Particle Diffusivity in Particulate Systems by Using Photon Correlation Spectroscopy

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Characterizing the mass transport of nanoparticles (NPs) in free media and in porous media (PM) requires the particle diffusivity D which can be affected by the morphology and surface functionalization of the NPs, the properties of the continuous phase, as well as the structure and wall functionalization of the pores. The influences of such structural and physicochemical characteristics on D need to be identified experimentally.

In this contribution, two photon correlation spectroscopy (PCS) techniques, namely dynamic light scattering (DLS) and differential dynamic microscopy (DDM), will be introduced for the determination of D. They are based on the analysis of intensity fluctuations of the scattered light originating from the particle density fluctuations governed by the Brownian motion in macroscopic thermodynamic equilibrium. While DLS analyzes the scattered light with a point detector in the far-field, DDM utilizes a pixelated detector placed in the near-field.

For both PCS techniques, experimental setups have been developed and applied for the determination of D in various particulate systems, e.g., aqueous solutions of poly(ethylene) glycol, unimodal dispersions of gold nanorods, bimodal dispersions of silica nanospheres, evaporating drops containing silica nanospheres, and unimodal dispersions of gold nanospheres in porous silica monoliths. This contribution highlights the necessity of a heterodyne detection scheme in PCS experiments to reliably determine D in particulate systems. For bimodal systems, the influence of the often neglected, yet sometimes relevant cross term occurring in homodyne DLS experiments on the determined D was identified. For the diffusion of NPs in PM, two distinct D, both smaller than that in free media, were found. The slowing-down of the diffusion processes of NPs was identified to be associated with the geometric hindrance and particle-wall interactions. Based on the results, the applicability and limitations of the two PCS techniques to different particulate systems will be discussed.