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Radiative Properties of Silica Nanoporous Matrices

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Abstract Superinsulating materials are currently of much interest because of the price of energy on the one hand and CO_2 emissions attributed to offices and houses cooling and heating on the other hand. In this work, we aim at understanding and modeling the radiative transfer within silica nanoporous matrices that are the principal components of nanoporous superinsulating materials. We first elaborate samples of various thicknesses from a pyrogenic silica powder. These samples are characterized using two spectrophotometers on the whole wavelength range [250 nm; 20 μm]. Using a parameter identification technique, we compute the radiative properties of the various samples. Then, our samples being made of packed quasi-spherical particles, we use the Mie theory to model the radiative properties of these materials. Due to the observed discrepancies between the experimental radiative properties and those computed from the Mie theory with a uniform value of 10 nm for the scatterer diameter (value derived from TEM images), we determine an effective scatterer diameter that allows a good agreement between the experimental radiative properties and the Mie results. Nevertheless, in the short wavelength range, the Mie theory gives results that significantly differ from the experimental radiative properties. This behavior is attributed to structure effects as the wavelength is of the same order of magnitude as the diameter of the scatterer that is now regarded as an aggregate of nanoparticles. Hence, to take into account these effects, we use the discrete dipole approximation (DDA). The DDA extinction coefficient spectra appear to be much closer to the experimental results than the Mie spectra, and these first results are quite encouraging.

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1 Introduction

Nanoporous superinsulating materials are currently the subject of much attention because of their superb thermal insulation properties [1]: up to five times better than air that is generally regarded as an excellent thermal insulator, when they are placed under primary vacuum. These materials are made of nanoporous matrices of amorphous silica nanoparticles, fibers to provide mechanical reinforcement, and micrometric particles to improve opaqueness in the infrared wavelength region. The aim of our research is to determine experimentally and to model the radiative properties of such nanoporous materials that are semi-transparent media in the considered wavelength range. In the preliminary study reported here, we consider only the nanoporous matrix.

We first present the relevant characteristics of our samples under study and the method we use to measure their optical properties. Then, after a brief description of the radiative transfer equation (RTE) and of the parameter identification technique that we have used, we discuss the radiative property spectra obtained. Finally, these experimentally determined spectra are compared to the radiative properties computed using two different theoretical methods.

2 Measurement of the Optical Properties of Silica Nanoporous Matrix Samples

The studied material is a silica nanoporous matrix obtained by packing pyrogenic silica nanoparticles supplied by the German company Wacker (reference of the powder: HDK-T30). TEM images allowed estimation of the diameter of the primary nanoparticles, which is between 10 nm and 15 nm. The material is highly porous (porosity of around 90 %), and different samples were fabricated with thicknesses ranging between 2.0 nm and 10.5 mm. All these samples were then optically characterized using two different spectrometers covering an overall spectral band of [250 nm; 20 μm]. The quantities measured were the hemispherical transmittance and reflectance properties; the two spectrometers were equipped with integrating spheres that collect hemispherically the radiation traveling through or reflected by the samples.

Figure 1 shows the spectra obtained for three samples of thicknesses 2.8 mm, 5.9 mm, and 10.5 mm. These spectra are in accordance with what was expected. As far as the transmittance is concerned, we can point out that this quantity decreases as the sample thickness increases, which is quite consistent. In the neighborhood of the 3 μm wavelength, the transmittance almost vanishes; this large absorption spectral zone is attributed to the presence of water within the pores and/or at the surface of the silica nanoparticles (see later). Above 8 μm, the transmittance vanishes because of the bulk absorption of silica that strongly increases in this wavelength range. With regard to the reflectance, we note that this quantity increases with the sample thickness; this behavior is consistent and finds its explanation in the fact that the quantity of backscattered photons increases with the sample thickness. Above 8 μm, the reflectance does

