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Particle Optics in the Rayleigh Regime

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ABSTRACT

Light scattering and absorption by particles suspended in the atmosphere modifies the transfer of solar energy in the atmosphere, thereby influencing global and regional climate change and atmospheric visibility. Of particular interest are the optical properties of particles in the Rayleigh regime, where particles are small compared with the wavelength of the scattered or absorbed light, because these particles experience little gravitational settlement and may have long atmospheric lifetimes. Optical properties of particles in the Rayleigh regime are commonly derived from electromagnetic theory using Maxwell's equations and appropriate boundary conditions. The size dependence of particle scattering and absorption are derived here from the most basic principles for coherent processes such as Rayleigh scattering (i.e., add amplitudes if in phase) and incoherent processes such as absorption (i.e., add cross sections), at the same time yielding understanding of the upper particle size limit for the Rayleigh regime. The wavelength dependence of Rayleigh scattering and absorption are also obtained by adding a basic scale invariance for particle optics. Simple consequences for particle single-scattering albedo ("whiteness") and the optical measurement of particle mass densities are explained. These alternative derivations complement the conventional understanding obtained from electromagnetic theory.

IMPLICATIONS

The simple derivation of optical properties of small particles from coherence and scale invariance considerations allows scientists to develop a simpler, more intuitive understanding of their optical properties and of changes of such optical properties during atmospheric processes changing particle morphology and size distribution. This increased understanding can be used in applications including atmospheric visibility, radiative forcing, optical particle characterization, and optical remote sensing.

INTRODUCTION

The name "Rayleigh scattering" is mostly associated with light scattering by molecular and atomic gases and the related question "Why is the sky blue?"[1,2] In addition, the name Rayleigh is commonly attached to scattering by small particles in the expressions "Rayleigh regime" or "Rayleigh limit," in which small refers to a size parameter $x \ll 1$, with $x = 2\pi r/\lambda$ being the ratio of particle circumference $2\pi r$ to wavelength λ for spherical particles. The name "Tyndall scattering" has also been suggested for the scattering by small particles.[1]

The scattering and absorption properties of small particles are well known, and there is no controversy as to the validity of the theory. However, this does not mean that the physical understanding of Rayleigh scattering and absorption could not be improved by considering different explanations. In this article, the following two questions are investigated with simple approaches:

(1) Why are the Rayleigh scattering and absorption cross sections proportional to the square of the particle volume and the particle volume, respectively (i.e., sixth and third power of the particle radius for spherical particles)?
(2) Why are the Rayleigh scattering and absorption cross sections inversely proportional to the fourth and first power of the scattered wavelength, respectively?

These questions are commonly answered using electromagnetic theory, which is based on Maxwell's equations,[3] or as a limiting case of Mie theory.[4] Although this results in correct answers, the simple alternative approach taken here complements the understanding gained from those conventional approaches.

Applications of the derived properties include the propagation of electromagnetic radiation in the atmosphere, including atmospheric visibility and radiative forcing, the probing of small particles with electromagnetic radiation, and atmospheric remote sensing, a combination of the first two applications. Examples of particles in the Rayleigh regime range from nuclei-mode aerosols interacting with visible light to rain drops being probed by radar.[5,6]

SIZE DEPENDENCE OF RAYLEIGH SCATTERING AND ABSORPTION CROSS SECTIONS

Any particle can be conceptually divided into many small regions, here called scatterers. In practice, one may choose atoms or molecules as individual scatterers and take advantage of their known scattering and absorption cross sections. If light is incident on the particle, a dipole moment is induced in each scatterer by the applied oscillating field. These induced dipole moments oscillate at the frequency of the incident light, thereby radiating (i.e., scattering) in many directions. The light scattered by the particle is due to the superposition of the radiation of the individual scatterers, taking phase differences and the resulting interferences into account. Absorption is due to the damping of the oscillating dipoles and the incoherent process that transfers electromagnetic energy into thermal energy.

For small particles ($x \ll 1$), each consisting of n scatterers, the situation is simplified as all individual scatterers radiate in phase, resulting in constructive interference between the scattered waves. Therefore, the individual scattering amplitudes $(\sigma_{sca\_i})^{0.5}$, here defined as the square root of the scattering cross section σ_{sca_i} of an individual scatterer, add up to the scattering amplitude $(\sigma_{sca})^{0.5}$ of the particle (eq 1a).[7] For particles composed of n identical scatterers with identical scattering cross sections σ_{sca_i} for all i, this results in the scattering cross section σ_{sca} of the particle being the product of the individual scattering cross section σ_{sca_i} and the square of the number of scatterers n^2.

