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Absorption in multiple scattering systems of coated spheres: design applications

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Abstract

We illustrate the utility of some recently derived transfer matrix methods for electromagnetic scattering calculations in systems composed of coated spherical scatterers. Any of the spherical coatings, cores, or host media may be composed of absorbing materials. Our formulae permit the calculation of local absorption in either orientation fixed or orientation averaged situations. We introduce methods for estimating the macroscopic transport properties of such media, and show how our scattering calculations can permit 'design' optimization of macroscopic properties.

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The considerable progress in theoretical treatments of multiple scattering [1–7] pave the way to the theoretical design of inhomogeneous media with tailor made electromagnetic properties. Single multiple coatings are a means of obtaining fundamental scatterers with novel properties, and henceforth enlarging the domain of macroscopic properties obtainable in such materials. In this work, we present some illustrative calculations with a particular emphasis on absorption properties.

In Section 1, we present a numerically stable recursive algorithm for treating spheres with multiple coatings. Reliable recursive algorithms will also be presented for treating the multiple scattering interactions between coated spheres. Formula for local absorption cross-sections are also presented. We then demonstrate in Section 2 some potential applications by employing our formulae to estimate the design properties which minimize the effective absorption lengths in both dense and tenuous coated sphere media.

1. Recursive transfer matrix algorithms

An arbitrary incident field in a homogeneous external medium can be developed in terms of regular partial waves developed about some point **0** chosen as the origin of the system of scatterers: $\mathbf{E}_{\text{inc}}(\mathbf{r}) = E\,\text{Rg}\{\Xi^{\text{t}}(k_0\mathbf{r})\}.a$, where '$a$' is a column vector composed of the coefficients of the incident wave development [7]. The abstract row vector

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$\Xi^{t}(k\mathbf{r})$ is composed of the *normalized* basis set [8] of *outgoing* vector partial waves,

$$\Xi^{t}(k\mathbf{r}) \equiv [\mathbf{M}_{1,-1}(k\mathbf{r}), \mathbf{M}_{1,0}(k\mathbf{r}), \ldots, \mathbf{N}_{1,-1}(k\mathbf{r}), \mathbf{N}_{1,0}(k\mathbf{r}), \ldots]. \quad (1)$$

In this notation, waves scattered waves from a coated scatterer centered on $\mathbf{x}_1^{(j)}$ (see Fig. 1) are expressed: $\mathbf{E}_s(\mathbf{r}_1^{(j)}) = E\,\Xi^{t}(k_0\mathbf{r}_1^{(j)}).f$, where $\mathbf{r}_1^{(j)} \equiv \mathbf{r} - \mathbf{x}_1^{(j)}$ and 'f' is a column vector of composed of the scattered wave coefficients.

The T-matrix of a coated scatterer (Fig. 1), $\tau_{1,0}^{(j)}$, connects the scattered field coefficients to those of the locally incident or "excitation" field coefficients, 'e', i.e., $f^{(j)} = \tau_{1,0}^{(j)}.e$, where $^{(j)}$ is a particle label, and the indices $_{(1,0)}$ indicate a scattered wave in medium 0 scattered from the outermost layer (1).

Dropping for the moment the particle index $^{(j)}$, the total transfer matrix of a sphere with multiple spherical coatings is obtained recursively via the formula

$$\tau_{l+1,l} = \left[\frac{T_{l+1,l} + Q_{l,l+1}.\beta_{k_{l+1}}^{[l+1,l+2]}.\tau_{l+2,l+1}.\beta_{k_{l+1}}^{[l+2,l+1]}.V_{l+1,l}}{\mathrm{I} - Q_{l,l+1}.\beta_{k_{l+1}}^{[l+1,l+2]}.\tau_{l+2,l+1}.\beta_{k_{l+1}}^{[l+2,l+1]}.U_{l+1,l}}\right] \quad (2)$$

and is initialized by a homogeneous sphere T-matrix of the innermost sphere, $\tau_{L,L-1} = T_{L,L-1}$. The $\beta_{k_i}^{[l,m]} \equiv \beta(k_i(\mathbf{x}_l - \mathbf{x}_m))$ matrices are the normalized regular addition matrices [7,8], with $\mathbf{x}_l$ denoting the center of the outer spherical interface