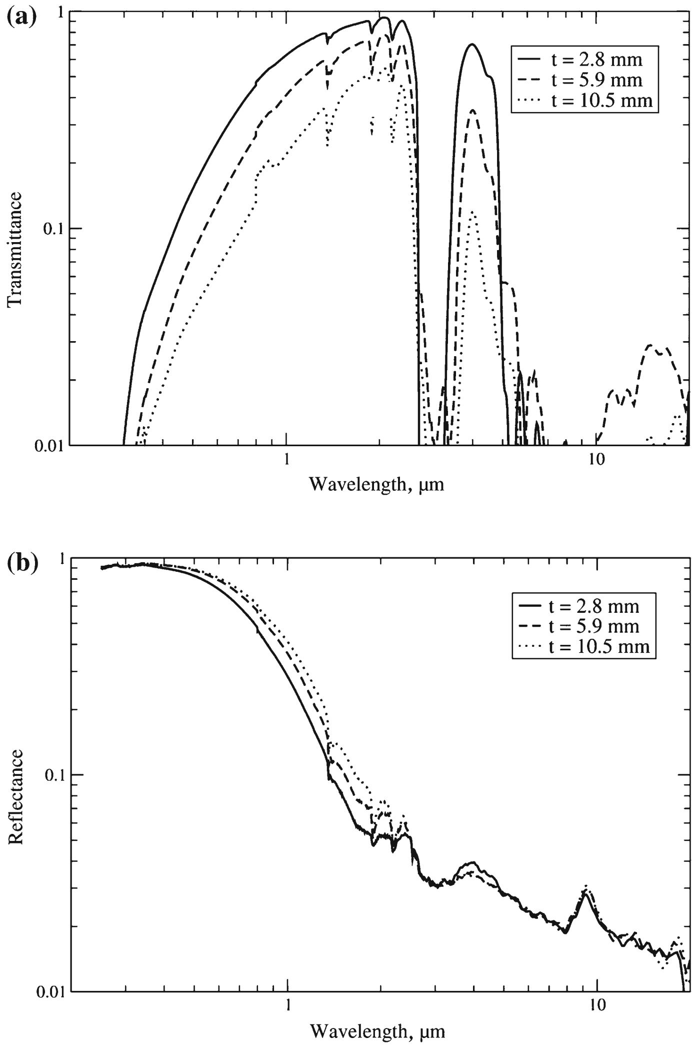

Fig. 1 (**a**) Hemispherical transmittance and (**b**) reflectance spectra in the spectral band [250 nm; 20 µm] for three samples of different thicknesses

not depend on the sample thickness: silica being very absorbing in this wavelength range, even the thinnest sample can be considered as optically thick.

3 Determination of the Radiative Properties of the Silica Nanoporous Matrix from the Experimental Optical Data

Once the optical properties of the samples were determined, we have transcripted these data into radiative properties of the silica nanoporous matrix. To this end, we have used the radiative transfer equation (RTE) formalism and a parameter identification technique.

First, we consider the sample as a homogeneous medium. Moreover, we assume one-dimensional radiative transfer with azimuthal symmetry. Finally, we ignore the self-emission term. Under these assumptions, we can write the RTE as follows:

$$\frac{\mu}{\beta_\lambda}\frac{\partial L_\lambda(z,\mu)}{\partial z} + L_\lambda(z,\mu) = \frac{\omega_\lambda}{2}\int\limits_{\mu'=-1}^{1} \Phi_\lambda\left(\mu',\mu\right) L_\lambda\left(z,\mu'\right)\,\mathrm{d}\mu' \tag{1}$$

where L_λ is the space and direction dependent intensity field, z is the spatial coordinate (lying between 0 and the thickness t of the sample), β_λ is the spectral extinction coefficient, ω_λ is the spectral scattering albedo, Φ_λ is the spectral scattering phase function, and μ is the cosine of the polar angle.

Since the diameter of the silica particles constituting the material is close to 10 nm and the wavelengths considered are, at least, 250 nm, the radiation-particle interaction lies clearly within the Rayleigh regime; consequently, for all the wavelengths investigated, the spectral phase function Φ_λ was given the value of the Rayleigh phase function.

The material being very porous (porosity $\approx$ 90 %), the optical constants of the optically equivalent homogeneous material are close to those of air, so that reflections at the interfaces may be neglected. Under these circumstances, the boundary conditions are simply as follows:

- At the front surface of the sample $z = 0$, i.e., the surface submitted to the illumination: $L_\lambda\,(z = 0, \mu > 0) = \Psi_\lambda\,(\mu)$, where Ψ_λ is the direction and wavelength dependent illumination function;
- At the back surface of the sample $z = t$: $L_\lambda\,(z = t, \mu < 0) = 0$.