$$\sigma_{sca} = \left(\sum_{i=1}^{n} \sqrt{\sigma_{sca\_i}} \right)^2 = n^2 \sigma_{sca\_i} \,, \tag{1a}$$

where n equals the product of number density N and particle volume V. This n^2 dependence may be counterintuitive, but is explained by the facts that (1) the "amount" of light scattered by an individual scatterer refers to the total energy of that scattered light; and (2) this energy is proportional to the square of the electric field, or to the square of the amplitude of the scattered light wave (as is characteristic of wave motion in general). When multiple individual scatterers emit light that is in phase, the emitted light waves interfere constructively, meaning the amplitudes of these light waves add. The total energy associated with the sum of these scattered light waves is proportional to the square of the amplitude of the summed light wave. So the amplitude of the scattered light is proportional to the number of scatters, but the energy, or "amount" of scattered light, is proportional to the square. More simply expressed, for coherent scattering—sum first, then square.

For a spherical particle with radius r, the number of scatterers n can be written as

$$n = NV = N \frac{4}{3} \pi r^3 \,, \tag{1b}$$

and the scattering cross section σ_{sca} becomes

$$\sigma_{sca} = (NV)^2 \sigma_{sca\_i} = \left(\frac{4}{3} \pi N \right)^2 r^6 \sigma_{sca\_i} \,. \tag{1c}$$

This equation relates the cross section σ_{sca_i} of an individual scatterer (e.g., atom or molecule), to the cross section σ_{sca} of a small particle in the Rayleigh regime, neglecting effects due to the interaction between scatterers.

For incoherent processes such as light absorption, no interferences between scattered waves occur, because for light absorption there are no scattered waves and the incident electromagnetic energy is absorbed and transferred to random thermal motion. Therefore, cross sections (not amplitudes) are added (i.e., sum the squares), yielding the particle absorption cross section as the sum of the absorption cross sections of its individual scatterers, or for n identical scatterer, as the product of n and the individual absorption cross sections σ_{abs_i}.

$$\sigma_{abs} = \sum_{i=1}^{n} \sigma_{abs\_i} = n \sigma_{abs\_i} \,, \tag{1d}$$

and for a spherical particle the absorption cross section becomes

$$\sigma_{abs} = (NV) \sigma_{abs\_i} = (\frac{4}{3} \pi N) r^3 \sigma_{abs\_i} \,. \tag{1e}$$

Thus the r^6 (for spherical particles) or more general V^2 size dependence of Rayleigh particle scattering has been obtained from two simple facts: (1) the scattering cross section is proportional to the number of identical scatterers squared (i.e., n^2); and (2) the number of scatterers (or molecules) in a particle is proportional to its volume, or to its radius cubed for a spherical particle. In addition, it becomes clear that for spherical particles, Rayleigh scattering theory is no longer applicable when the size parameter x becomes comparable to (or larger than) the scattered wavelength and the individual scatterers do not radiate in phase anymore. In this case, the contributions of individual scatterers can still be added if their phase relation and the coupling between their electromagnetic fields are accounted for. Light absorption by larger particles is not limited by coherence considerations as in the case of Rayleigh scattering but by the incomplete penetration of the particle by light. For larger homogeneous spherical particles, scattering and absorption can be calculated with Mie theory,[8] whereas for arbitrarily shaped and potentially inhomogeneous particles, powerful numerical approaches are available for the calculation of scattering and absorption.[9]

WAVELENGTH DEPENDENCE OF RAYLEIGH SCATTERING AND ABSORPTION CROSS SECTIONS

The well-known λ^{-4} wavelength dependence of the Rayleigh scattering cross section (Why is the sky blue?) and the less well-known λ^{-1} wavelength dependence of the Rayleigh absorption cross section are usually derived from electromagnetic oscillator theory in the long-wavelength approximation.[7] However, Lord Rayleigh originally derived this wavelength dependence with a simple dimensional analysis.[10] Here, an alternative derivation without the use of electromagnetic theory is presented. First, the particle scattering efficiency Q_{sca} and absorption efficiency Q_{abs} are defined as the ratio of scattering (absorption) cross section σ_{sca} (σ_{abs}) and geometric particle cross section $\sigma_{geometric}$ as

$$Q_{sca} = \frac{\sigma_{sca}}{\sigma_{geometric}} = \frac{\left(\frac{4}{3}\pi N\right)^2 r^6 \sigma_{sca\_i}}{\pi r^2} = \frac{16}{9}\pi N^2 r^4 \sigma_{sca\_i} = \frac{N^2 x^4}{9\pi^3}\lambda^4 \sigma_{sca\_i}(\lambda), \tag{2a}$$

