RADIATIVE PROPERTIES OF SILICA NANOPOROUS MATRICES

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Nanoporous superinsulating materials are currently the subject of much attention because of their awesome thermal insulation properties[1]: up to five times better than air, 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, fibres to provide mechanical reinforcement and micrometric particles to improve opaqueness in the infrared wavelength region. Our aim is to determine experimentally and to model the radiative properties of such nanoporous materials, which are semi-transparent media in the considered wavelength range. In the simplified approach presented here, we consider the nanoporous matrix alone.

To measure the spectral transmittance and reflectance properties, we used two different spectrometers covering an overall spectral band of [250 nm ; 25 μm] and equiped with integrating spheres that collect hemispherically the radiation travelling through or reflected by the samples. These samples were made by compacting powders of 10 nm diameter particles (supplier : german company Wacker) and were of different thicknesses. The porosity of each sample was about 90%. Using the radiative transfer equation formalism and a parameter identification technique based on the Newton-Raphson algorithm, we determined the spectral radiative properties (*i.e.* the extinction coefficient and albedo spectra) of the nanoporous matrix from the experimental values of the spectral hemispherical transmittances and reflectances. For the resolution of the radiative transfer equation, we assumed one-dimensional radiative transfer in an absorbing, scattering, non-emitting semi-transparent medium with azimuthal isotropy.

The experimentally determined radiative properties of the nanoporous matrix were then compared to the results of the well-known Mie theory[2]. As the primary particles used to prepare the samples were hydrophilic silica particles, we had to take into account the water contribution, so we used a coated sphere model[3] (a water coating of 2 Å was retained). The only way that we found to get a good agreement between the theoretical and experimentally obtained radiative property spectra was to consider a particle diameter of 55 nm instead of 10 nm (figure 1). Consequently, from the point of view of the interaction with electromagnetic waves, our material behaves approximately as a cloud of uniform size particles of about 55 nm diameter. Although this value is significantly different from the diameter of the primary particles, it is not an absurd value: indeed during the silica powder fabrication process the primary nanoparticules 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 the one of the matrix, the volume of silica contained in such an aggregate is equivalent to the volume of a dense silica sphere of 55 nm diameter. Hence, we can venture the hypothesis that the nanoporous matrix scatters as a cloud of primary scatterers, the primary scatterer being here the aggregate obtained during the production process.

In order to confirm this hypothesis, we are currently working on the Discrete Dipole

Approximation[5,6,7] (DDA) to compute the radiative properties of an aggregate. The DDA is a flexible method that allows to compute the absorption and scattering properties of irregular targets (particles of complex shapes, clusters of spheres) approximated by arrays of point dipoles. DDA calculations require the localization of the 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[6]. This method has been shown to be superior to the other polarizability prescriptions for a cluster of spherical monomers replaced by single dipoles[6]. 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.

Prior to DDA calculations, the dipoles must be localized in space. To obtain valuable results, the material structures on which DDA calculations are performed must be representative of our nanoporous material in terms of porosity (≈ 90%), specific surface area (≈ 250 $m^2.gr^{-1}$) and fractal dimension (≈ 1.8 according to the litterature[8]). As no tomographic characterization is currently possible at that length scale, we have resorted to the numerical generation of 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 function and hence in the polarizability function of the particles with the help of the Maxwell-Garnett mixing rule. We have generated clusters of 170 particles of 10 nm diameter with the equivalent of 2 Å water coatings. The number of 170 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 properties spectra (figure 2) is quite encouraging, and is a first step toward a reasonable representation of the material organization within our nanoporous matrices.

SUMMARY AND PERSPECTIVES

We have determined the spectral radiative properties of silica nanoporous matrices from experimentally obtained reflectances and transmittances using a parameter identification. These data have been compared to the Mie theory assuming a uniform diameter distribution of 10 nm for the particles. To get a good agreement between the experimental values and the Mie theory, we had to increase the particle diameter up to 55 nm.

