Inhomogeneity structure and the applicability of effective medium approximations in calculating light scattering by inhomogeneous particles

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Abstract

Atmospheric aerosols commonly occur as inhomogeneous particles with significant internal variations of refractive indices. For the purpose of light-scattering calculations, effective medium approximations (EMAs) have been developed that seek to model an inhomogeneous particle with an internal variation of refractive index using a homogeneous particle with a single “effective” refractive index, one whose value is expected to yield approximately the same scattering properties. Here the applicability of four EMAs is investigated in the relatively simple case that the particle is a mixture of materials having just two different indices of refraction, and consideration is given to the effects of the spatial arrangement of these on the reliability of results obtained using the EMAs. The EMAs considered are based on the Bruggeman theory, the Maxwell–Garnett theory, and two different Wiener bounds. The mixing states considered are relatively regular forms of “layering,” as well as states that involve varying degrees of more irregular “mixing.” Just two overall particle shapes are considered: spheres and spheroids. For each inhomogeneous particle two sets of scattering calculations are performed: calculations treating the inhomogeneous particle itself exactly, and calculations treating an effective homogeneous particle with the same shape and size but a single refractive index determined using one of the EMAs. The first kind is done using the core–mantle Mie theory in the case of stratified composition and the pseudo-spectral time-domain method in the more irregular mixing cases. The second kind of calculation is done using the Lorenz–Mie or T-matrix method.

Calculated values of extinction efficiencies, asymmetry factors, and phase matrices of both a single particle and an ensemble of particles are compared. In comparisons of the EMAs with each other, the Bruggeman model and Maxwell–Garnett model give similar results, results which differ by small but noticeable amounts from the results obtained from the Wiener bounds. This suggests that the particular choice of one of the EMAs over another is not critical in calculating the scattering properties of atmospheric particles, especially the bulk-scattering properties. Comparison with the numerically exact results shows that the applicability of the EMAs is largely independent of the particle shape, size, or volume fraction of the components, but is significantly affected by different mixing states. It is found that the Bruggeman and...
1. Introduction

Atmospheric aerosols (e.g. mineral dust, black carbon, and sea salt) affect the climate directly by scattering and absorption of solar radiation and terrestrial infrared emission and indirectly by aerosol–cloud interaction [1–3]. However, quantification of the impact of atmospheric aerosols remains questionable because of the variations in aerosol particle shape, size, and composition. The scattering and absorption properties of complicated particles are vital to our understanding of the direct and indirect effects of aerosols [4,5].

Quantitative information about the shape, size, number of components, and mixing state of natural aerosols is usually unknown [6–8], and, in general, the particles occur as mixtures of various components whose optical properties may vary significantly. However, in radiative transfer and remote sensing applications, these inhomogeneous particles are represented using “equivalent homogeneous” particles having the same shapes and sizes but uniform refractive indices, making the optical properties much easier to estimate [9,10]. This is done by using some form of effective medium approximation (EMA) to calculate an effective refractive index for the mixture, a value which when given to homogeneous particle is expected to result in similar optical properties to those of the inhomogeneous particle [11,12]. A variety of EMAs have been developed and used for atmospheric aerosols.

The first EMA, based on the Maxwell–Garnett (MG) theory, was developed over a century ago [13,14], and was used on dust aerosols by Longtin et al. [15]. A model based on the Bruggeman (BR) theory [16,17] is another EMA that has also been widely used to study the radiative properties of mineral aerosols [18,19]. In addition to the MG and BR theories, Sokolik and Toon [18] chose a simple volume average approximation to calculate the effective refractive indices of aerosols. Additional EMAs have been proposed: the performances of nine EMAs, developed for a variety of different shapes, size distributions, physical properties, and mixing structures, have been reviewed by Kolokolova and Gustafsson [12].

Although the EMAs and the equivalent homogeneous approximations are widely used [9,10,12,18,19], their applicability and accuracy in atmospheric light-scattering studies are still uncertain. Chylek et al. [20] and Kolokolova and Gustafsson [12] compared the EMA results with experiments for spheres with small inclusion amounts and sizes, and both found acceptable agreement between the calculated and measured values. From numerical investigations, Perrin and Lamy [21] found the application of the EMAs to the study of the interaction of light with inhomogeneous dust particles to be limited. However, Voshchinnikov et al. [22,23] indicated that the EMAs could be used to simplify the computation of the optical properties of aggregates containing only Rayleigh inclusions. The EMAs have also been applied to some specific cases, i.e. water coated soot aggregates by Yin and Liu [24] and Liu et al. [25], and the MG was found to provide more accurate approximations for the single-scattering properties of coated aggregates than the BR. More detailed discussion of effective medium theories can be found in [11] and its references. However most of the foregoing studies used the EMAs with significant limitations on particle size, shape, mixing structure, or volume fraction of the components, and, in fact, drew substantially different conclusions.

This study focuses on the case of just two constituents with different refractive indices, and considers how the internal arrangement of the constituents affects the ability of the EMAs to reliably treat problems of light scattering by inhomogeneous atmospheric aerosols. Four EMAs, three mixing states, and two particle shapes will be investigated, and we consider cases of the two components having volume fractions that vary from 0 to 1. For each inhomogeneous particle, approximate and exact methods are used to calculate its scattering properties. The approximate method treats the inhomogeneous particle as its equivalent homogeneous counterpart, and uses the EMAs to find the effective refractive indices, with which its scattering properties are calculated by the Lorenz–Mie theory [26] and the T-matrix theory [27,28]. It should be noticed that the Lorenz–Mie and the T-matrix results are understood as the approximations in this study, because they are used for the equivalent homogeneous particles, not the original inhomogeneous ones. Representing standards of “truth” for the scattering properties of the inhomogeneous particle itself, the core–mantle Mie [29,30] theory and the pseudo-spectral time domain method (PSTD) [31,32] are applied. Then the applicability and accuracy of the EMAs can be evaluated by comparing the results from the PSTD/core–mantle Mie methods with the results from a combination of the EMAs and Lorenz–Mie/T-matrix theories. The scattering properties examined in making these comparisons are the extinction efficiency ($Q_{ext}$), asymmetry factor ($g$), and phase matrix elements $P_{11}$ and $P_{12}$ of both a single and an ensemble of inhomogeneous particles. Definitions of these scattering properties are given in [33].

