review paper (van Kranendonk and Sipe, 1977) and even an expository article (Russakoff, 1970). What follows is therefore far from being exhaustive; my hope is merely to shed some light on the inconsistencies that were unearthed in the preceding section.

Matter is composed of an enormous number of rapidly moving charged particles bound together in more or less stable atoms and molecules. On an atomic scale electric and magnetic fields vary wildly in space and time. Instruments measure averages over regions containing many atoms and over time intervals long compared with characteristic atomic times. It is a formidable task to go from the microscopic Maxwell equations, which apply to a vacuum peppered with many point charges, to macroscopic Maxwell equations, which apply to matter in bulk.

Composite media, the kinds to which effective-medium theories are applied, contain grains. They are sufficiently large that the fields inside them are macroscopic. Yet grains may be looked upon as merely very large atoms. And we may, of course, define average fields over regions containing many grains. Microscopic fields are often denoted by lower case letters **e** and **h**. The macroscopic fields are then denoted by upper case letters **E** and **H**. To remind ourselves that even coarser averages are taken for composite media, we denote such average fields by $\langle\mathbf{E}\rangle$ and $\langle\mathbf{H}\rangle$, which William Doyle has suggested be called *megascopic* fields.

Let us now suppose that the average fields $\langle\mathbf{E}\rangle$ and $\langle\mathbf{H}\rangle$ satisfy the familiar field equations, even though this has not, to the best of my knowledge, been demonstrated rigorously. And suppose that we are able to obtain solutions to these equations for specified boundary conditions. Would the results be useful?

Wherever there are averages there are variances lurking in the background. We ignore them at our peril. Averages are meaningful only if they are large compared with variances. The average field is often denoted as the *coherent* part of the field, and its variance as the *incoherent* part (for discussions of this see Foldy, 1945; Lax, 1951; Ishimaru, 1978; Ishimaru and Kuga, 1982). Rather than launch into a lengthy discussion of coherent and incoherent fields, the point can be made more simply by appealing to a few experiments.

Imagine a laser beam incident on an air–water interface. The path of the refracted beam is evident because of light scattered out of the plane of incidence. This light is unaccounted for by Snell's law; it is the incoherent part of the scattered light, the coherent part being the refracted light. Thus Snell's law is not exact, even for homogeneous media free of all contaminants (e.g., pure water). It is nevertheless a good approximation when the incoherent field is small compared with the coherent field.

When a few drops of milk are added to pure water the intensity of laterally scattered light greatly increases.

Milk is a suspension of fat globules in water. They are spherical, small compared with the wavelengths of visible light, and only weakly absorbing. Moreover, at visible wavelengths the refractive indices of fats and water are not vastly different. Milk is therefore an ideal system to which the Maxwell-Garnett theory may be applied. But the MG effective dielectric function is not sufficient to interpret observations of a glass of milk. This dielectric function applies to the coherent part of the field whereas the incoherent part may dominate the total field. For experiments in which the coherent part of the field is the quantity under observation, the MG dielectric function may be useful. But it fails completely to predict the appearance of a glass of milk.

Implicit in the preceding paragraphs is the condition under which effective-medium theories for heterogeneous media are likely to have unrestricted applicability. Recall that $\langle \mathbf{E} \rangle$ and $\langle \mathbf{H} \rangle$ are average fields. For an average to have any meaning it must be taken over a large number of elements. In this instance, the elements are the grains in a heterogeneous medium. The characteristic length scale for any problem involving a heterogeneous medium interacting with an electromagnetic wave is its wavelength. Therefore, there must be many grains in a cube one wavelength on a side if the heterogeneous medium can be described by a dielectric function with unrestricted validity. This condition cannot be satisfied if grain sizes are comparable with the wavelength.

Nearly a century ago Planck stated quite clearly in his masterly *Theory of Heat Radiation* the condition under which a particulate medium may be taken to be homogeneous:

> . . . . "turbid" media, i.e., such as contain foreign particles, may be quite properly regarded as optically homogeneous, provided only that the linear dimensions of the foreign particles as well as the distances of neighboring particles are sufficiently small compared with the wave lengths of the rays considered. As regards optical phenomena, then, there is no fundamental distinction between chemically pure substances and the turbid media just described. No space is optically void in the absolute sense except a vacuum. Hence a chemically pure substance may be spoken of as a vacuum made turbid by the presence of molecules.