As the thickness of the sample and the spectral phase function are known, if we know the values of β_λ and ω_λ, we can solve the RTE and compute the intensity field L_λ. From that field, the hemispherical transmittance and reflectance can be computed using the following expressions:

$$T_\lambda^h = \frac{\int_0^1 L_\lambda\,(t,\mu)\,\mu\,\mathrm{d}\mu}{\int_0^1 \Psi_\lambda\,(\mu)\,\mu\,\mathrm{d}\mu} \quad R_\lambda^h = -\frac{\int_{-1}^0 L_\lambda\,(0,\mu)\,\mu\,\mathrm{d}\mu}{\int_0^1 \Psi_\lambda\,(\mu)\,\mu\,\mathrm{d}\mu} \tag{2}$$

The intensity field L_λ is computed using the discrete ordinate method (DOM) that consists of replacing the angular integrals by quadratures:

$$\int\limits_{4\pi} f\left(\vec{\Delta}\right)\,\mathrm{d}\Omega \approx \sum_{i=1}^{N} w_i f\left(\vec{\Delta}_i\right) \tag{3}$$

Using the DOM, the new form of the RTE is

$$\frac{\mu_j}{\beta_\lambda}\frac{\partial L_\lambda\left(z,\mu_j\right)}{\partial z} + L_\lambda\left(z,\mu_j\right) = \frac{\omega_\lambda}{2}\sum_{i=1}^{N} w_i\ \Phi_\lambda\left(\mu_i,\mu_j\right)\ L_\lambda\left(z,\mu_i\right) \tag{4}$$

In the same way, the expressions of the hemispherical transmittance and reflectance become

$$T_\lambda^h = \frac{\sum_{i=1}^{\frac{N}{2}} w_i L_\lambda\left(t,\mu_i\right)\mu_i}{\sum_{i=1}^{\frac{N}{2}} w_i \Psi_\lambda\left(\mu_i\right)\mu_i} \qquad R_\lambda^h = -\frac{\sum_{i=\frac{N}{2}+1}^{N} w_i L_\lambda\left(0,\mu_i\right)\mu_i}{\sum_{i=1}^{\frac{N}{2}} w_i \Psi_\lambda\left(\mu_i\right)\mu_i} \tag{5}$$

The whole procedure that we have described above, which allows the evaluation of the optical properties of our samples from the knowledge of their radiative properties, must be regarded as the direct problem; the inverse problem is numerically solved using a method based on the Newton–Raphson algorithm. The radiative property spectra obtained that way are shown in Figs. 2 and 3.

4 Comparison Between the Experimentally Determined Radiative Property Spectra of the Silica Nanoporous Matrix and the Spectra Derived from Two Different Models

One of the main goals of our work is to be able to predict the radiative behavior of our silica nanoporous matrix material on the basis of its morphological description. As a first step, we will compare the experimentally determined radiative properties to those computed via the well-known Mie theory. Due to discrepancies observed between the experimental and Mie data in the short wavelength range, we are presently working on an alternative modeling technique based on the discrete dipole approximation (DDA); we will present the first results derived from this new approach in the second part of this section.

4.1 Comparison of the Experimentally Determined Radiative Properties of the Silica Nanoporous Matrix to Those Derived from the Mie Theory

The studied material being made of packed-spherical nanoparticles, it appears quite natural to try the Mie theory [2] (that allows computation of the interaction (scattering and absorption) between an electromagnetic wave and a homogeneous sphere) to predict the radiative properties of the matrix.

The pyrogenic silica used to fabricate the samples is very hydrophilic; in order to take into account the water contribution in our calculations, we have made use of the coated sphere model developed by Bohren et al. [3]. We chose a water coating thickness in order to respect the water volume fraction that can be determined from the experimental radiative properties, more precisely from the small step at 4.7 μm and the peak at 6.1 μm which are directly related to two peaks of the water extinction index