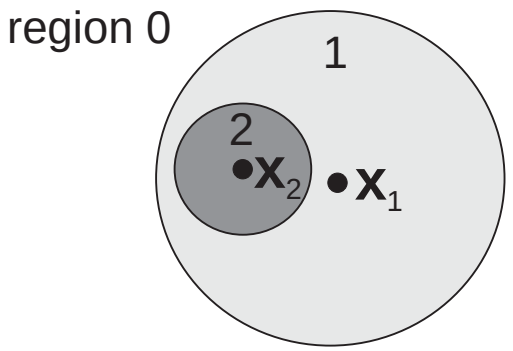

Fig. 1. Coated spherical scatterer in a homogeneous external medium (labeled 0). The first coating, 1 fills a spherical region centered on $\mathbf{x}_1$, the second coating is centered on $\mathbf{x}_2$, etc., until one encounters the innermost homogeneous sphere, labeled L.

bounding the lth layer. Expressions for the $T_{l+1,l}$, $Q_{l,l+1}$, $U_{l+1,l}$, and $V_{l+1,l}$ matrices are given in the appendix.

The solution of an electromagnetic wave interacting with a N scatterer system can be formulated in terms of N-*body* transfer matrices, $\tau_N^{(j,k)}$, containing all the multiple-scattering information and which satisfy [1,4], $f^{(j)} = \sum_{k=1}^{N} \tau_N^{(j,k)}.\beta^{(k,0)}.a$. The $\tau_N^{(j,k)}$ are constructed starting from the transfer matrices of isolated scatterers, $\tau_{1,0}^{(j)}$. The label indices $_{1,0}$ are repetitive in the multiple scattering context, and we henceforth adopt the notation $\tau_1^{(j)}$ for an individual transfer matrix, index 1 indicating that the $\tau_1^{(j)}$ describes the scattering by an isolated 1-*body* system.

The recursive solution for the N-body matrices, $\tau_N^{(j,k)}$, is to add a new scatterer, N, to a known solution of $\tau_{N-1}^{(j,k)}$ matrices describing a system of $N-1$ scatterers

$$\tau_N^{(N,N)} = \tau_1^{(N)}\left[I - \sum_{j,k=1}^{N-1} \alpha^{(N,k)}.\tau_{N-1}^{(k,j)}.\alpha^{(j,N)}.\tau_1^{(N)}\right]^{-1}, \quad (3)$$

where the $\alpha^{(N,k)}$ are the irregular addition matrices [7,8]. All the other $\tau_N^{(i,j)}$ matrices are found by matrix multiplications involving $\tau_N^{(N,N)}$:

$$\tau_N^{(N,k)} = \tau_N^{(N,N)} \sum_{j=1}^{N-1} \alpha^{(N,j)}.\tau_{N-1}^{(j,k)},$$

$$\tau_N^{(j,N)} = \sum_{k=1}^{N-1} \tau_{N-1}^{(j,k)}.\alpha^{(k,N)}.\tau_N^{(N,N)},$$

$$\tau_N^{(j,k)} = \tau_{N-1}^{(j,k)} + \sum_{i=1}^{N-1} \tau_{N-1}^{(j,i)}.\alpha^{(i,N)}.\tau_N^{(N,k)},$$

$$j \neq N, \quad k \neq N. \quad (4)$$

The above method is presented in detail in Refs. [1,3], and unlike previous recursive transfer matrix methods, it is not subject to severe numerical instabilities [9].