Section 2 defines the four EMAs that will be used in this study. The particle shapes and mixing states of the
inhomogeneous model are introduced in Section 3. We describe the numerical methods for the light scattering simulations and the validation of them for inhomogeneous particles in Section 4. The results are discussed in Section 5, and Section 6 concludes the study.

2. The effective medium approximations

Models using the EMAs try to replace a dielectric inhomogeneous particle, i.e. a particle having internal variations of refractive indices, with a homogeneous one that has a single “effective” refractive index and approximately the same scattering properties as the inhomogeneous counterpart. The MG [13,14], whose history dates back to 1904, was one of the first attempts to approximate the optical properties of inhomogeneous materials. It considers a mixture of two components, with permittivities ε₁ and ε₂, and defines the effective permittivity εₑff to satisfy the relation

\[ \frac{εₑff - ε₂}{εₑff + 2ε₂} = f_1 \frac{ε₁ - ε₂}{ε₁ + 2ε₂}, \]

where \( f_1 \) is the volume fraction of the first component. The asymmetry evident in the formula reflects the intent of the original MG theory to treat the case that the first component is the “medium,” the second component is the “inclusion,” and the inclusion has a volume fraction that is assumed to be “small” [34]. We will not make this restriction in our examination of the MG-based EMAs. The BR, on the other hand, treats the two components of an inhomogeneous particle symmetrically [16,17], defining an effective permittivity εₑff to satisfy

\[ f_1 \frac{ε₁ - εBR}{εBR + s(ε₁ - εBR)} + f_2 \frac{ε₂ - εBR}{εBR + s(ε₂ - εBR)} = 1, \]

where \( ε₁ \) and \( ε₂ \) are the permittivities of the two components, and \( f_1 \) and \( f_2 \) are their volume fractions. In Eq. (2), \( s \) is a geometric factor related to the shape of the inclusion, and, for three-dimensional spherical inclusions, \( s = 1/3 \).

In addition to these two popular EMAs, we consider the lower and upper limits of the effective permittivites given by the Wiener bounds [35]. The absolute bounds \( ε_{min} \) and \( ε_{max} \) are given by

\[ ε_{min} = \frac{f_1 ε₁ + f_2 ε₂}{f_1 + f_2}, \]

\[ ε_{max} = f_1 ε₁ + f_2 ε₂. \]

All four of these EMAs are formulated in terms of the permittivities of constituents. In studies of atmospheric aerosols, the complex refractive index \( m \) is also commonly used, and is related to the complex permittivity \( ε \) by \( m^2 = ε \). Thus

\[ m = Re[m] + Im[m]i = \sqrt{ε}. \]

When we wish to refer to the effective permittivity without specifying the particular version, we will use the symbol \( ε_{eff} \). We define the corresponding refractive index to be \( m_{eff} \).

In addition to these four EMAs, there are more complicated ways to specify effective permittivity, and an extensive review of their homogenization strategies can be found in [12]. While differences in results obtained using one or another may occur in special circumstances, most of the approaches give values for effective permittivity that generally differ from each other by relatively small amounts. Here we just consider two popular ones and the two Wiener bounds, together given by Eqs. (1)-(4).

Before comparing the optical properties of the inhomogeneous and equivalent homogeneous particles, we directly compare the effective refractive indices given by the four EMAs. In our comparisons we will be extending some earlier work [36] that considered just volume fraction variations. Figs. 1 and 2 show two different ways of making the comparison, each with the same assumed value of the refractive index of the component whose properties are denoted by the subscript “1.” Specifically, both figures assume \( m₁ = 1.5 + 0.0001i \) (a typical value for mineral dust at visible wavelength [37]). Variations of the real and imaginary parts of the index of refraction of the other component are then considered in separate figures. In Fig. 1 \( Im[m₂] = 0 \) and variations of the volume fraction \( f₁ \) of the first component (horizontal axis in each subplot) and real part \( Re[m₂] \) (vertical axis in each subplot) of the index of refraction of the second component are considered. In Fig. 2, instead \( Re[m₂] \) is held at the value \( Re[m₂] = 1.3 \) (water or ice at visible wavelength [38]). \( Im[m₂] \) (now on the vertical axis in each subplot) is allowed to vary, while again \( f₁ \) varies on the horizontal axes.

In each of the two figures the top row of panels shows values for the real parts of the effective refractive indices as predicted by the different EMAs, and the bottom row shows values for the corresponding imaginary parts. Rather than showing the actual values for these quantities in the case of each EMA, which would result in rows of plots that would be visually indistinguishable, we show in the first panel of each row the result provided by the Bruggemann approach, and in the remaining panels of the same row show the value given by the corresponding EMA relative to the Bruggemann value, i.e. as a ratio to it. Thus it is important to note from the scaling indicated on the color bars that what by color contrast appears to be a large variation in relative values reflects in fact quite small differences in absolute values: this is an example of the feature mentioned above, that different EMAs in common use generally give only small differences in effective refractive index.