5. The albedo of soot-contaminated snow

At visible wavelengths the albedo of pure snow can only decrease when a strongly absorbing contaminant, such as soot, is added to it. This is so obvious that further elaboration is unnecessary. But what is so easy to state qualitatively evades precise quantification: How much soot reduces the visible albedo of snow by a given amount? Warren and Wiscombe (1980) calculated this using their snow albedo model. To obtain agreement with measurements, however, required about 2–5 times as much soot as was actually measured by Grenfell et al. (1981). Warren and Wiscombe attributed a factor of two difference to their use of graphite density instead of soot density. Thus, a discrepancy of about a factor of 2 remained to be explained. An attempt to do so was made by Warren (1982), who listed possible sources of discrepancy, one of which is that the location of soot particles inside grains "might enhance their absorption of light." This statement was the impetus for Chýlek et al. (1983) to compute the albedo of soot-contaminated snow using the effective-medium theory of Chýlek and Srivastava (1983), which is an extension of a theory of Stroud and Pan (1978).

In this theory the effective dielectric function is expressed as an infinite series in the Mie scattering coefficients. No statement is made in the Chýlek-Srivastava paper or in succeeding papers (e.g., Chýlek et al., 1983, 1984b) that perhaps these expressions are invalid if more than the first or second terms are retained. Indeed, they refer to their extended effective-medium theory as "the proper generalization" without qualification. Thus, the implication is that they consider their expressions to have unrestricted validity. Although they apply them to soot grain size distributions with *mode* radii smaller than the wavelength, some of the grains are larger than the wavelength. These large grains are much fewer in number than the small ones, but each one contributes much more to absorption. If the grains are sufficiently large to give rise to magnetic dipole and higher order multipole radiation then the effective relative permeability of the composite medium cannot be unity (see section 2). This was not recognized by Chýlek et al. (1983), which by itself casts doubts on their results. Further doubt arises from the fact that extended effective-medium theories predict absorption where none exists (section 3). Nevertheless, the test of a theory is agreement with experiment, and by this criterion Chýlek et al. (1983) claim success: "with our new model for snow containing impurities, we have been able to obtain good agreement between the field measurements of spectral snow albedo and calculated albedo and between the amount of graphitic carbon measured and the amount needed in our calculations." Their explanation is the correct one, however, only if no reasonable alternative explanations exist. They mention none. But such alternatives do exist, as I shall show in the following sections. Note that only a factor of 2 discrepancy is at issue. This is insignificant in view of the uncertainties about soot absorption. Moreover, these uncertainties will always plague attempts to predict albedo reduction by soot contamination. The most that one can hope for is *bounds* on the amount of soot it takes to reduce the albedo of snow by a given amount.

a. A simple explanation of why soot grains inside ice are more absorbing than when outside

The absorption cross section of a small sphere, with radius a, relative to its geometrical cross section is

$$Q_{abs} = \frac{24a\pi}{\lambda} \epsilon_m^{3/2} \frac{\epsilon''}{(\epsilon' + 2\epsilon_m)^2 + \epsilon''^2}, \tag{9}$$

where $\epsilon' + i\epsilon''$ is the dielectric function of the particle and ϵ_m is that of the surrounding medium (assumed to be nonabsorbing) at the wavelength λ. The condition that $\partial Q_{abs}/\partial \epsilon_m$ be positive is

$$3\epsilon'^2 + 3\epsilon''^2 + 4\epsilon'\epsilon_m > 4\epsilon_m^2.$$

This condition is certainly satisfied if $\epsilon' > \epsilon_m$. In particular, it is satisfied for "soot" in ice if $\epsilon_m = \epsilon_{ice} = 1.72$ and $\epsilon = \epsilon_{soot} = 2.99 + i1.8$. The absorption cross section of a small soot sphere in ice is therefore about 1.4 times its cross section in air. This is consistent with the calculations of Chýlek et al. (1983).