The individual absorption cross-sections, $\sigma_a^{(j)}$, for a coated scatterer are calculated by integrating the normal component of the Poynting vector of the *total* field at the outermost interface of the jth scatterer,

$$\sigma_a^{(j)} \equiv -\frac{1}{I_{inc}(\mathbf{0})}\oint_A \hat{\mathbf{r}}_1^{(j)} \cdot \mathbf{S}^{(j)}\,\mathrm{d}A, \quad (5)$$

where $I_{\rm inc}(\mathbf{0})$ is the irradiance of the incident wave at the origin of the system. Calculations on the partial wave basis, [2] yield the orientation fixed and orientation averaged formulae for $\sigma_{\rm a}^{(j)}$:

$$\sigma_{\rm a}^{(j)} = \frac{1}{|k_1^{(j)}|^2}\,{\rm Re}\left\{\sqrt{\frac{\mu_0}{\varepsilon_0}} f^{(j),\dagger}.\Gamma^{(j)}.f^{(j)}\right\},$$

$$\langle \sigma_{\rm a}^{(j)} \rangle_{\rm o} = \frac{2\pi}{|k_1^{(j)}|^2} \times \sum_{i,l=1}^{N} {\rm Re}\left[\sqrt{\frac{\mu_0}{\varepsilon_0}}{\rm Tr}\{[\tau_N^{(j,l)}]^{\dagger}.\Gamma^{(j)}.\tau_N^{(j,i)}.\beta^{(i,l)}\}\right], \tag{6}$$

where the $\Gamma^{(j)}$ matrix is given in the appendix. The orientation averaged cross-section $\langle \sigma_{\rm a}^{(j)} \rangle_{\rm o}$, was obtained by integrating over all possible incident directions and polarizations [1,4].

2. Reduction of the absorption length in coated spheres systems

We now demonstrate through calculations, that the absorption properties of inhomogeneous media can be enhanced via the use of coated spheres. Our chosen model problem is to minimize the dimensionless effective absorption length, $k_{\rm vac} l_{\rm a}^{\rm eff}$ of an absorbing media, of index $n_1 = 1.5 + 0.01i$, dispersed within a non-absorbing host material of index $n_0 = 1.5$.

For the purpose of comparison, let us first consider material n_1 to be fashioned into grains much smaller than the wavelength, and dispersed within media n_0. The small particle assumption means that scattering by the index n_1 grains is essentially negligible, and that the absorption length within this inhomogeneous material is $k_{\rm vac} l_{\rm a} \simeq k_{\rm vac}/(N_1 \sigma_{\rm abs}^{\rm disp}) = 1/(2 f_1 n_1'')$, where N_1 and f_1 are, respectively, the number density and volume density of the absorbing material 1. For our model refraction indices, we have then $k_{\rm vac} l_{\rm a} \simeq 50/f_1$.

We now propose to decrease the effective absorption length by placing material 1 as concentric coatings around spherical grains of a high index scatterer like TiO_2 ($n_2 \simeq 2.5$). The coated grains are then randomly dispersed in medium n_0. At low concentrations, the scattering mean-free path within the medium is $l_{\rm s} = 1/N_{\rm s}\sigma_{\rm s}$, where $\sigma_{\rm s}$ and $N_{\rm s}$ are, respectively, the scattering cross-section, and the number density of the coated scatterers. The absorption mean-free path is likewise $l_{\rm a} = 1/N_{\rm s}\sigma_{\rm a}$. The average number of scatterings that the light undergoes before being absorbed, denoted v, is therefore $v = l_{\rm a}/l_{\rm s} = \sigma_{\rm s}/\sigma_{\rm a}$.

The asymmetry parameter, g, gives the projection of the scattered component of light along the direction of incidence after a single collision. Making the usual transport assumption that after m collisions, the projection of the scattered light along the initial direction of incidence is g^m, a summation of the average distance traveled by a photon during the v collisions undergone before it is absorbed yields that the average travel distance, henceforth referred to as the 'effective' absorption length, $l_{\rm a}^{\rm eff}$, is given by

$$k_{\rm vac} l_{\rm a}^{\rm eff} = \frac{\chi_1 \sqrt{v + 2(g(v-1) - vg^2 + g^{v+1})/(1-g)^2}}{n_0 f_{\rm s} Q_{\rm s}}, \tag{7}$$