From the very little we know about the silica powder, we have proposed an explanation that seems to be confirmed by the first DDA calculations. Nonetheless, these results must be toned down because they are based on the use of a structure with a given fractal dimension, that is close to what is usually found in the literature. As many other different fractal dimension values can be found, depending notably on the particle size and volume fraction, fractal dimension measurements of our samples are in progress using X-ray and neutron scattering techniques.

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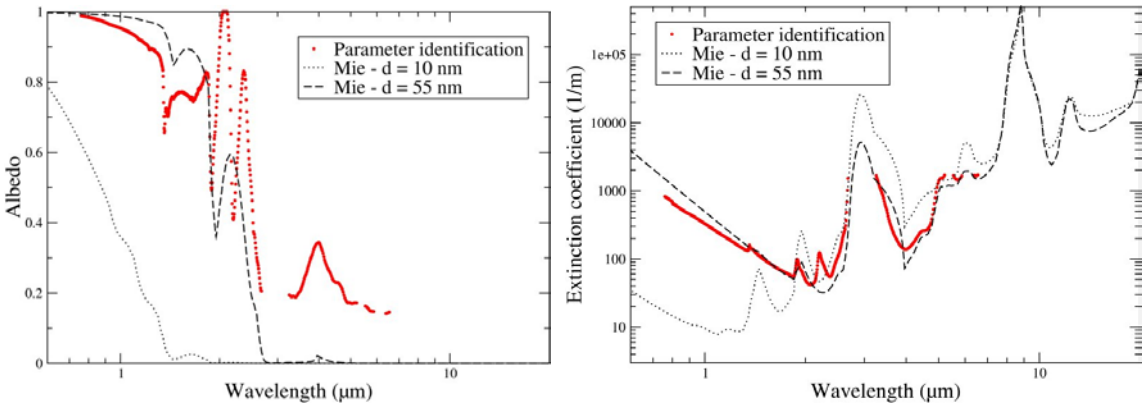

Figure 1: Comparison of the experimental albedo and extinction coefficient spectra (red dots) and the results of the Mie theory for two particle diameters. Data used for the Mie calculations: particles of 10 nm and 55 nm diameters coated with 2 Å of water, volume fraction = 10%.

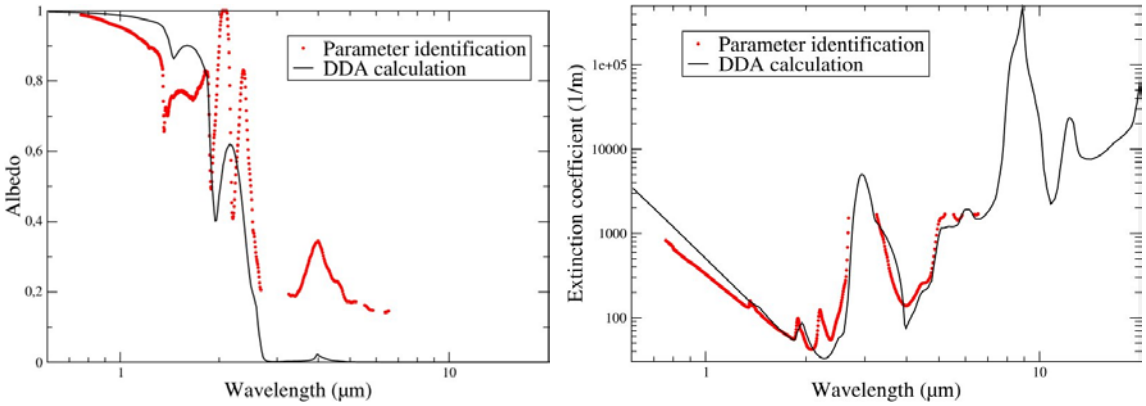

Figure 2: Comparison of the experimental albedo and extinction coefficient spectra (red dots) and the results of a DDA calculation for an aggregate of 170 particles of 10 nm diameter.