Additional enhancement may be obtained depending on the position of the soot grains within an ice particle. For example, if we ignore reflections, it follows from simple geometrical optics that n^2 more light is incident on a small sphere when it is at the center of a much larger transparent sphere with refractive index n than when it is in air. Of course, all soot in an ice grain will not necessarily lie at its center; the focussing (or defocussing) effect depends on the position of a grain. If the grains are uniformly distributed throughout the transparent sphere, we expect no focussing effect: on average, all soot grains are illuminated by a beam with the irradiance of that of the external beam.

b. Uncertainties about the optical constants of soot

The most important quantity in computations of absorption by soot is its complex refractive index (or, equivalently, dielectric function), particularly the imaginary part. The value used by Chýlek et al. (1983) $m = 1.8 + i0.5$ ($\epsilon = 2.99 + i1.8$) [in a subsequent paper, Chýlek et al. (1984b) switch to $1.94 + i0.66$ without comment], has been widely used by many investigators as if "soot" were an invariable substance with a fixed composition and structure. But soot is merely a convenient, although imprecise, term for the carbonaceous products of combustion. The value $1.8 + i0.5$ for the refractive index of "soot" was recommended in a compilation by Twitty and Weinman (1971) as the "constant value" for wavelengths between 0.25 and 15 μm. Yet the basis for this recommendation, for visible wavelengths, is measurements made in 1917 on coal by Senftleben and Benedict. More recent measurements indicate that this single value is far from being representative. For example, Roessler and Faxvog (1980) state that "the literature is replete with optical data on carbon soots . . . there is a wide variation in the reported values of these optical parameters at any given wavelength." These same authors give a table (their Table II) of measured values (at $\lambda = 0.5145$ μm) in support of this assertion. It is clear from this table that there is about a factor of 5 uncertainty in the imaginary part of the refractive index of carbonaceous substances that are lumped together under the general heading of "soot." It therefore follows from (9) that this implies the same factor of uncertainty in the absorption cross section of small soot particles. Thus, the factor of 2 discrepancy in the amount of soot necessary to reduce the albedo of snow by a specified amount can be accounted for solely by uncertainties in the refractive index of soot.

c. Uncertainties about the shape of soot particles

The extended effective-medium theory of Chýlek and Srivastava (1983) is based on the assumption of spherical grains. Yet in Fig. 2 of the paper by Roessler and Faxvog (1980) there is a scanning electron micrograph of "typical acetylene soot." One looks in vain for spheres. To what extent does shape affect the absorption cross section of soot particles?

This question cannot be answered once and for all because there is no end to the possible shapes of soot particles. But we can at least estimate the effect of shape by considering some limiting cases. The (average) absorption cross sections of small, randomly oriented spheres, needles, and disks are (Bohren and Huffman, 1983, p. 350):

$$\langle C_{abs}\rangle_{sphere} = \frac{kv}{3}\left(\frac{27}{(\epsilon' + 2)^2 + \epsilon''^2}\right)\epsilon'',$$

$$\langle C_{abs}\rangle_{needle} = \frac{kv}{3}\left(\frac{8}{(\epsilon' + 1)^2 + \epsilon''^2} + 1\right)\epsilon'',$$

$$\langle C_{abs}\rangle_{disk} = \frac{kv}{3}\left(\frac{1}{\epsilon'^2 + \epsilon''^2} + 2\right)\epsilon'',$$

where v is the volume of a particle, ϵ is its dielectric function relative to that of the surrounding medium, and k is the wavenumber of the incident light. Suppose that the particles are in air. Then for a dielectric function $\epsilon = 2.99 + i1.8$ the cross sections are in the ratio (sphere:needle:disc) 1:1.48:2.17; if the particles are in ice the cross sections are in the ratio 1:1.08:1.25. A more detailed discussion of absorption by small carbon spheroids is given by Roessler et al. (1983).

If the particles are platelike and separate from the ice grains in a snowpack, then they will be more than twice as absorbing, per unit mass, than if they were spherical. Thus, shape alone can account for the discrepancy noted by Warren and Wiscombe (1980). Until evidence is brought forth that all soot particles in snow are spherical, shape cannot be brushed aside as being insignificant.

d. Uncertainties about the porosity of soot particles

Soot particles are not necessarily homogeneous; they may contain voids. To what extent does this affect absorption per unit mass of soot?