where $f_{\rm s}$ is the volume density occupied by the coated spheres, and the scattering "efficiency" is defined $Q_{\rm s} \equiv \sigma_{\rm s}/(\pi R_1^2)$. Were the scatterings to completely randomize the light propagation, $g = 0$, and one obtains the classical diffusion result that the average distance traveled is proportional $\sqrt{v}$, with $k_{\rm vac} l_{\rm a}^{\rm eff} = k_{\rm vac} l_{\rm s} \sqrt{v}$. The limit of entirely forward scattering, i.e., $g \to 1$, yields $k_{\rm vac} l_{\rm a}^{\rm eff} \to k_{\rm vac}/N_{\rm s}\sigma_{\rm a}$, as one would expect.

With the above model parameters, calculations indicate that $k_{\rm vac} l_{\rm a}^{\rm eff}$ is minimized for 'optimal' values of (see Fig. 2): $R_1 - R_2 \simeq 0.18 R_2$, and $\chi_1 = k_0 R_1 \simeq 2.2$. With these values, one obtains $k_{\rm vac} l_{\rm a}^{\rm eff} \simeq 5.1/f_1$, i.e., a factor of 10 decrease in the absorption length per unit volume compared to that of homogeneous absorbing grains.

The predictions of Eq. (7) apply only in the low scatterer density limit. At high densities, coherent scattering effects will come into play. Since these effects are largely limited to nearest-neighbor interactions, we shall model them by taking a

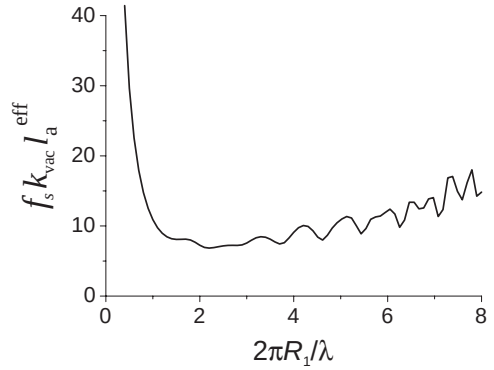

Fig. 2. The dimensionless effective absorption length is plotted as a function of the size parameter, $\chi_1 = 2\pi R_1/\lambda_0$ for $R_1 - R_2 = 0.18R_2$.

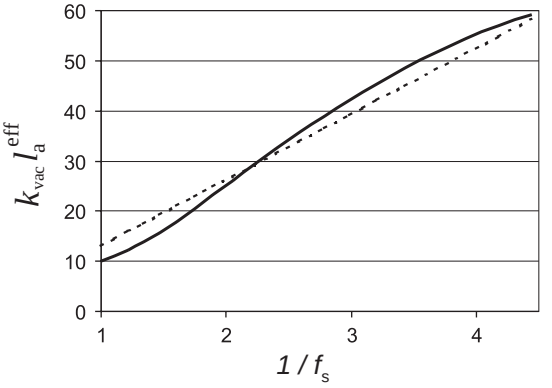

Fig. 3. Coherent scattering calculation of $k_{vac}l_a^{eff}$ plotted as a function of the density $1/f_s$. The independent scattering prediction is plotted as a dashed line for comparison.

coated sphere with the above 'optimized' parameters and surrounded by eight identical 'neighbors', and varying the interparticle distance. As a first approximation, we can employ Eq. (7) if we take care to define our individual cross sections so as to avoid over-counting of the multiple scattering effects.

The effective absorption length from the multiple scattering calculations is given in Fig. 3 as a function of the inverse volume fraction of coated spheres with the scale being modified such that close packing corresponds to $f = 1$. The results indicate that even at high filling fractions, the absorption path length is a near linear function of $1/f$, presumably due in part to the fact that the rather thick coatings create a natural separation of the strong scattering cores. Inspection of Fig. 3 predicts that coherent scattering effects can actually shorten the effective absorption length in the high-density limit. In the limit of close packing ($f_1 \approx 25\%$), the calculations indicate that l_a^{eff} could be as much as a factor of five smaller than that of a pure n_1 index material.

