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Applicability of the effective medium theory for optimizing thermal radiative properties of systems containing wavelength-sized particles

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ABSTRACT

The effective medium theory (EMT) can be used for fast and approximate calculations of inhomogeneous media's optical properties, which is helpful for considerably reducing computation times for designing the thermal radiative properties of particulate materials. Because EMT has mostly been limited to systems with characteristic sizes considerably smaller than the studied wavelength, this study explores the possibility to extend EMT's applicability in particulate materials having structural sizes comparable to the radiation wavelength. Calculations are demonstrated for two types of thermal radiative properties: the extinction coefficient of a thermal insulating material and the reflectance of film solar absorbers. The results of the modified Clausius–Mossotti equation and Maxwell Garnett mixing rule are compared with methods based on more rigorous material structures and physical models. The applicable domains and limitations of the studied EMT methods are analyzed to provide a guide for utilizing EMT's potential in aiding thermal radiative property design.

1. Introduction

Thermal radiative properties of materials containing micro-/nanometer sized particles are important in many energy related applications. The radiative properties of these particulate media depend on the composing particles' optical characteristics, sizes and volume fractions. For a comprehensive literature review of experimental and theoretical works on the optical properties of heterogeneous media, one can refer to the review articles by Brosseau et al. [1,2] and Sacadura et al. [3,4]. In the engineering design of the radiative properties of particulate materials, a main challenge is to determine the optimal component parameters to achieve the desired radiative performance, such as maximizing the extinction coefficient for infrared radiation in a thermal insulation film or designing spectrally selective absorptivity to improve the efficiency of a solar absorber. The search for optimal component parameters usually requires optical calculations for a great many input cases involving different particle parameters and wavelength points. Moreover, the complicated non-ideal internal structures of particulate materials further lead to very heavy computation loads for optimization calculation of radiative properties.

Many numerical optical calculation methods are able to address the complicated material structures, such as the discrete dipole approximation (DDA) [5] and finite difference time domain method (FDTD) [6]. However, these methods require structure characterization, discretization and lengthy numerical calculations, which are too complex for large scale design optimization. Methods based on the simplified geometry model, such as the Mie theory for spherical particles with single-scattering approximation, have much smaller computation loads but are still not efficient enough for calculation involving many groups of input parameters. For example, Baneshi et al. [7] suggested using database interpolation to replace repeated Mie calculations in the design of a selectively reflecting pigment coating. Moreover, the calculation complexity may further increase if more practical material models are considered, such as multi-layer structures containing different size particles, as proposed by Wang et al. [8], to minimize the radiative transfer in opacified aerogel insulation. In this case, the optimization process would be more prohibitive to account for all design parameters.

One way to significantly accelerate the calculation is the effective medium theory (EMT) [9,10], which approximates the inhomogeneous media as homogenous ones with effective optical properties. Because the light-matter interaction is greatly simplified in a homogenous medium, calculations using EMT are much easier and faster than more rigorous methods. However, because classical EMT methods ignore structural details and particle scattering, they are only applicable to weakly scattering systems with typical structural sizes much smaller than the incident wavelength

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[9,10]. Recently, several improved models have been developed with the potential to extend the traditional application range of EMT [11–13]. Newer models have now been applied for more complicated and even anisotropic media, such as carbon nanotubes [14,15] and metamaterials [13,16,17]. Many studies examined the results of EMT by other theoretical methods and experimental results to explore its applicability for various systems [15,18–22]. Even without good quantitative accuracy, qualitative predictions by EMT are still of significant help in material design, as demonstrated by Mirmoosa et al. [17] in their theoretical study of wire metamaterials.

The aim of this work is to apply EMT to radiative property design calculations for media containing wavelength-sized particles. This type of material is important for thermal engineering applications due to their relatively easy preparation, low cost and the strong light-matter interaction caused by wavelength-sized particles. In this work, EMT is examined in calculating the extinction coefficient of the opacified aerogel and the spectral absorptance of solar absorber films. The opacified aerogel, as high temperature thermal insulation [23,24], contains micrometer opacifier grains to minimize infrared (IR) radiative transfer for 1–8 μm wavelengths. Film absorbers for solar radiation use submicron carbon aggregates to provide selective visible-to-IR absorption [25–28]. EMT calculations are applied to both systems to search for the optimal particle diameter, d, and particle volume fraction, f_{vp}. The results are compared against more rigorous computational methods, which can characterize the structure details of the studied systems. The studied EMT formulations include the modified Maxwell–Garnett mixing rule and modified Clausius–Mossotti equations. This study evaluates the accuracy of radiative property results, concludes the most appropriate EMT formulations for parameter optimization and discusses EMT's applicability and limitations in the studied material systems.