As just explained, the left-most panels of Fig. 1 show \( Re[m_{BR}] \) and \( Im[m_{BR}] \), where the subscript “BR” indicates that values are calculated by the BR. We see immediately that \( Im[m_{BR}] \) is sensitive primarily to volume fraction, while \( Re[m_{BR}] \) is sensitive to both volume fraction and \( Re[m₂] \). In considering the sensitivity of \( Re[m_{BR}] \), it is important to recall that \( Re[m₁] = 1.5 \), which is the value assigned to the color green in the color bar. This explains the value and weak sensitivity of \( Re[m_{BR}] \) to variations of \( Re[m₂] \) at volume fractions \( f₁ \approx 1 \), in which case the particle is almost entirely composed of the first component, as well as the extension of the green region all the way to \( f₁ = 0 \) at \( Re[m₂] = 1.5 \). The variation of \( Re[m_{BR}] \) follows that of \( Re[m₂] \) for small values of \( f₁ \), when the aerosol is almost completely made up of the second component.
When $|\text{Re}[m_2] - \text{Re}[m_1]| < 0.1$, the three comparison ratios are all approximately 1. This indicates that the four EMAs all produce essentially the same $\text{Re}[m_{\text{eff}}]$. When $|\text{Re}[m_2] - \text{Re}[m_1]| > 0.1$, the differences between values for $\text{Re}[m_{\text{eff}}]$ given by the different EMAs become more noticeable and increase with an increase of $|\text{Re}[m_2] - \text{Re}[m_1]|$. However, the magnitude of the relative differences between the MG results and those given by the BR is no more than 0.8%. Furthermore, the relative difference of $\text{Re}[m_{\text{min}}]$ from the BR value is less than 5%, and the
relative difference of \( \text{Re}[m_{\text{max}}] \) from the BR value is less than 3%.

With imaginary parts for both components fixed at relatively small (0.0001 and 0) values, the value for \( \text{Im}[m_{\text{BR}}] \) is almost independent of \( \text{Re}[m_{j}] \), and the values of \( \text{Im}[m_{\text{eff}}] \) given by the BR and MG are relatively close, although the differences do increase as \(|\text{Re}[m_{2}] - \text{Re}[m_{1}]|\) increases. Note from Fig. 1 that the Wiener “minimum” method can give a value for \( \text{Im}[m_{\text{eff}}] \) that is for some \( f \) larger than the BR value, and for other \( f \) smaller than the BR value. Similarly, the Wiener “maximum” method can also produce values below as well as above the BR value: relative ratio of \( \text{Im}[m_{\text{max}}] \) to \( \text{Im}[m_{\text{BR}}] \) ranges between 0.5 and 2. Note that we have chosen not to explore absorption properties in any detail as part of this study, so only very small imaginary parts will be used. Small values are typical of many atmospheric aerosols at visible wavelengths. However, some atmospheric particles are highly absorptive, and the influences of the EMAs on the scattering properties of absorptive particles could be an interesting topic for future study.

Fig. 2 shows variations of the real and imaginary parts of the effective refractive indices, displayed in the same manner as in Fig. 1, this time with the fixed value \( \text{Re}[m_{2}] = 1.3 \) and allowing \( \text{Im}[m_{2}] \) to vary. The range of these variations is indicated on the vertical axis in each of the sub-panels. As in Fig. 1, \( m_{1} \) is \( 1.5 + 0.0001i \). Although the real part of each component is fixed, the \( \text{Re}[m_{\text{eff}}] \) does show some variation with an increase of \( \text{Im}[m_{2}] \) at fixed volume fraction \( f_{1} \), and this variation becomes larger when \( \text{Im}[m_{2}] \) becomes close to 1. When \( \text{Im}[m_{2}] \) is smaller than 0.2, all four EMAs give almost the same \( \text{Re}[m_{\text{eff}}] \). The differences become more noticeable when \( \text{Im}[m_{2}] \) is larger than 0.4. The MG may give either smaller or larger \( \text{Re}[m_{\text{eff}}] \) values than the BR by 1%, while much larger differences are noticed for the values given by the Wiener bounds. The \( \text{Re}[m_{\text{max}}] \) can be over 10% larger than the BR result with \( \text{Im}[m_{2}] \) larger than 0.7 and \( f_{1} \) around 0.5, while the \( \text{Re}[m_{\text{max}}] \) may be more than 5% smaller than the BR result. For \( \text{Im}[m_{\text{eff}}] \), the values given by the four EMAs differ significantly, and the differences are sensitive both to \( \text{Im}[m_{2}] \) and to \( f_{1} \). With the small value chosen for the imaginary part for the component 1, \( \text{Im}[m_{\text{BR}}] \) of course decreases with increasing volume fraction \( f_{1} \).

For simple mixtures with two components, there are as many as five variables (\( \text{Re}[m_{1}], \text{Im}[m_{1}], \text{Re}[m_{2}], \text{Im}[m_{2}] \) and \( f_{1} \)), making it a complicated undertaking to consider variations of all those parameters. This study will instead just consider the effects of different volume fractions, while the refractive indices will be fixed. In this consideration, Figs. 1 and 2 will become very useful to infer the relative performance of the four EMAs for cases with refractive indices different from those we discuss.

3. The inhomogeneous particles considered

As is clear from the definitions of effective permittivities in the previous section, there is no attention paid to mixing state or particle shape, and one or another of the four EMAs has been used for more than one kind of particle shapes and/or mixing state. But it is certainly conceivable that the scattering properties of inhomogeneous particles with different mixing states may be substantially different, and it would seem therefore that the applicability of effective permittivity approaches should have their limits. This study is an exploration of these limits, with a restriction of focus to spherical and spheroidal particles, these being the shapes most widely used particle geometries for aerosol particles [9,10], with further restriction of the spheroids to those with an aspect ratio of 0.5. We will, however, include variations in size.