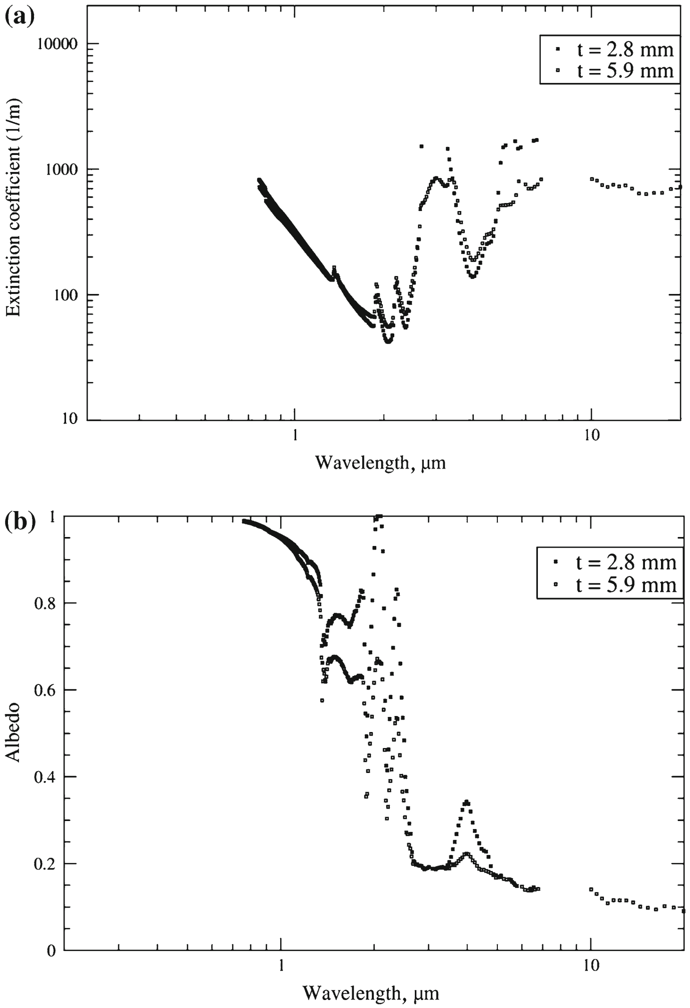

Fig. 2 (**a**) Extinction coefficient and (**b**) scattering albedo spectra of two samples of different thicknesses obtained by parameter identification (optical measurements performed in November 2005)

spectrum. On Fig. 4, we have plotted the extinction spectra computed for various water volume fractions (from 0 % to 6 %) in the wavelength range [3.0 µm; 7.0 µm]. From Fig. 4a that shows three experimental extinction spectra and those computed with the Mie theory for water volume fractions of 0 %, 2 %, 4 %, and 6 %, we clearly see that the water volume fraction is more important than 2 % and less than 6 %. Hence, on Fig. 4b, we have plotted the three experimental extinction coefficient spectra and those computed with the Mie theory for water volume fraction of 3 %, 4 % and 5 %. Figure 4b allows a refinement of the evaluation of the water volume fraction: with a water volume fraction of 3 %, the computed peak at 6.1 µm is a little weak as compared to its experimental counterpart, whereas for a volume fraction of 5 %, this peak as well as the extinction step around 4.7 µm appear to be more pronounced on the Mie

