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Determination of diffusivities in fluid mixtures using light scattering techniques in and out of equilibrium

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For the understanding and design of numerous natural and technical processes, accurate knowledge about diffusivities in fluid mixtures is important. In general, the experimental and theoretical determination of transport properties including mass and thermal diffusivity as well as thermodiffusion coefficient remains quite challenging until today. Even in the case of binary liquid mixtures, discrepancies can be found between the mutual diffusivity data obtained by different techniques, which are clearly outside their combined uncertainties. Thanks to the advancement of light sources and detection units, contactless light scattering techniques relying on the analysis of equilibrium, non-equilibrium, and forced fluctuations have attracted great attention for the characterization of several diffusive processes during the past two decades. Nevertheless, the different light scattering techniques have not been compared in a rigorous manner so far, although they possess individual pros and cons in connection with their applicability for a given thermodynamic state and diffusivity range as well as their precision, accuracy, and uncertainty.

In the present contribution, at first, the methodological principles and the experimental realization of dynamic light scattering (DLS), shadowgraphy, and forced Rayleigh scattering (FRS) will be presented. Then, the different techniques will be compared focusing on their application for the determination of diffusivities in fluid mixtures. The measurement of thermal and mutual diffusivity by DLS is based on the analysis of statistical fluctuations in temperature or entropy and composition in macroscopic thermodynamic equilibrium. It depends on the fluid characteristics and thermodynamic state whether or not both properties can be accessed simultaneously. In the presence of a macroscopic gradient at steady state, the analysis of long-ranged non-equilibrium fluctuations by shadowgraphy allows the simultaneous determination of the thermal and the mutual diffusivity as well as of the thermodiffusion coefficient. The application of a macroscopic gradient, however, restricts corresponding investigations to the one-phase region. The third light scattering technique, the FRS technique, involves gratings induced by the interference of two laser beams. From the analysis of the formation and relaxation of the resulting temperature and concentration gratings, the thermal and the mutual diffusivity as well as the thermodiffusion coefficient of mixtures can be determined. For performing FRS measurements, the addition of an absorbing dye contaminating the fluid of investigation is often necessary. While the use of small disturbances prevents advective flows, the FRS method might be inefficient close to first- or second-order phase transitions. By identifying the capabilities of each technique, guidelines for their reliable application within thermophysical property research are given for specific conditions. For this, the different techniques were examined by their application for different reference systems including binary mixtures of toluene and isooctane.