What are called “external” and “internal” mixtures are the most widely used structures to model inhomogeneous aerosols [7,39], e.g. the internally mixed sulfate and organic particles [40], sea salt and silicate mineral component [41], and externally mixed mineral dust and black carbon [42]. Stratified particles are also very common in the atmosphere, e.g. aerosol particles surrounded by condensed water vapor [43] and black carbon coated by sulfate [44]. This study will consider three mixing states:

- **Stratified particles**: One component is coated by the other. In our representation the core and mantle parts are concentric, and (for spheroids) they have the same aspect ratios.
- **Externally mixed**: Two parts with different components attached to each other, with the connecting surface being planar and perpendicular to the symmetric axis of the spheroids, i.e. a sphere or spheroid separated into two parts different refractive indices by a plane.
- **Internally mixed**: Elements of the two components are mixed uniformly throughout the entire particle. The spherical or spheroidal particle is formed by randomly arranged small elements of the two components, and the individual elements are small enough to lie in the Rayleigh scattering regime.

Fig. 3 illustrates inhomogeneous spheres (upper panels) and spheroids (lower panels) with the three mixing states. The dark and light regions represent the two components with refractive indices of \( m_{1} \) and \( m_{2} \), respectively. For the stratified particles, one component can be either the core or the mantle, and the scattering properties of both cases will be studied. Of course both the mixing states and overall particle shapes we are considering are much simpler than occur in real aerosol particles. But they do include the most important and general mixing cases seen in atmospheric aerosols, and the consideration of only such ideal versions will not, we believe, fundamentally affect the significance of conclusions we will draw concerning the applicability of the EMAs in cases of these three basic mixing states.

4. The scattering models

In the homogenization approach, equivalent homogeneous particles with their effective refractive indices calculated by the EMAs are intended to have similar optical properties to their inhomogeneous counterparts. With the particle shapes taken to be spherical or spheroidal, the scattering properties of equivalent homogeneous...
particles can be calculated efficiently and accurately by the Lorenz–Mie [26] and T-matrix [27,28] theories. The accuracy of the homogeneous approximation can be evaluated by comparing with the exact scattering properties of the inhomogeneous particles. A number of numerical methods can be used to calculate the optical properties of inhomogeneous particles, for example the core–mantle Mie theory [29,30], the finite-difference time domain method (FDTD) [45,46], the PSTD method [31,32,47], or the discrete dipole approximation (DDA) [48,49]. We choose to use the core–mantle Mie theory, a rigorous method that can be efficiently applied, for example to stratified spheres, and use the PSTD for other kinds of inhomogeneous particles. The PSTD is a numerically exact method, where we recall that in electromagnetic studies the term “numerically exact” refers to a computational method that is based on solving some form of Maxwell’s equations (hence the adjective “exact”) using a numerically convergent scheme. Other examples of numerically exact methods are the DDA and T-matrix methods. This is in contrast to, say, geometric optics methods, which are based on some form of ray-tracing equations, and hence an “inexact” physical model that only applies in a limited range of particle sizes.

The PSTD, which solves Maxwell’s curl equations in the time domain, can simulate the scattering of light by arbitrarily shaped particles [31,50]. The PSTD has been applied to spheres with size parameters up to 200 at ice refractive indices with real parts close to 1.3 [31]. Here we define the size parameter $x$ for a sphere as

$$x = \frac{2\pi r}{\lambda};$$

where $r$ is the radius of the sphere and $\lambda$ is the incident wavelength. Liu et al. [32] compared the PSTD with the DDA for homogeneous spheres and spheroids, and found the PSTD to be more efficient for numerical simulations of particles with refractive indices larger than 1.4 and small refractive indices but large sizes. In view of these comparisons of the relative applicability and efficiency of the two methods, we have chosen to use primarily the PSTD in calculating the numerically exact scattering properties of the inhomogeneous particles, using the DDA only at the outset for validation, as explained next.

Inhomogeneous particles are numerically specified in terms of the spatial distribution of the refractive indices, a specification that is straight-forward in a discretized spatial domain. The DDA has been applied for arbitrary particle shapes and compositions [52]. In this study the Amsterdam DDA implementation (ADDA) is used [53]. Because the results mentioned above concerning better performance by the PSTD for large particles considered only homogeneous particles, we will first verify the applicability of the PSTD for inhomogeneous particles by comparing the PSTD results with the core–mantle Mie results for stratified spheres and results from the DDA for externally and internally mixed particles.

The PSTD, DDA and core–mantle Mie results of stratified spheres with a size parameter of 50 are shown in Fig. 4: the volume fractions of the spherical core, i.e. $f_c$, are 0.01, 0.1, 0.5, and 0.9. The refractive index of the core is 1.2 and that of the mantle is 1.1. For the validation, relatively
small refractive indices will be used because the DDA is very accurate and efficient when the refractive indices of the particles are less than 1.2 [54,55]. The left panels show the normalized phase function $P_{11}$, and the right panels show the ratios $P_{12}/P_{11}$. Results concerning the other non-zero phase matrix elements show similar agreement and will not be shown. For all four cases with volume fractions ranging from 0.01 to 0.9, both the PSTD and DDA results show overall good agreement with the rigorous solutions, with only slight differences with $f_c = 0.9$ at some scattering angles. Similar results are found for the ratios $P_{12}/P_{11}$. Fig. 4 indicates both the PSTD and DDA to be robust and accurate methods for calculating the scattering properties of inhomogeneous particles with stratified structures and can be applied over the entire range of the volume fractions.

The conclusions are a little different if larger refractive indices are used: Fig. 5 is the same as Fig. 4 but with more realistic refractive indices of atmospheric components. The refractive index of the core is $1.5 + 0.0001i$ (mineral dust at visible wavelength [37]) and of the mantle is $1.3 + 0i$ (water or ice at visible wavelength [38]). In Fig. 5, it is clear that the PSTD results still agree very well with the analytic solutions, whereas the DDA does not perform as well. Furthermore, when $f_c$ reaches 0.9, i.e. the components with refractive index of $1.5 + 0.0001i$ becomes the predominant component, the DDA converges too slowly, and no DDA result is obtained. This indicates that the PSTD simulations and their accuracy are less sensitive to the refractive indices of the particles, while the DDA encounters difficulty as the refractive index increases.