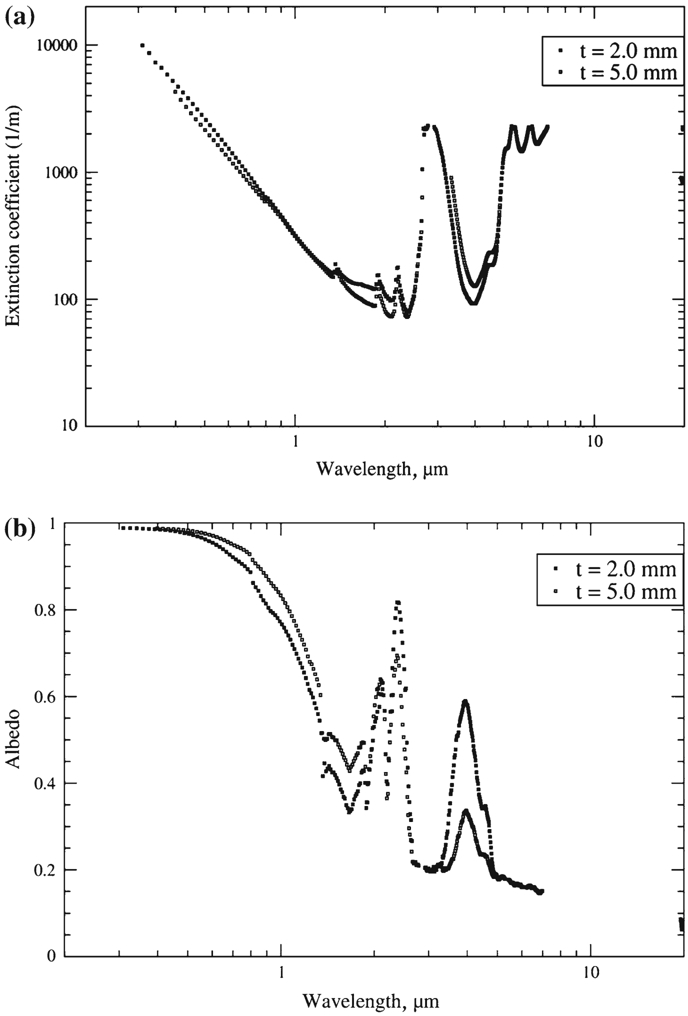

Fig. 3 (**a**) Extinction coefficient and (**b**) scattering albedo spectra of two other samples of different thicknesses obtained by parameter identification (optical measurements performed in December 2006)

calculation than on the experimental spectrum. Hence we conclude with a value of the water volume fraction of 4 %, which could be derived from the experimental extinction spectra with a precision of about ±1 %. This value of 4 % is quite consistent with the 1.5 % water mass fraction value reported by the manufacturer of the silica powder that we have used to elaborate our samples [4].

Assuming a uniform nanoparticle diameter of 10 nm, the radiative properties that we obtained from the Mie theory appeared to be quite far from the experimentally determined ones, notably in the wavelength range over which scattering dominates the radiative transfer (see Fig. 5). On the other hand, we found that an increase in the particle diameter in our Mie calculations up to a value of 45 nm resulted in a very

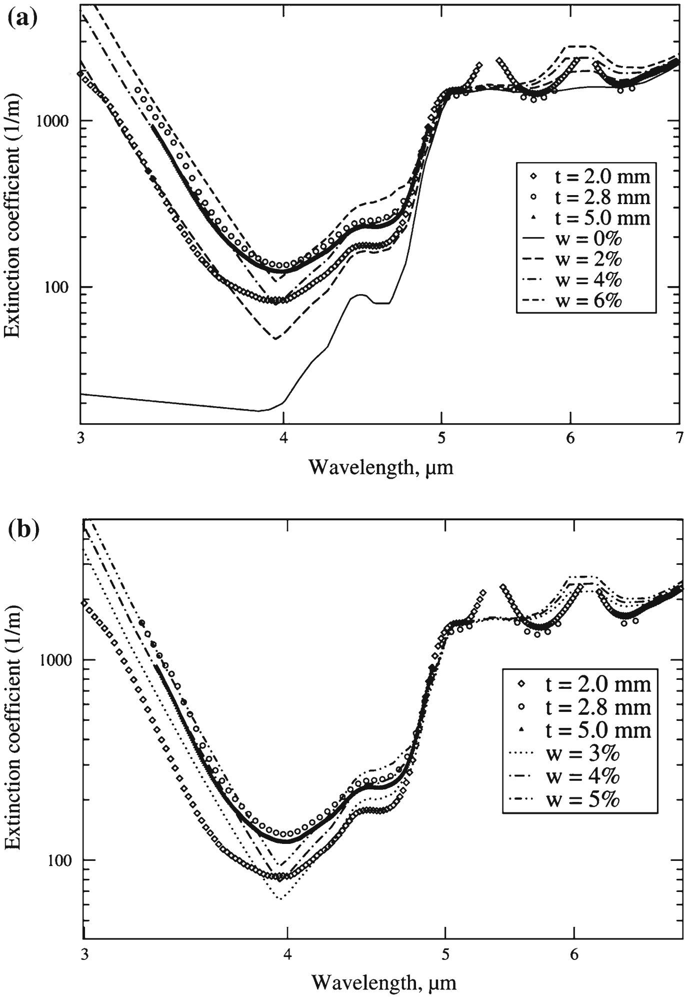

Fig. 4 Comparison of the experimental extinction coefficient spectra for three samples of various thicknesses to those computed with the Mie theory for various water volume fractions: **(a)** 0 %, 2 %, 4 %, and 6 % and **(b)** 3 %, 4 %, and 5 %

satisfactory agreement between the experimental and calculated data, for wavelengths above 1 µm and for both the extinction and albedo spectra (see Fig. 6). In other words, it may be said that, from the point of view of the interaction with electromagnetic waves, our material behaves approximately as a cloud of uniform size particles with a diameter of about 45 nm. Although this value is significantly different from the diameter of the primary particles, it is not an absurd one: indeed, during the silica powder fabrication process, the primary nanoparticles of 10 nm diameter fuse together to form larger units of approximately 120 nm hydrodynamic equivalent sphere diameter [4]. If we assume that the porosity of these aggregates is the same as that of the matrix, the volume of

