Methodology for optical characterization of multi-scale morphologically complex heterogeneous media – Application to snow with soot impurities

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Abstract. The radiative characterization of heterogeneous media with complex morphologies on multiple scales is of interest in a variety of areas such as solar energy conversion technologies or environmental sciences. An in-depth understanding and decoupling of the multi-scale morphological effects, bulk material properties, and operating conditions on the macroscopic behaviour provides pathways for morphology tailoring on multiple scales for improved application performance. We introduce a multi-scale methodology for the characterization of the spectral radiative transport in heterogeneous media with complex morphologies on two distinct scales characterized by size parameters ($\pi \cdot \text{diameter/wavelength}$) significantly above and below one. The methodology incorporates the exact morphology at the various scales and utilizes volume-averaging approaches with the corresponding effective properties to couple the scales. At the large scale the volume-averaged coupled radiative transfer equations are solved utilizing i) effective radiative transport properties obtained by direct Monte Carlo simulations at the middle scale (mm range), and ii) averaged bulk material properties obtained at the small scale (submicron scale) by discrete dipole approximation calculations. The method is exemplary applied to snow containing agglomerated soot impurities. A quantification and decoupled understanding of the morphological effect on the radiative transport is achieved and a significant influence of the dual-scale morphology on the macroscopic optical behaviour is observed.

1. Introduction
Radiative transfer in heterogeneous media is observed in a variety of significant technical applications such as in solar energy conversion processes functioning as high temperature solar absorbers or photovoltaics devices, or in naturally occurring systems such as snow pack or porous soil. The maximization of the absorption in solar energy conversion devices or the accurate characterization of the reflection behavior of earth surfaces for climate modelling are the objectives and have particular relevance in today’s society. The radiative characterization of such media is challenging as the exact incorporation of the real morphology is needed for an accurate radiative characterization. Tomography-based approaches have recently been successfully used to provide the detailed morphological information for radiative characterization down to a scale of micrometers [6]. Volume-averaging approaches provide a theoretical basis for the radiative characterization in such complex heterogeneous media through the introduction of effective transport properties, which account for the detailed morphology [9]. An additional complexity is added to radiative transport problems in
heterogeneous media when the morphologies exhibit morphological details at various scales. We provide a methodology for the investigation of such media exhibiting morphological details at two distinct scales described by their size parameters ($\chi = \pi \cdot \text{diameter/wavelength}$) significantly above and below one.

2. Methodology
The methodology accounts for three scales described as small ($\chi<1$), middle ($\chi>1$), and large scale ($\chi>>1$), and consists of the following steps: i) obtaining the detailed 3D morphology of the sub-micron scaled structures ($\chi<1$) and its incorporation into the solution of the Maxwell’s equations for the determination of the extinction- and scattering-efficiencies and scattering phase function, ii) obtaining the detailed 3D morphology of the micron sizes structures ($\chi>1$) and its incorporation into the solution of the discrete-scale radiative transfer equations (RTEs) for the determination of the effective extinction- and scattering coefficients and effective scattering phase functions, and iii) incorporation of the two-scale radiative transport properties into the coupled multi-phase volume-averaged RTEs for the determination of the averaged intensity vector field and heat transfer fluxes.

On the large-scale (continuum-scale) the intensity vector field within a heterogeneous medium composed of two different phases or components, is given by two volume-averaged RTEs [9]:

$$\hat{s} \cdot \nabla I_{i,A}(x,\hat{s}) = -\left[\kappa_{d,i} + \sigma_{s,i},d + \sigma_{s,int,i} + \sigma_{s,int,i} \phi_{d,i} \right]I_{i,A}(x,\hat{s}) + n_{d,i}^2 \kappa_{d,i} I_{s,i,B_i}(x)$$

$$+ \frac{1}{4\pi} \int I_{i,A}(x,\hat{s}_m) \left[\sigma_{s,i,d} \phi_{d,i} (\hat{s}_m,\hat{s}) + \sigma_{s,int,i} \phi_{int,i} (\hat{s}_m,\hat{s})\right]d\Omega_m$$

$$+ \frac{\sigma_{s,int,i}}{4\pi} \int I_{i,A}(x,\hat{s}_m) \phi_{int,i} (\hat{s}_m,\hat{s})d\Omega_m,$$

where $I_i$ represents the volume-averaged intensity of phase $i$; $\kappa$, $\sigma$, $\beta$, $\Phi$, represent the absorption coefficient, scattering coefficient, and extinction coefficient, and the scattering phase function, respectively; the subscript d represents bulk properties of the phases which incorporate morphological characteristics at the small scale ($\chi<1$); the subscript int represents the effective properties which incorporate morphological characteristics with dimensions at the middle scale ($\chi>1$). The coupled RTEs can be solved using path-length based Monte Carlo methods with appropriate large-scale boundary conditions [5].