Figs. 4 and 5 show the angular-dependent phase matrix elements of the inhomogeneous particles and their integral scattering properties, i.e. the extinction efficiency $Q_{ext}$ and asymmetry factor $g$; the relative errors are listed in Table 1. The accuracy of both methods is excellent for the coated spheres with relatively small refractive indices (all relative errors are less than 1.5%), whereas the relative errors of the DDA results become as large as 6.8% for the large refractive indices’ cases with $f_c = 0.1$. To show the relative efficiency of the PSTD and DDA at the two refractive index groups, Table 1 also includes the ratios
of the computational times used by the PSTD to DDA (all computations done on the same machine). From the ratios of the computational times used by the two methods, we can see that the PSTD is more efficient for spheres with large refractive indices (and also more accurate), whereas the DDA outperforms the PSTD for the small refractive indices (i.e. faster with a similar accuracy). Similar results on relative performance were found in the homogeneous case [32,56].

Fig. 6 shows $P_{11}$ and $P_{12}/P_{11}$ of the externally (upper panels) and internally (lower panels) mixed spheres given by the PSTD and DDA. For internally mixed particles the element size here and below, unless otherwise explicitly mentioned, is $D=0.2$ (see definition in Section 5.2). The size parameters of the spheres are 50, and the volume fractions of the two components are both 0.5. The refractive indices of the two parts are 1.2 (dark region) and 1.1 (light region). The incident directions are illustrated in the figure. The curves calculated by the PSTD and DDA are almost undistinguishable for $P_{11}$ in both cases, but the $P_{12}/P_{11}$ ratio of the internally mixed sphere differs slightly at a few scattering angles. Again, the excellent agreement indicates the applicability of the PSTD for externally and internally mixed particles. The integral scattering properties for the two cases are listed in Table 2, and the relative differences of the two methods are less than 1%.

We now turn to consideration of internally mixed particles. For the construction of these particles, once the volume fractions of the two components are fixed, the distribution of each component is randomly determined. Two different realizations of these randomly generated particles can appear to be very different, and the effects of the particle realization on the scattering properties are unknown. We used a Monte-Carlo method to generate five internally mixed spheres with a chosen volume fraction and size parameter of 50, and Fig. 7 shows the $P_{11}$ and $P_{12}/P_{11}$ of the spheres with the different mixing realizations. (More details on this construction are provided in Section 5 below.) The volume fractions of the component having a refractive index of $1.5 + 0.0001i$ are 0.1 (upper panels) and 0.5 (lower panels) and the other component has a refractive index of $1.3 + 0i$. The figure clearly shows the five spheres with the same size and volume fractions, but different mixing realizations, to have almost the same $P_{11}$.
The indication is that the optical properties of the internally mixed particles do not depend on the mixing realizations, and the light scattering by one realization of the internally mixed particles can be used to represent those of an ensemble with the same volume fraction.

The previous results indicate that the PSTD is a robust and accurate method to calculate the light scattering.

Table 1
The integral scattering properties as well as their relative errors of the stratified spheres given by the PSTD and DDA compared with the core–mantle Mie solutions, and the ratios of the CPU times used for the PSTD to DDA calculations.

<table>
<thead>
<tr>
<th>m</th>
<th>g</th>
<th>Q_{ext}</th>
<th>f_{c}</th>
<th>0.01</th>
<th>0.1</th>
<th>0.5</th>
<th>0.9</th>
</tr>
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<tbody>
<tr>
<td>1.2+0.0i</td>
<td>Core–mantle Mie</td>
<td>2.289</td>
<td>1.765</td>
<td>2.551</td>
<td>1.981</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PSTD</td>
<td>(-0.73)</td>
<td>(-0.84)</td>
<td>(0.05)</td>
<td>(1.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DDA</td>
<td>2.306</td>
<td>1.779</td>
<td>2.527</td>
<td>1.946</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(RE [%])</td>
<td>(0.0)</td>
<td>(0.056)</td>
<td>(0.0)</td>
<td>(0.36)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1+0.0i</td>
<td>Core–mantle Mie</td>
<td>0.9480</td>
<td>0.9202</td>
<td>0.9068</td>
<td>0.8916</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PSTD</td>
<td>0.9480</td>
<td>0.9177</td>
<td>0.9068</td>
<td>0.8930</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>DDA</td>
<td>0.9493</td>
<td>0.9215</td>
<td>0.9102</td>
<td>0.8986</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(RE [%])</td>
<td>(0.14)</td>
<td>(0.13)</td>
<td>(0.95)</td>
<td>(0.79)</td>
<td></td>
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<tr>
<td>1.5+0.0001i</td>
<td>Core–mantle Mie</td>
<td>2.344</td>
<td>1.957</td>
<td>1.976</td>
<td>2.205</td>
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<td></td>
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<tr>
<td></td>
<td>PSTD</td>
<td>2.342</td>
<td>1.958</td>
<td>1.978</td>
<td>2.226</td>
<td></td>
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</tr>
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<td>2.262</td>
<td>2.091</td>
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<tr>
<td></td>
<td>(RE [%])</td>
<td>(-3.5)</td>
<td>(6.8)</td>
<td>(10.0)</td>
<td>(10.0)</td>
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<td></td>
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<tr>
<td>1.3+0.0i</td>
<td>Core–mantle Mie</td>
<td>0.8582</td>
<td>0.7831</td>
<td>0.7803</td>
<td>0.8380</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>PSTD</td>
<td>0.8642</td>
<td>0.7894</td>
<td>0.7967</td>
<td>0.8357</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>DDA</td>
<td>(0.0)</td>
<td>(0.0)</td>
<td>(0.0)</td>
<td>(0.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(RE [%])</td>
<td>(-0.44)</td>
<td>(2.0)</td>
<td>(0.036)</td>
<td>(0.06)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>T_{PSTD}/T_{DDA}</td>
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<td>12.7</td>
<td>13.3</td>
<td>2.30</td>
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Fig. 6. \(P_{11}\) (left panels) and \(P_{12}/P_{11}\) (right panels) of the externally and internally mixed spheres with size parameters of 50 given by the ADDA and PSTD. The volume fractions of both components are 0.5. The refractive indices of the two components are 1.1 (light region of the sphere) and 1.2 (dark region).
properties of inhomogeneous particles. Considering the relative efficiency of the PSTD and DDA, as well as the refractive indices considered, this study uses the PSTD as the exact method to calculate the scattering properties of the inhomogeneous particles. Results obtained with the PSTD are then regarded as the “truth” in exploring the applicability of the EMAs to the simulation of the scattering properties of inhomogeneous particles.