In conclusion, some of the new results of this work are the formulae for recursive calculations of absorption in multiple scattering composed of coated spheres (including the possibility of eccentric coatings). Another new result was the formula in Eq. (7) which permits an estimation of the average propagation distance (along the direction of incidence) of light before it is absorbed. Although based upon well-established transport theory arguments, the comparison of this formula with experimental results should prove of capability.

We would like to emphasize that the possibility to accurately calculate the scattering–absorption properties of interacting coated sphere systems opens up the possibility of performing simulations which can potentially economize both time and effort in the elaboration of heterogeneous materials composed of coated spheres. More sophisticated simulations are currently underway, and with the elaboration of new fabrication techniques of coated scatterers, we hope to be able to compare our predictions with experimental values.

Appendix A. Matrices for transfer matrices and absorption

The $T_{l+1,l}$, $Q_{l,l+1}$, $V_{l+1,l}$, and $U_{l+1,l}$ are all diagonal matrices of the form $[O]^{\mathbf{A},\mathbf{B}}_{\nu,\mu;n,m} = \delta_{n,\nu}\delta_{m,\mu}\delta_{\mathbf{A},\mathbf{B}}[O_{l,l+1}]^{\mathbf{A}}_n$. The $[T_{l+1,l}]^{\mathbf{A}}_n$ are the Mie coefficients of a homogeneous sphere [10]:

$$[T_{l+1,l}]^{\mathbf{M}}_n = \frac{\psi_n(k_l R_{l+1})}{\xi_n(k_l R_{l+1})} \times \frac{\frac{\mu_{l+1}}{\mu_l}\Phi_n(k_l R_{l+1}) - \rho_{l+1,l}\Phi_n(k_{l+1}R_{l+1})}{\rho_{l+1,l}\Phi_n(k_{l+1}R_{l+1}) - \frac{\mu_{l+1}}{\mu_l}\Psi_n(k_l R_{l+1})},$$

$$[T_{l+1,l}]_n^{\mathbf{N}} = \frac{\psi_n(k_l R_{l+1})}{\xi_n(k_l R_{l+1})} \times \frac{\rho_{l+1,l}\Phi_n(k_l R_{l+1}) - \frac{\mu_{l+1}}{\mu_l}\Phi_n(k_{l+1}R_{l+1})}{\frac{\mu_{l+1}}{\mu_l}\Phi_n(k_{l+1}R_{l+1}) - \rho_{l+1,l}\Psi_n(k_l R_{l+1})}, \quad \text{(A.1)}$$

where $\rho_{l+1,l} \equiv k_{l+1}/k_l = \sqrt{\varepsilon_{l+1}\mu_{l+1}/\varepsilon_l\mu_l}$ are the dielectric contrasts, and the functions Φ and Ψ are the logarithmic derivatives of the Ricatti–Bessel functions, $\Phi_n(z) = \psi_n'(z)/\psi_n(z)$ and $\Psi_n(z) = \xi_n'(z)/\xi_n(z)$, $\psi_n(z) = zj_n(z)$, $\xi_n(z) = zh_n^{(1)}(z)$. We remark that the $[T_{l+1,l}]_n^{\mathbf{N}}$ are obtained from the $[T_{l+1,l}]_n^{\mathbf{M}}$ by simply exchanging $\rho_{l+1,l}$ and μ_{l+1}/μ_l factors. The elements of $Q_{l,l+1} \equiv P_{l,l+1}^{-1}$, $V_{l+1,l}$ and $U_{l+1,l}$ are

$$[P_{l,l+1}]_n^{\mathbf{M}} = \mathrm{i}\psi_n(k_{l+1}R_{l+1})\xi_n(k_l R_{l+1}) \times \left\{\rho_{l+1,l}\Phi_n(k_{l+1}R_{l+1}) - \frac{\mu_{l+1}}{\mu_l}\Psi_n(k_l R_{l+1})\right\},$$

$$[V_{l+1,l}]_n^{\mathbf{M}} = \mathrm{i}\psi_n(k_l R_{l+1})\xi_n(k_{l+1}R_{l+1}) \times \left\{\frac{\mu_{l+1}}{\mu_l}\Phi_n(k_l R_{l+1}) - \rho_{l+1,l}\Psi_n(k_{l+1}R_{l+1})\right\},$$