The effective properties, $\sigma_{ii}$, $\sigma_{ij}$, $\beta$, $\Phi_{ii}$, $\Phi_{ij}$, are postulated when deriving the volume-averaged RTEs [9] and a collision-based Monte Carlo method is used for the determination of the effective properties [4]. The exact morphology is incorporated by using a level-set approach for the discretization and X-ray tomography for obtaining the 3D morphology [10].

The bulk properties account for morphological characteristics at the sub-micron scale ($\chi<1$) and are determined by solving the Maxwell’s equations [1]. The Maxwell’s equations are solved by using the discrete dipole approximation (DDA) where the complex structures are approximated by a large numbers of dipoles and the calculated dipole moments are used for the determination of the scattering and extinction efficiencies, and scattering phase function [2, 3].

3. Application to snow with soot impurities
The methodology introduced is applied to snow layers with soot impurities. The importance for the characterization of the radiative behaviour of snow is related to the fact that the total net anthropogenic radiative forcing is predicted to be 1.6 ±0.8/-1.0 W/m², of which in average 0.1 W/m² are associated to changes in surface albedo due to soot impurities in snow but with a large uncertainty of +/-0.1 W/m² [7]. Snow and agglomerated soot have both very complex and stochastic morphologies as shown and characterized in Table 1. We choose two distinct snow samples: i) metamorphosed snow (ml), and ii) wet snow (ws), which have been incorporated using X-ray tomography [5]; and two types of soot agglomerates, each composed of 400 primary particles of 10 nm diameter and randomly accumulated [8]. Additionally, the soot agglomerates have been approximated by an equivalent sphere with the
same volume as the agglomerates, and by 400 single particles with the primary particle diameter. A volume fraction of soot in the ice of $10^{-6}$ was exemplary chosen. The spectral complex refractive index of ice and soot has been extracted from literature [12, 11].

**Table 1. Morphological characteristics and refractive index of snow and soot agglomerates.**

| Morphology          | Porosity | Specific surface | Particle size | Anisotropy | Fractal dimensionality | Refractive index |
|---------------------|----------|------------------|---------------|------------|------------------------|-----------------|
| Metamorphosed snow (ml) | 0.85     | 6 mm$^{-1}$      | 80 µm [5]     | 0.157      | -                      | Ice [12]        |
| Wet snow (ws)       | 0.38     | 3 mm$^{-1}$      | 666 µm [5]    | 0.035      | -                      | Ice [12]        |
| Agglomerate 1 (a1)  | 0.85     | 89 µm$^{-1}$     | 10 nm         | 0.141      | 2.412                  | Soot [11]       |
| Agglomerate 2 (a2)  | 0.95     | 31 µm$^{-1}$     | 10 nm         | 0.514      | 2.175                  | Soot [11]       |

The spectral scattering and extinction efficiencies and scattering phase function of the soot agglomerates have been calculated using DDSCAT [2, 3] or BHMIE [1]. Together with the spectral effective scattering and extinction coefficients and scattering phase functions, these properties are used to solve eqs. (1). The calculated hemispherical-hemispherical reflectivity of an infinite ml and ws 4cm-thick snow slab diffusely irradiated is depicted in Figure 1. The difference in reflectance was up to 275% for wavelengths below 1.5 µm solely based on the middle scale morphology. For the same mid-scale morphology, variations in small scale morphologies lead to differences of up to 18%.

**Figure 1.** Reflectance of a diffusely irradiated 4 cm-thick ml and ws snow layer without (dashed) and with soot impurities modeled as i) uniformly distributed single soot primary particles (black solid), ii) uniformly distributed agglomerates modeled by an equivalent large sphere (black dashed), and iii) uniformly distributed agglomerates with high (grey solid) and low (grey dotted) fractional dimensionality.

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