5. Results

This section compares the scattering properties of inhomogeneous and corresponding equivalent homogeneous particles. Both single- and bulk-scattering properties will be considered, and the integral scattering properties as well as the phase matrix elements will be discussed. The comparison will focus on two issues: (1) the relative performance of the four EMAs, and (2) the performance of the EMAs to approximate the scattering properties of the inhomogeneous particles. The refractive indices of the two components will be \( m_1 = 1.5 + 0.0001i \) and \( m_2 = 1.3 + 0i \).

In what follows, when we refer to the volume fraction, we mean the fraction \( f_1 \) of component with refractive index \( m_1 \) (the volume fraction of the other component being then \( f_2 = 1 - f_1 \)). The two parameters we use to describe a spheroid with equatorial radius \( a \) and semi-length of symmetry axis are the size parameter \( x \) and the aspect ratio \( \rho \), defined by

\[
x = \frac{2\pi b}{\lambda},
\]

\[
\rho = \frac{a}{b}
\]

We will take \( \rho = 0.5 \). It should be noticed that, with this definition spheres and spheroids with the same value for size parameter can have different volumes. For stratified particles, the term “stratified 1” will refer to the case when the component with refractive index \( m_1 \) forms the core, and “stratified 2” will refer to the case when that component instead forms the mantle. All scattering properties considered are for “randomly oriented” particles, which means that averages are taken over a set of random orientations of the particle with respect to the incident direction: in the PSTD simulations, the single-scattering

<table>
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<th>( m )</th>
<th>Mixing state</th>
<th>Externally mixed</th>
<th>Internally mixed</th>
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<tr>
<td>Q_{ext}</td>
<td>PSTD</td>
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<td>1.976</td>
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<tr>
<td></td>
<td>DDA</td>
<td>1.978</td>
<td>1.977</td>
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<tr>
<td>( g )</td>
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<td>0.7884</td>
<td>0.8983</td>
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<tr>
<td></td>
<td>DDA</td>
<td>0.7932</td>
<td>0.9034</td>
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Table 2

The integral scattering properties of internally and externally mixed spheres given by the PSTD and DDA.

![Graphs showing scattering properties](image-url)
properties of spheroids with three mixing states, as well as the externally mixed spheres are each averaged over 180 scattering planes for 16 particle orientations.

5.1. Scattering from a single particle

Fig. 8 shows $Q_{\text{ext}}$ (upper panels) and $g$ (lower panels) of inhomogeneous spheres (left panels) and spheroids (right panels) with a size parameter of 30 as functions of the volume fraction. The markers in the figure indicate the core–mantle Mie and PSTD results of inhomogeneous particles with the three mixing states. The values of $Q_{\text{ext}}$ and $g$ vary dramatically with the change in volume fraction. Particles with various mixing states have significantly different integral scattering properties, especially the two stratified cases. The four curves in Fig. 8 are the results given by the EMAs for equivalent homogeneous particles (combined with the Lorenz–Mie theory for spheres and the T-matrix theory for spheroids). Of the four EMAs, the MG and BR have almost the same $Q_{\text{ext}}$ and $g$ for all volume fractions from 0 to 1. However, when the volume fraction is between 0.1 and 0.9, the $Q_{\text{ext}}$ and $g$ based on the two Wiener bounds are significantly different from those given by the other two, especially for spheres. The discrepancy can be explained by the relatively large differences in the effective refractive indices between the Wiener bounds and the other two methods. Comparing the results of the inhomogeneous and equivalent homogeneous particles, we notice that only in the cases of internal mixing do the results from the equivalent homogeneous cases (based on the BR and MG) agree well with those from the PSTD calculations; this agreement is good over the entire range of volume fractions. The relative errors given by the MG and BR compared with the PSTD results for the internally mixed cases are less than 5% for the spheres and 2% for the spheroids. However, the PSTD values of $Q_{\text{ext}}$ and $g$ for the two stratified and the externally mixed particles are very different from those of the equivalent homogeneous particles, and may be over 30% larger or smaller at some volume fractions. Thus, the EMAs appear to be able to give accurate approximations for only the internally mixed particles, and are very poor for the stratified and externally mixed particles. Because the same results are obtained for both the spheres and spheroids over the entire range of volume fractions, we expect that similar conclusions regarding the applicability of the EMAs is independent of particle shape, but have chosen not to investigate other shapes in this study.