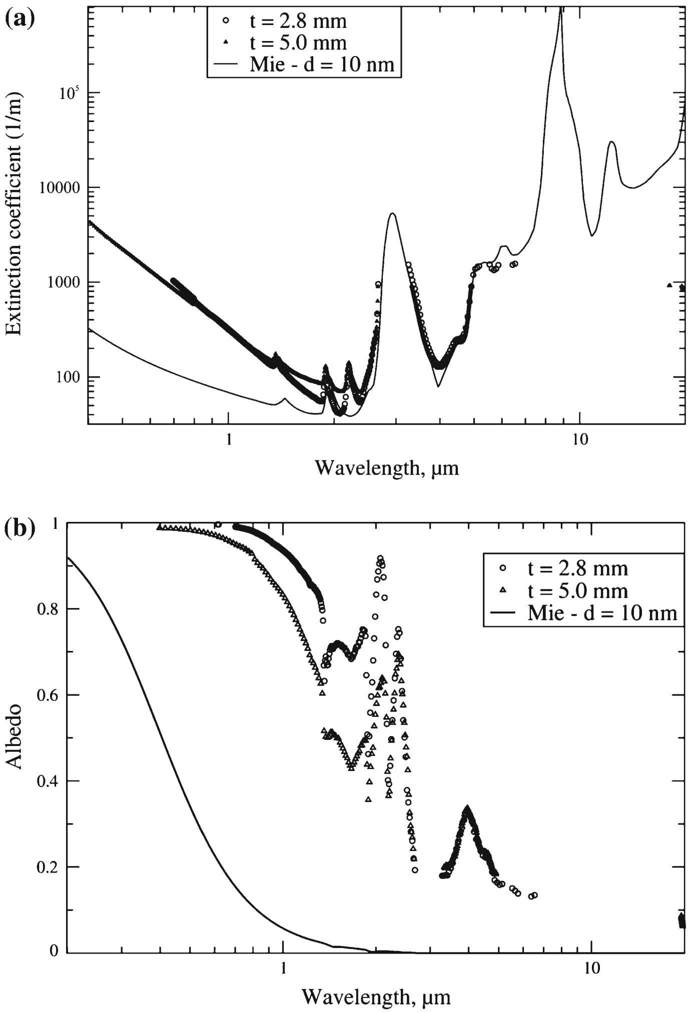

Fig. 5 Comparison of (**a**) extinction coefficient and (**b**) scattering albedo spectra. Symbols: experimental results collected on two samples; solid curve: Mie theory predictions. Parameters used for the Mie calculation are 10 nm diameter nanoparticles and 4 % water volume fraction

silica contained in such an aggregate is approximately equivalent to the volume of a dense silica sphere of 45 nm diameter.

For wavelengths below 1 µm, we still observe an unsatisfactory agreement between the experimental radiative property spectra and the predicted ones. This may be interpreted as nanostructure effects and tends to show the limit of the Mie theory: as long as the wavelength is superior to 1 µm, the interaction between the wave and the scatterer is not sensitive to the shape of the scatterer because the latter is significantly smaller than the wavelength; on the contrary, when the wavelength is below 1 µm, the wavelength and the size of the aggregate are of the same order of magnitude, so the scattering properties become aggregate shape sensitive. The Mie theory can not