$$Q_{abs} = \frac{\sigma_{abs}}{\sigma_{geometric}} = \frac{\left(\frac{4}{3}\pi N\right) r^3 \sigma_{abs\_i}}{\pi r^2} = \frac{4}{3} N r \sigma_{abs\_i} = \frac{2Nx}{3\pi}\lambda \sigma_{abs\_i}(\lambda), \tag{2b}$$

where the scattering (absorption) cross section σ_{sca_i} (σ_{abs_i}) is written as function of wavelength (i.e., as $\sigma_{sca\_i}(\lambda)$ and $\sigma_{abs\_i}(\lambda)$), although its wavelength dependence is to be determined. Invoking scale invariance,[11] that is, the scattering (absorption) efficiency Q exclusively depends on particle size and wavelength through their ratio (i.e., through the size parameter x; this implies that the refractive index is independent of wavelength), it can be concluded that the scattering cross section σ_{sca} must be proportional to λ^{-4} and the absorption cross section σ_{abs} must be proportional to λ^{-1} and can be written as

$$\sigma_{sca\_i}(\lambda) = \sigma_{sca\_0}\frac{\lambda_0^4}{\lambda^4}, \tag{2c}$$

$$\sigma_{abs\_i}(\lambda) = \sigma_{abs\_0}\frac{\lambda_0}{\lambda}, \tag{2d}$$

where σ_{sca_0} and σ_{abs_0} are constants (equal to the scattering and absorption cross sections at a fixed wavelength λ_0), resulting in proper, scale-invariant expressions for scattering and absorption efficiencies Q_{sca} and Q_{abs} as

$$Q_{sca} = \frac{\lambda_0^4 \sigma_{sca\_0}}{9\pi^3} N^2 x^4, \tag{2e}$$

$$Q_{abs} = \frac{\lambda_0 \sigma_{abs\_0}}{3\pi} 2Nx. \tag{2f}$$

These equations correspond to the following expressions for the scattering and absorption cross sections.

$$\sigma_{sca} = (NV)^2 \frac{\lambda_0^4 \sigma_{sca\_0}}{\lambda^4} = \left(\frac{4}{3}\pi N\right)^2 r^6 \frac{\lambda_0^4 \sigma_{sca\_0}}{\lambda^4}. \tag{3a}$$

$$\sigma_{abs} = (NV)\frac{\lambda_0 \sigma_{abs\_0}}{\lambda} = \left(\frac{4}{3}\pi N\right) r^3 \frac{\lambda_0 \sigma_{abs\_0}}{\lambda}. \tag{3b}$$

It follows that the λ^{-4} and λ^{-1} wavelength dependencies of Rayleigh scattering and absorption have been derived solely from the r^6 and r^3 dependencies of the Rayleigh scattering and absorption cross sections, respectively, and from the notion of scale invariance. Inversely, one could obtain the wavelength dependencies from electromagnetic theory and derive the size dependencies through use of scale invariance. In other words, scale invariance couples the size and wavelength dependencies of Rayleigh scattering and absorption.

The value of the constants used in equations 2e, 2f, and 3 can be determined through comparison with the conventional equations derived from electromagnetic theory as[4]

$$N^2 \lambda_0^4 \sigma_{sca\_0} = 24\pi^3 \left|\frac{m^2 - 1}{m^2 + 2}\right| \quad \text{and} \tag{3c}$$

$$N \sigma_{abs\_0} \lambda_0 = 6\pi Im\left\{\frac{m^2 - 1}{m^2 + 2}\right\}, \tag{3d}$$

where m is the complex refractive index of the particles and Im represents the imaginary part of the term in the curly brackets.

APPLICATIONS

Because the scattering cross section for Rayleigh scattering is proportional to the particle volume squared, the scattering mass efficiency (cross section per mass) is proportional to the volume and does not easily lend itself to the measurement of particle mass concentrations, where one would ideally like a scattering mass efficiency independent of particle size. Calibration of a scattering measurement in the Rayleigh regime for the determination of mass concentration is only possible if the particle size distribution stays approximately constant.[12] For incoherent processes such as light absorption by small particles, the absorption cross section σ_{abs} is proportional to the particle volume or mass yielding a direct measurement of particle mass concentrations.[13]