Fig. 9 illustrates the angular-dependent $P_{11}$ (left panels) and $P_{12}/P_{11}$ (right panels) of inhomogeneous and equivalent homogeneous spheres with volume fractions of 0.5 and size parameters of 30. The ratio $P_{12}/P_{11}$ is a measure of the degree of linear polarization of the scattered light. For a clearer comparison, the results are shown in three panels: (1) the upper panels are approximations of the equivalent homogeneous spheres given by a combination of the four EMAs and the Lorenz–Mie method; (2) the middle panels are results from the two stratified spheres and the homogeneous sphere based on the effective refractive index given by the BR; and (3) the lower panels
are the same as the middle ones but for externally and internally mixed spheres. The upper panels of Fig. 9 indicate that the BR and MG give quite similar results for both phase matrix elements, but these results differ from the ones based on the Wiener bounds, especially around some peaks. The middle and the lower panels compare \( P_{11} \) and the ratio \( P_{12}/P_{11} \) for the equivalent homogeneous and inhomogeneous particles. The stratified spheres (middle panels) give totally different phase matrix elements from the equivalent homogeneous spheres for both the oscillations and the overall angular dependence. Similar to the case of integral scattering properties, the results from a combination of EMAs and Lorenz–Mie theory agree very well with those of the internally mixed sphere, except for slight differences in \( P_{12}/P_{11} \) at some scattering angles. The phase function of the externally mixed sphere follows the same overall angular dependence as the homogeneous sphere, but shows much weaker oscillations, and the \( P_{12}/P_{11} \) ratio appears very different. Comparisons for other non-zero phase matrix elements show qualitatively similar patterns of agreement and disagreement to those of \( P_{12}/P_{11} \), and will not be shown. Overall, we see from Fig. 9 that the EMAs, specifically the BR and MG, provide an accurate approximation for the phase matrix elements \( P_{11} \) and \( P_{12}/P_{11} \) of the internally mixed spheres, but cannot be reliably applied to the stratified or externally mixed cases.

Similar to Fig. 9, the \( P_{11} \) and \( P_{12}/P_{11} \) of randomly oriented spheroids with a size parameter of 30 and volume fractions of 0.5 are given in Fig. 10. Here, the effective refractive indices from the EMAs are used for the T-matrix method. The agreement between the four EMAs becomes much better for spheroids, and the \( P_{11} \) given by the Wiener bounds shows a little difference from the other three at scattering angles about 170°. Furthermore, Fig. 10 indicates that EMA applicability for calculating the phase matrix of non-spherical particles is also limited to the internally mixed ones, and both \( P_{11} \) and \( P_{12}/P_{11} \) of the stratified and externally mixed particles are significantly different from the ones given by the EMAs.

The previous results are for particles with the same size parameter and varying volume fractions. In Fig. 11 we show the results for \( Q_{\text{ext}} \) and \( q \) in the case of inhomogeneous spheres (left panels) and spheroids (right panels) as functions of the particle size parameter. The size parameter increases from 1 to 100, and the volume fraction is fixed at 0.5. As in Fig. 8, the EMA results are given by
curves with different markers to indicate the two stratified cases as well as the externally and internally mixed cases. When the size parameter is small \( \times 5 \), the \( Q_{\text{ext}} \) and \( g \) of inhomogeneous particles in the three mixing states are quite similar, and the homogeneous approximations based on the EMAs are close to those of the results of PSTD calculations for the actual inhomogeneous particles. However, the differences become significant for particles with larger size parameters, except for the case of internally mixed particles. For particles with \( \times 5 \), the EMAs can give accurate approximations only for the internally mixed particles. For the stratified or externally mixed cases, their scattering properties agree with those of their homogeneous counterparts only at some size parameters.

5.2. The scale of internal mixing

It seems that only the scattering properties of the internally mixed particles can be approximated using the EMAs, whereas the definition of the internally mixed particles are still incomplete. As we have mentioned in Section 3, the internally mixed particles we consider are made up of randomly distributed small elements that individually have sizes in the Rayleigh scattering range. Earlier studies have shown that the EMAs give reliable results for particles with such small inclusions \([22,23]\). But how large can the inclusions be before the EMAs lose their ability to represent scattering properties well? The basic elements are defined as cubes, and the size parameter of an element is defined as

\[
D = \frac{\pi d}{\lambda},
\]  

(9)

where \( d \) is the length of the cube side.

We did calculations over a range of sizes from \( D=0.2 \) to 3 in increments of 0.2 and compared with the results given by the BR. Fig. 12 shows the comparison of the \( P_{11} \) and \( P_{12}/P_{11} \) of the internally mixed spheres with just four different choices for element size. The cross sections of four such inhomogeneous spheres are also illustrated in the figure. To construct a realization of the inhomogeneous sphere with a chosen volume fraction for one component, we randomly add small cubic particles with given size in the spherical space until their total volume produces the desired fraction: that total volume is assigned to the component and the remaining volume is assigned to the other component. If only a part of a randomly positioned cube lies inside the edge of the sphere, only that part is used. A volume fraction of 0.5 is used for the simulation. For \( P_{11} \) and \( P_{12}/P_{11} \), only the sphere with very small elements \( (D=0.2) \) shows essentially the same
scattering properties as the BR results, whereas definite differences emerge when $D$ becomes 0.4, especially at scattering angles between 80° and 140°. While a choice of cubes as elementary units may seem arbitrary and special, it may be expected that, at such small sizes, the shape of the elements is not important: in fact we have found that similar results to the ones we report here are obtained with spherical basic elements. Generally, as $D$ increases the angular region of disagreement expands, and when inclusion elements have size parameter of 3, the phase function of the inhomogeneous particle becomes very smooth and significantly different from the equivalent inhomogeneous sphere calculation resulting from BR. A rough qualitative judgment based on the results in Fig. 12 would be that mixing must occur down to a scale of $D/250$ for the internally mixed particles to have the same angular-dependent scattering properties as those equivalent homogeneous ones.