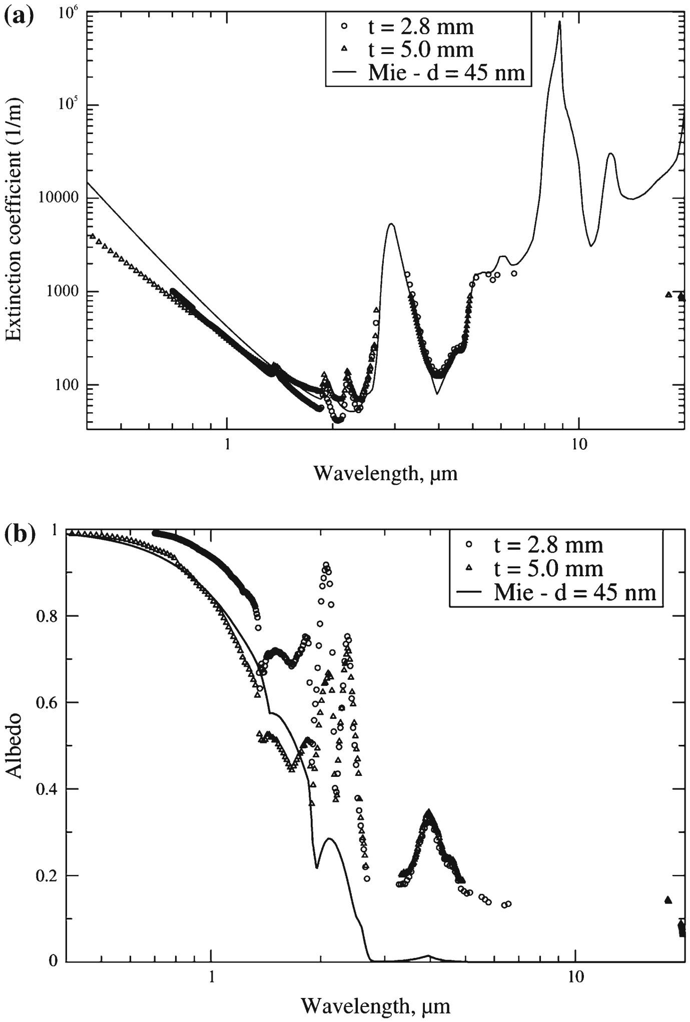

Fig. 6 Comparison of (**a**) extinction coefficient and (**b**) scattering albedo spectra. Symbols: experimental results collected on two samples; solid curve: Mie theory predictions. Parameters used for the Mie calculation are 45 nm diameter nanoparticles and 4 % water volume fraction

take into account the microstructure of these aggregates. Hence, we can propose the hypothesis that the nanoporous matrix scatters radiation in the same way as a cloud of primary scatterers, the primary scatterer being here the aggregate obtained during the silica powder production process.

In order to evaluate the sensitivity of the radiative properties to the structure of the aggregates at small wavelengths, we are currently working on an alternative way to compute the radiative properties of the silica nanoporous matrix that takes into account the material microstructure: the discrete dipole approximation.