$$[U_{l+1,l}]_n^{\mathbf{M}} = \mathrm{i}\xi_n(k_l R_{l+1})\xi_n(k_{l+1}R_{l+1}) \times \left\{\frac{\mu_{l+1}}{\mu_l}\Psi_n(k_l R_{l+1}) - \rho_{l+1,l}\Psi_n(k_{l+1}R_{l+1})\right\}$$

and as above, the $[O_{l,l+1}]_n^{\mathbf{N}}$ elements are obtained from the $[O_{l,l+1}]_n^{\mathbf{M}}$ by exchanging the $\rho_{l+1,l}$ and μ_{l+1}/μ_l factors.

The absorption matrices in Eq. (6) are expressed as

$$\begin{aligned}\Gamma^{(j)} = {} & [P_{0,1}^{(j)}.(I - T_{1,0}^{(j)}.[\tau_1^{(j)}]^{-1})]^{\dagger}.C^{(j)} .[P_{0,1}^{(j)}.(I - T_{1,0}^{(j)}.[\tau_1^{(j)}]^{-1})] \\ & + [V_{1,0}^{(j)}.[\tau_1^{(j)}]^{-1} + U_{1,0}^{(j)}]^{\dagger}.D^{(j)} .[V_{1,0}^{(j)}.[\tau_1^{(j)}]^{-1} + U_{1,0}^{(j)}] \\ & + [V_{1,0}^{(j)}.[\tau_1^{(j)}]^{-1} + U_{1,0}^{(j)}]^{\dagger}.F^{(j)} .[P_{0,1}^{(j)}.(I - T_{1,0}^{(j)}.[\tau_1^{(j)}]^{-1})] \\ & + [P_{0,1}^{(j)}.(I - T_{1,0}^{(j)}.[\tau_1^{(j)}]^{-1})]^{\dagger}.G^{(j)}.[V_{1,0}^{(j)}.[\tau_1^{(j)}]^{-1} + U_{1,0}^{(j)}]. \quad \text{(A.2)}\end{aligned}$$

The $C^{(j)}$, $D^{(j)}$, $F^{(j)}$ and $G^{(j)}$ are diagonal matrices with elements

$$[C^{(j)}]_n^{\mathbf{A}} \equiv \mathrm{i}[\tilde{\eta}_1^{(j)}]^{\mathbf{A}}\xi_n^*(k_1^{(j)}R_1^{(j)})\xi_n'(k_1^{(j)}R_1^{(j)}),$$
$$[D_l^{(j)}]_n^{\mathbf{A}} \equiv \mathrm{i}[\tilde{\eta}_1^{(j)}]^{\mathbf{A}}\psi_n^*(k_1^{(j)}R_1^{(j)})\psi_n'(k_1^{(j)}R_1^{(j)}),$$
$$[F^{(j)}]_n^{\mathbf{A}} \equiv \mathrm{i}[\tilde{\eta}_1^{(j)}]^{\mathbf{A}}\psi_n^*(k_1^{(j)}R_1^{(j)})\xi_n'(k_1^{(j)}R_1^{(j)}),$$
$$[G_l^{(j)}]_n^{\mathbf{A}} \equiv \mathrm{i}[\tilde{\eta}_1^{(j)}]^{\mathbf{A}}\psi_n'(k_1^{(j)}R_1^{(j)})\xi_n^*(k_1^{(j)}R_1^{(j)}),$$

where the $[\tilde{\eta}_1^{(j)}]^{\mathbf{A}}$ factors are $[\tilde{\eta}_l^{(j)}]^{\mathbf{M}} \equiv \sqrt{\varepsilon_1^{(j)}/\mu_1^{(j)}}$, $[\tilde{\eta}_1^{(j)}]^{\mathbf{N}} \equiv \sqrt{\varepsilon_1^{(j),*}/\mu_1^{(j),*}}$.

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