Bohren and Wickramasinghe (1977) showed that a small hollow sphere is equivalent to a sphere described by the Maxwell-Garnett dielectric function for a porous medium with the same void volume fraction. We can therefore estimate the effect of porosity by considering a small, hollow sphere. It follows from the expression for the polarizability of such a sphere given by Bohren and Huffman (1983, p. 149) that the absorption cross section per unit particle volume is

$$\frac{C_{abs}}{v} \propto \mathrm{Im}\left(\frac{\dfrac{\epsilon-1}{\epsilon+2}}{1-f\dfrac{\epsilon-1}{\epsilon+2}\dfrac{\epsilon-1}{\epsilon+1/2}}\right)$$

where f is the void volume fraction and ϵ is the dielectric function; the particle is in air. If we define R as the volumetric absorption of a hollow sphere relative to that of a solid sphere, both with the same composition, then a power series expansion for R gives

$$R = 1 + 0.76f + O(f^2),$$

if $\epsilon = 2.99 + i\,1.8$. Thus, a small porous carbon particle is more absorbing than a solid carbon particle with the same volume. To a first approximation, the amount of enhanced absorption is equal to the void volume fraction. Porosity is therefore another uncertainty in absorption by soot particles.

6. Conclusions

The concept of a refractive index (or dielectric function) is so familiar in optics that its foundations are rarely examined. We have no qualms about using refractive indices for all kinds of calculations: reflection by optically smooth surfaces; absorption and scattering by particles, to name just a few. Yet we may do so only because matter is composed of units so small compared with the wavelengths of light that they may be considered to be point dipoles. This is indeed a stroke of luck, for it enables us to circumvent what would otherwise be complicated electromagnetic many-body problems. But simplicity is a two-edged sword. On the one hand it allows us to solve problems without worrying about fine details. On the other hand, it ignores fine details that may not be without observable consequences.

The concept of a refractive index may be extended to macroscopically heterogeneous media composed of units (grains or inclusions) much larger than ordinary atoms and molecules—so large that they possess refractive indices—but still sufficiently small to be considered point dipoles. That is, the grains may be looked upon as merely molecules with very large molecular weights and with polarizabilities determined by their refractive indices. Effective refractive indices of such heterogeneous media may sometimes be used for the same purposes that we use refractive indices of homogeneous media.

As the size of the grains in heterogeneous media increases, the range of applicability of the associated effective dielectric functions becomes ever more severely constrained. Stroud and Pan (1978) and Niklasson et al. (1981) formulated effective-medium theories that go beyond the Maxwell-Garnett and Bruggeman theories. But these authors appear not to have invested the resulting effective dielectric function with more significance than it legitimately possesses. Their aims were limited: determining attenuation of electromagnetic waves in unbounded heterogeneous media. Thus, the imaginary part of the effective dielectric function is a measure of attenuation but not necessarily of absorption.

Chýlek et al. (1983) applied the Chýlek-Srivastava (1983) mixing rule, which is based on that of Stroud and Pan (1978), to the problem of determining absorption by ice grains in which soot is embedded. If the soot grains—indeed, any grains—are sufficiently large then there are appreciable differences between the Chýlek-Srivastava and MG or Bruggeman dielectric functions. Unfortunately, for such grains the validity of an effective dielectric function is highly questionable. For example, even if the grains are nonabsorbing and embedded in a nonabsorbing medium, extended effective-medium theories predict absorption.

What is at issue here is not *which* effective-medium theory is applicable to a given heterogeneous medium, but whether or not *any* of them are. It has been argued here that *none* of them are unless the grains are quite small. And even this condition is not sufficient; it is merely necessary.

The conclusion is inescapable, although perhaps unpalatable, that if problems of absorption and scattering by nonhomogeneous particles must be solved, and if the heterogeneities are not electric dipoles, then we must abandon the fruitless search for extended effective-medium theories and tackle such problems by other methods. An example of one such method is that of Varadan et al. (1983).

Chýlek et al. (1983) claim to have explained a factor of 2 discrepancy between measurements of the albedo of soot-contaminated snow and calculations based on the snow albedo model of Warren and Wiscombe (1980). Yet this discrepancy has alternative explanations, which were not entertained by Chýlek et al. (1983): (i) soot is not an invariable substance; measured refractive indices of carbonaceous materials vary appreciably; (ii) absorption by a small soot particle depends on its shape, varying by as much as a factor of two; and (iii) absorption by a soot particle may be enhanced by porosity. To predict exactly how much a given amount of soot reduces the visible albedo of snow therefore requires more detailed information about soot than is likely to be readily obtainable. It is unreasonable to expect better than a factor of 2 agreement between theory and measurement except by accident; the many uncertainties can easily combine to give discrepancies greater than a factor of 2.

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