The coagulation of n small particles into one (still small) particle increases the collective scattering cross section (or the scattering mass efficiency) by a factor of n, whereas the collective absorption cross section (or the absorption mass efficiency) does not change. Consequently, particle single-scattering albedo ω (ratio of scattering and extinction, a measure of the particle "whiteness") in the Rayleigh regime is a function of particle size as

$$\omega = \frac{\sigma_{sca}}{\sigma_{sca} + \sigma_{abs}} = \frac{n^2 \sigma_{sca\_i}}{n^2 \sigma_{sca\_i} + n\sigma_{abs\_i}} = \frac{1}{1 + \frac{\sigma_{abs\_i}}{n\sigma_{sca\_i}}} = \frac{1}{1 + \frac{3}{4\pi N r^3}\frac{\sigma_{abs\_i}}{\sigma_{sca\_i}}} = \frac{1}{1 + \frac{3}{4\pi N r^3}\frac{\sigma_{abs\_0}\lambda^3}{\sigma_{sca\_0}\lambda_0^3}}. \tag{4a}$$

Replacing the ratio of particle circumference $2\pi r$ and wavelength λ with the size parameter x demonstrates that the single-scattering albedo ω is scale invariant (i.e., ω depends on particle size and wavelength exclusively through their ratio (i.e., through the size parameter x) and can be written as

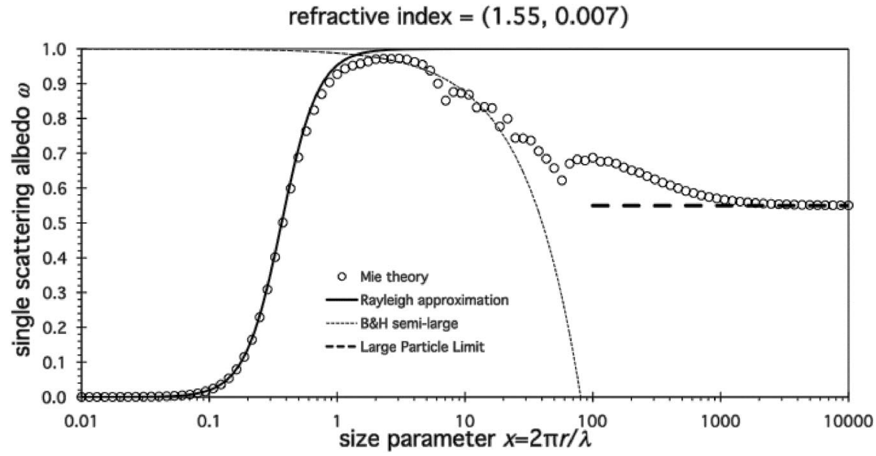

Figure 1. Calculation of single-scattering albedo for a refractive index of (1.55, 007) as function of particle size parameter *x*. Shown are calculations using Mie theory covering the whole size range (open circles), the Rayleigh approximation for small particles (solid line; as discussed in this article), Bohren and Huffman's semi-large approximation (thin dashed line), and the large particle limit (thick dashed line).

$$\omega = \frac{\sigma_{sca}}{\sigma_{sca} + \sigma_{abs}} = \frac{1}{1 + \frac{6\pi^2 \sigma_{abs\_0}}{N\lambda_0^3 \sigma_{sca\_0}} \frac{1}{x^3}}. \quad (4b)$$

Therefore, the particle single-scattering albedo increases (the particle becomes brighter) as its size parameter x increases within the Rayleigh regime, demonstrating that optical properties depend not only on material properties but also the size parameter or the ratio of particle size and wavelength. A comparison of this Rayleigh approximation with Mie theory calculations is shown in Figure 1 for particles with a refractive index of $m = 1.55 - i\,0.007$. This figure shows excellent agreement between the Rayleigh approximation and Mie theory for size parameters $x \ll 1$, with differences in albedo smaller than 1% for $x < 0.15$ and smaller than 5% for $x < 0.5$. As complement to the Rayleigh approximation discussed here, Bohren and Huffman's semi-large approximation and the large particle limit for the albedo are also shown.[4] The constants in eq 4b can be calculated from the complex refractive index as[4]

$$\frac{1}{N\lambda_0^3} \frac{\sigma_{abs\_0}}{\sigma_{sca\_0}} = \frac{Im\left\{\frac{m^2 - 1}{m^2 + 2}\right\}}{4\pi^2 \left|\frac{m^2 - 1}{m^2 + 2}\right|^2}. \quad (4c)$$

CONCLUSIONS

The basic size (i.e., r^6 and r^3) and wavelength dependencies (i.e., λ^{-4} and λ^{-1}) of particle scattering and absorption, respectively, in the Rayleigh regime have been derived from the properties of constructive interference and scale invariance with a minimum of mathematics. Differences of particle scattering in the Rayleigh regime from incoherent processes such as absorption and some simple consequences such as the size and wavelength dependence of particle albedo in the Rayleigh regime have been pointed out.

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