Particle diffusivities in free and porous media from dynamic light scattering applying a heterodyne detection scheme

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Diffusive processes in particulate systems play a significant role in a large variety of natural and technical processes. It is well known that the diffusive mass transport is slower in porous media in comparison to that in free media, i.e. in absence of confinements induced by a porous solid material. Porous media may consist of a myriad of interconnected structures with different pore sizes, pore geometries, and degrees of disorder, where each structure results in a characteristic diffusive mass transport. Diffusive transport on different length scales is hard to probe and differentiate experimentally. At present, fluorescence correlation spectroscopy (FCS) and dynamic light scattering (DLS) relying on a homodyne detection scheme are used to study diffusive mass transport in porous media. These techniques, however, are restricted to confined particulate systems containing fluorescent particles for FCS experiments, and to solvents with a refractive index matching the one of the porous matrix for homodyne DLS experiments. In a homodyne detection scheme, the scattered light detected and analyzed has to be sufficiently pure to ensure the validity of the corresponding working equation evaluated in context with DLS measurements. Owing to the effects of stray light, this condition is no longer given if the refractive indices of the solvent and the porous medium are different. In principle, this restriction can be overcome by ensuring a heterodyne detection scheme for DLS measurements, where the scattered light is superimposed with sufficiently strong coherent reference light.

In the present contribution, the applicability of a heterodyne detection scheme has been demonstrated for a dispersion saturating a porous medium consisting of inverse opals. These possess spherical pores with a diameter of 300 nm being approximately equal to the diameter of the pore opening. The binary particulate system consists of spherical gold nanoparticles with a hydrodynamic diameter of about 20 nm dispersed in water with a particle volume fraction of 3×10^{-6}. The hydrodynamic diameter was determined via the Stokes-Einstein relation using diffusivity values measured for the dispersion in free medium. For the porous medium, the measurements performed with a heterodyne detection scheme document that even if the refractive index of the dispersion is not matching the refractive index of the inverse opals, signals related to the particle diffusive process are observable in the intensity correlation functions. Studies performed under the same conditions with pure water saturating the porous medium demonstrated that the signals observed for the dispersion are rising from the diffusion of particles under the confinement of the porous skeleton and are not related to experimental artefacts. Heterodyne DLS experiments on the confined dispersion were conducted at different scattering angles in order to probe diffusive processes on different length scales. On average, the diffusive process in the confined dispersion was found to be 6.2 times slower than that in free medium. In addition, clear differences were observed between diffusive processes at the subpore length scale and at a larger length scale also integrating interconnected pores, cracks, and channels. The structures of the porous media were characterized by scanning electron microscopy and conventional microscopy.