5.3. Scattering from a distribution of particles

Previous results indicate that the EMAs cannot be used to approximate the single-scattering properties of stratified and externally mixed particles, and Fig. 13 shows their performance for the bulk phase matrix elements for spherical particles, i.e. scattering properties averaged over a collection of spherical particles with a given size distribution. In comparison with single particle results, the averaging results in scattering angle dependencies of matrix elements that are more smooth and relatively featureless. The incident wavelength is 0.6328 μm and the volume fraction is 0.5. The size distribution of feldspar given by the ALSD [37] is used, and the ensemble particles have an effective radius of 1.0 μm and a variance of 1.0. Fig. 13 is organized similar to Figs. 9 and 10. For the bulk phase matrix elements $P_{11}$ and $P_{12}/P_{11}$, the four EMAs are equivalent. However, the results of the homogeneous particles are dramatically different from the two stratified cases. For externally mixed particles, the EMA results in this bulk scattering case are quite close to the exact solutions given by the PSTD, but some differences are noticed at scattering angles from 90° to 150°. As expected, the $P_{11}$ given by the EMAs and Lorenz–Mie theory agree very well with those for the internally mixed particles, but the agreement becomes relatively poor for the ratio $P_{12}/P_{11}$.

Fig. 14 is the same as Fig. 13, but the overall particle shape is a spheroid with an aspect ratio of 0.5. The same incident wavelength and particle size distribution are used to give the bulk phase matrix. The upper panels of Fig. 14 show the consistency of the four EMAs to approximate the bulk scattering properties of the inhomogeneous spheroids. As seen in the middle panels, neither stratified result for $P_{11}$ or $P_{12}/P_{11}$ agrees with values given by the combination of the EMAs and T-matrix method, although the overall angular dependences differ less than is seen in the case of spherical particles. The lower left panel shows that the bulk $P_{11}$ of externally mixed spheroids and the homogeneous results good agreement for forward scattering, but the homogeneous particle values significantly underestimate the backward scattering. Similar results
Fig. 12. Comparison of the $P_{11}$ (left panels) and $P_{12}/P_{11}$ (right panels) of the internally mixed spheres with different element sizes. The volume fraction 0.5 is used for the simulation; the realizations used for different values of $D$ are illustrated in the top panel.

Fig. 13. The bulk $P_{11}$ and $P_{12}/P_{11}$ of an ensemble of spheres with effective radius of 1.0 $\mu$m and variance of 1.0.
was observed at the phase function of the single spheroid with size parameter of 30 (see Fig. 10). Considering the exact solutions of the inhomogeneous particles with the three mixing states, only the internally mixed results, both $P_{11}$ and $P_{12}/P_{11}$, coincide with the ones given by the homogeneous approximations, and the choice of the EMAs is not essential.

Figs. 8–14 compare both the single- and bulk-scattering properties of the inhomogeneous and equivalent homogeneous particles. The scattering properties of particles with the three different mixing states show significant differences. Homogeneous approximations based on the EMAs can only be applied for internally mixed particles, and are not accurate enough for the stratified and externally mixed particles. Once again we stress that we have not investigated a wider range of geometries than spheres and spheroids, but we nevertheless expect that our qualitative conclusions will extend to other shapes.

6. Conclusion

This study investigates the applicability of EMAs for calculating the scattering properties of inhomogeneous atmospheric particles, and four EMAs, three mixing states, and two overall particle shapes are considered. The EMAs are combined with the Lorenz–Mie or T-matrix theories to approximate the scattering properties of the equivalent homogeneous particles, and the results are verified by comparing with the standards-of-truth provided by calculations based on the core–mantle Mie theory or the PSTD, which consider the exact inhomogeneous mixing structures of the particles. The four EMAs give effective refractive indices with only slight differences between each other. In fact, the four EMAs show essentially the same ability to approximate the bulk-scattering properties of the inhomogeneous particles, and only the single-scattering properties given by the Wiener bounds differ from those based on the Maxwell–Garnett theory and Bruggeman theory. Considering that the bulk-scattering properties are used for most applications and that the Wiener bounds give the upper and lower limits of the EMAs, the choice of one EMA rather than another appears not to be essential for atmospheric applications. The applicability of the EMAs is independent of the volume fractions of the components and size of particles, as well as the (admittedly limited) choice of overall shapes of the particles, but is determined by the mixing state. The scattering properties of the equivalent homogeneous particles are significantly different from those of stratified or externally mixed particles, but agree with those of internally mixed particles for which the mixing occurs at small scales within the particle (with relative errors in the integral scattering properties...
for spheres and spheroids less than 5% and 2% respectively). Not surprisingly, there is no clear boundary between scales small enough for application of EMAs and scales not small enough, but good representation by the EMAs seems to require that the scale $D$ characterizing the degree of mixing should be no larger than approximately $D_{crit} \approx 0.4$. It should be noted, however, that this particular threshold mixing scale $D$ is for the choices of refractive indices made in this study, and the threshold scale may shift somewhat for other refractive indices. A more complete survey over refractive indices would be needed to determine what sensitivity the threshold mixing scale has to refractive index changes.

We note that this study considers only non-absorptive or weakly absorptive particles, making the performance of the EMAs for particles with significant absorption (e.g., black carbon and metal) an interesting topic for future research. Furthermore, in view of the significant irregularity of the atmospheric particles, the particles considered in this study must be regarded as extremely idealized models, both in terms of mixing states and overall particle geometry. Nevertheless we believe that the cases considered in this study are sufficient to establish two main points: if the EMAs are to be used as an approximation for the bulk scattering properties, the particular choice of the EMAs will matter little, and to achieve accurate scattering properties of atmospheric particles, the detailed mixing states have to be considered and only in extremely well mixed cases will EMAs be reliable.

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References


