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Photon correlation spectroscopy for the characterization of diffusion processes in fluid mixtures and particulate systems

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For fluid mixtures and particulate systems in macroscopic thermodynamic equilibrium, the analysis of scattered light governed by microscopic fluctuations originating from the random thermal movement of molecules and/or particles represents a contactless technique to study diffusion processes. It is often called dynamic light scattering (DLS) because it accesses the dynamics of the fluctuations via the analysis of the scattered light. Here, the use of classical interference spectroscopy, where one first spectrally filters the scattered light and then measures the intensity at a given frequency transmitted by the filter resulting in the spectra of scattered light, seems to be the straightforward way to analyze the fluctuations. Since this pre-detection filtering scheme is only possible under very special conditions, it is more convenient to analyze the spectrum of the scattered light in a post-detection filtering scheme. Here, the total intensity is first detected and the detector signal is filtered and processed later on. In this type of detection, one measures optionally the second-order power spectrum of the scattered light or the time-dependent intensity correlation function which also is named second-order correlation function. The fundamentals of the latter option, known as photon correlation spectroscopy (PCS), will be discussed in the present contribution at first in some more detail, which serves as the basis for the design of corresponding PCS experiments and their evaluation for different systems.

At present, the most frequent application of PCS is the study of collective diffusion coefficients for the characterization of macromolecular or particle size and size distribution. In this regard, the application of PCS to the bulk of fluids can be found nowadays, for example, for aerosols, colloidal dispersions, polymer solutions, solutions and dispersions of biological macromolecules as well as for glasses, gels, and liquid crystals. In contrast to the application of PCS to study the dynamics and structure of diverse systems, there are currently only few research groups which use PCS to a greater or lesser extent for the determination of thermophysical properties. A fundamental advantage is given by the fact that PCS may be used to determine transport properties without applying a macroscopic gradient. In this case, PCS makes use of microscopic statistical fluctuations which can be related to various diffusive processes and, thus, to the transport properties to be measured. The basic justification for this relation is Onsager's regression hypothesis, which states that, on a statistical average, microscopic fluctuations are governed by the very same transport equations that are valid for macroscopic systems.

The second part of the present contribution summarizes and reviews research activities performed at the Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP) of the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU) mainly during the past four years by using PCS. These activities focus on the study of thermophysical properties of fluid mixtures, in particular on mass or mutual and thermal diffusivities, and on the characterization of particulate systems by measuring particle diffusion coefficients. Measurement examples are presented for a large variety of fluid mixtures and particulate systems, which represent, besides model or reference systems, especially systems relevant for process and energy technology. For the model systems, limitations of the method regarding the thermodynamic state and the accuracy will be discussed in detail. For example, the study of an equimolar methane–propane mixture examines the resolvability and separability of mutual and thermal diffusivity in different fluid regions including the critical region [1]. The systematic investigation of liquids with dissolved gases [2, 3] contributes to the identification of structure-property relationships up to the development of an empirical correlation for the mass diffusivity within about ±10%. Technical representatives of liquids with dissolved gases are studied in form of liquid organic hydrogen carriers (LOHCs) with hydrogen [4] as well as polymer melts with nitrogen as blowing agent [5]. A special class of systems are electrolyte systems which are of technological importance, e.g., for metal ion batteries or for underground hydrogen storage. They can contain multiple species which might be represented in a binary mixture consisting of two salts by up to four different ions. Here, molecular segregation and clustering can influence the molecular mass transport, as it is evidenced by a combination of PCS and molecular dynamics simulations [6]. Based on mixtures of water with polyethylene glycol (PEG) molecules, which can be understood as both molecular and particulate systems, dispersions of extremely small spherical nanoparticles are studied. The results from PCS show that monodisperse PEGs are suitable model systems for studying the diffusion behavior of bimodal and also multimodal particulate systems [7]. In the context of the study of thermophysical properties, the analysis of particle diffusion coefficients via the Stokes-Einstein equation can, in principle, provide information about the dynamic viscosity of the solvent, as documented for various pure ionic liquids and their mixtures with dissolved carbon dioxide [8]. For the latter system, even the simultaneous determination of mutual diffusivity and particle diffusion coefficient is demonstrated. This is also possible for the characterization of polyol-based microemulsions containing micelles swollen with carbon dioxide, which can be understood as spherical particles. For these technical systems, which serve for the production of polyurethane foams, the micelle size that correlates with the pore size in the foam can be successfully analyzed by PCS via the determination of the micelle diffusion coefficient under process-relevant conditions [9]. Recent research activities for particulate systems demonstrated also the applicability of PCS for the characterization of the particle aggregation kinetics in process technology by studying particle diffusion coefficients in evaporating single droplets [10]. Moreover, not only in free media, but also under the influence of confinement in porous materials, the application of PCS is demonstrated for studying particle diffusion coefficients without using any refractive index matching fluid [11].

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