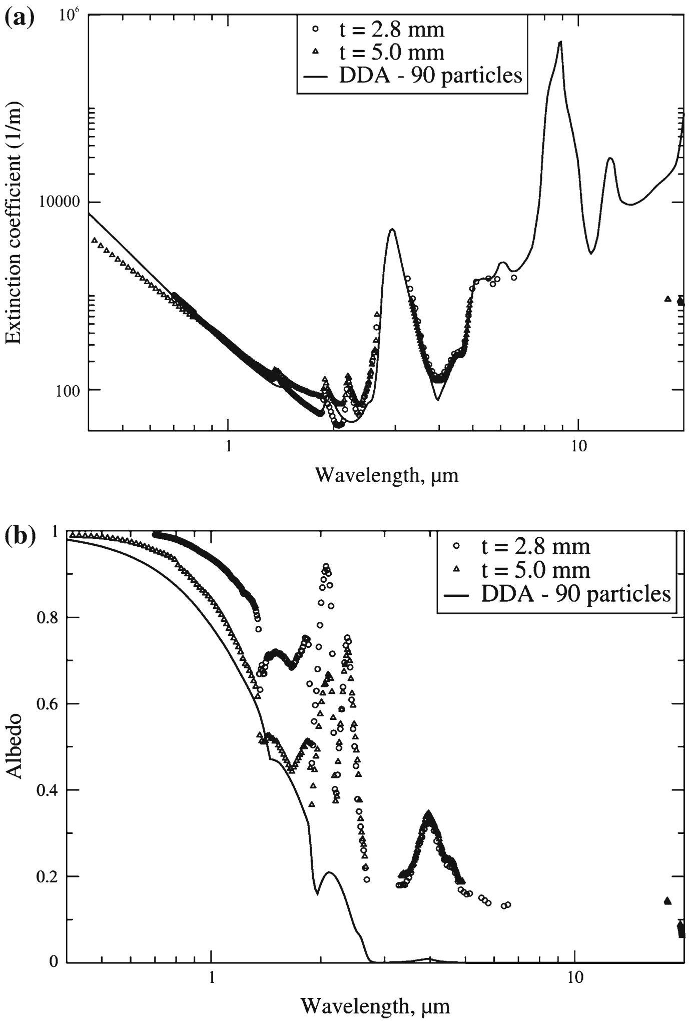

Fig. 7 Comparison of (**a**) extinction coefficient and (**b**) scattering albedo spectra. Symbols: experimental results collected on two samples; solid curve: DDA predictions. For this DDA calculation, we assume 10 nm diameter spherical nanoparticles that do not overlap. The water contribution is taken into account using a Maxwell–Garnett mixing rule on the relative dielectric function

4.2 Comparison of the Experimentally Determined Radiative Properties of the Silica Nanoporous Matrix to Those Derived from the Discrete Dipole Approximation

The discrete dipole approximation (DDA) [5,6] is a flexible method that allows computation of the absorption and scattering properties of irregular targets (particles of complex shapes, clusters of spheres) approximated by arrays of point dipoles. DDA calculations require a prior step consisting of the localization of dipoles in space and the evaluation of their polarizabilities. Concerning the polarizabilities, since we apply the DDA on a cluster of spherical particles that are small compared to the wavelength, we may treat each particle as a single dipole using the a_1 term method. This method has been shown to be superior to the other polarizability prescriptions for a cluster of spherical monomers replaced by single dipoles [7]. The dipole moments within the cluster result, on the one hand, from an incident electromagnetic field that activates them, and on the other hand, from the interaction between them; once these dipole moments are solved, it is possible to determine the radiative properties of the cluster.

As stated earlier, prior to DDA calculations, the dipoles must be localized in space. In order to obtain valuable results, the material structures on which DDA calculations are performed must be representative of our nanoporous matrix in terms of porosity ($\approx$90 %), specific surface area ($\approx$250 $\mathrm{m}^2 \cdot \mathrm{g}^{-1}$) and fractal dimension ($\approx$1.8 according to the literature [8]). To this end, we have generated numerical structures with the help of the diffusion limited cluster–cluster aggregation algorithm [9,10]. We have integrated the water contribution in the relative dielectric permittivity, and hence in the polarizability of the particles, with the help of the Maxwell–Garnett mixing rule. We have generated clusters of 90 particles of 10 nm diameter with a 4 % water volume fraction; the number of 90 particles was chosen in order to form clusters of 120 nm equivalent diameter and of 90 % porosity. The satisfactory correspondence between the experimental and simulated radiative property spectra (see Fig. 7) is quite encouraging, and is a first step toward a reasonable representation of the material organization within our silica nanoporous matrices.

5 Conclusion and Outlook

We have determined the spectral radiative properties of silica nanoporous matrices from experimentally obtained reflectances and transmittances by inversion of the radiative transfer equation. These experimental data have appeared to be substantially different from the predictions of the Mie theory assuming a uniform diameter distribution of 10 nm for the particles. On the other hand, Mie calculations with a particle diameter increased to 45 nm resulted in radiative property spectra in quite good agreement with the experimental values.

On the basis of the very little we know about the silica powder, we have proposed an explanation for this 45 nm equivalent diameter value that seems to be confirmed by our first DDA calculations. However, these satisfactory preliminary results must be toned down because they are based on the use of a particular structure with a fractal dimension of 1.8, i.e., a value that is close to what is usually found in the literature. However as many other fractal dimension values can also be found, depending notably on the particle size and volume fraction, fractal dimension measurements of our silica nanoporous matrices are in progress using X-ray and neutron scattering techniques.

Finally, from a more theoretical point of view, let us emphasize that the physical basis of the DDA makes this technique particularly suited for the examination of the interaction of an electromagnetic wave with an aggregate of particles that are small compared to the wavelength, independent of the particle concentration within the aggregate. The inter-dipole coupling effects within the aggregate are contained in the dipole moments resulting from the DDA calculation, so that phenomena generally referred to as “dependent effects” are accounted for with the DDA approach. It could be interesting in the future to study how the dependent effects derived from DDA calculations compare to more classical quantifications of these phenomena.

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