2. Fundamentals of effective medium theory

For inhomogeneous media, EMT uses mixing rules to derive the effective permittivity and permeability of the material, thus treating these inhomogeneous media as equivalent homogenous ones. This work studies the two most widely used EMT formulations: the Clausius–Mossotti (CM) relation and the Maxwell Garnett (MG) mixing rule, whose classical forms have been established for more than a century [10]. For a system containing particles dispersed in a homogeneous host medium, the CM relation gives the form of effective permittivity ε_{eff} as

$$\frac{\varepsilon_{eff}-\varepsilon_h}{\varepsilon_{eff}+2\varepsilon_h}=\frac{N\alpha}{3\varepsilon_h}=\frac{N(\alpha_E+\alpha_M)}{3\varepsilon_h} \tag{1}$$

where ε_h is the permittivity of the host medium, N is the particle number density and α is the particle polarisability, which is the sum of the polarisability caused by the electric field, α_E, and by the magnetic field, α_M. At the small particle limit, the polarisability α of an actual particle can be approximated by that of a dipole as [9]

$$\alpha = V\frac{3\varepsilon_h(\varepsilon_p-\varepsilon_h)}{\varepsilon_p+2\varepsilon_h} \tag{2}$$

where ε_p is the permittivity of the particle and V is the volume of a particle. Substituting Eq. (2) into Eq. (1) leads to the classical Maxwell Garnett mixing rule [10]

$$\frac{\varepsilon_{eff}-\varepsilon_h}{\varepsilon_{eff}+2\varepsilon_h}=f_{vp}\frac{\varepsilon_p-\varepsilon_h}{\varepsilon_p+2\varepsilon_h} \tag{3}$$

where $f_{vp} = NV$ is the volume fraction of particles.

The classical MG and CM formulas are still widely used for systems with weak scattering and particle size parameter $x = \pi d/\lambda \ll 1$ [21,29]. However, with given ε_p and ε_h, Eq. (3) implies that the effective permittivity is only determined by the particle volume fraction and not the particle sizes. Therefore, the classical formulations are incapable of describing the influence of particle sizes on the radiative properties and are only valid for very small particle sizes.

There have been many attempts to extend the capability of EMT formulations to characterize the influence of scattering and particle size. Mallet et al. [12] modified the MG mixing rule by a "radiative correction", adding a scattering loss term as an imaginary part of the effective permittivity:

$$\frac{\varepsilon_{eff}-\varepsilon_h}{\varepsilon_{eff}+2\varepsilon_h}=f_{vp}\frac{\varepsilon_p-\varepsilon_h}{\varepsilon_p+2\varepsilon_h}\left(1+\frac{2}{3}ix^3\frac{\varepsilon_p-\varepsilon_h}{\varepsilon_p+2\varepsilon_h}\right) \tag{4}$$

This correction is based on the modification of dipole polarisability in Eq. (2), where, for real ε_p and ε_h, Eq. (2) suggested that the polarisability α is also real, which disagrees with the fact that irradiated dipoles will scatter and attenuate EM waves and have non-zero imaginary parts. With this modification, Eq. (4) takes the size parameter x into consideration.

The classical CM relation can also be modified to consider the influence of particle sizes. Wheeler [11] suggested that the polarisability term in the CM relation should not be represented by the dipole polarisability but instead by the polarisability of actual spherical particles for better accuracy. The polarisability of spheres is expressed by the first Mie coefficients, a_1 and b_1:

$$\alpha=\alpha_E+\alpha_M=6i\pi a_1/k_h^3+6i\pi b_1/k_h^3 \tag{5}$$

where α_E is the part of polarisability corresponding to electrical fields and α_M is the part for magnetic fields. The first-order Mie coefficients, a_1 and b_1, are determined from the particle refractive index, m_p, and the size parameter, x [30]:

$$a_1=\frac{m_p\psi_1(m_px)\psi_1'(x)-\psi_1'(m_px)\psi_1(x)}{m_p\psi_1(m_px)\xi_1'(x)-\psi_1'(m_px)\xi_1(x)},\quad b_1=\frac{\psi_1(m_px)\psi_1'(x)-m_p\psi_1'(m_px)\psi_1(x)}{\psi_1(m_px)\xi_1'(x)-m_p\psi_1'(m_px)\xi_1(x)} \tag{6}$$

where ψ_1 and ξ_1 are first-order Riccati–Bessel functions. Wheeler [11] suggested that the polarisability could be characterized by using only the electric field term α_E. We examine this assumption by testing whether including α_M in the polarisability term will improve the results, i.e., whether one or two Mie coefficients should be used in the CM equations. The resulting two CM formulations are listed in Table 1.

In this work, EMT is used to derive the material's effective permittivity and further calculate the particulate media's goal radiative properties: the opacified aerogel's IR extinction coefficients and the solar absorber film's spectral reflectance. The derivation of thermal properties from dielectric properties is based on the common assumption that the optical properties of studied materials (carbon, silica, tungsten, etc.) will not change significantly with temperature. Refractive indices used in calculations are taken from the handbook by Palik [31].

3. Maximizing the extinction coefficient of the thermal insulation

The spectral extinction coefficient, β_λ, describes the attenuation rate of radiative energy along the propagation. To minimize the

Table 1
C-M equation formulations to be examined.

No.	Mie coefficients	C-M equation formulation
CM1	Only α_E	$\frac{\varepsilon_{eff}}{\varepsilon_h}=1+N\left[\frac{k_h^3\varepsilon_h}{6\pi i a_1}-\frac{N}{3}\right]^{-1}$
CM2	α_E and α_M	$\frac{\varepsilon_{eff}}{\varepsilon_h}=1+N\left[\frac{k_h^3\varepsilon_h}{6\pi i}\frac{1}{a_1+b_1}-\frac{N}{3}\right]^{-1}$