

Dynamic Light Scattering (DLS) for the characterization of diffusion processes

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Dynamic light scattering (DLS) represents a non-invasive technique to study diffusion processes in fluids. It is based on the analysis of microscopic fluctuations originating from the random thermal movement of molecules in macroscopic thermodynamic equilibrium. At present, the most frequent application of DLS is the study of collective diffusion coefficients for the characterization of macromolecular or particle size and size distribution. In this regard, the application of DLS from bulk fluids can be found nowadays, for example, for aerosols, colloidal dispersions, polymer solutions, solutions and dispersions of biological macromolecules and systems including viruses, protein-complexes, and membrane vesicles as well as for glasses, gels, and liquid crystals. In contrast to the application of DLS to study the dynamics and structure of diverse systems, there are currently only few research groups which use DLS to a greater or lesser extent for the determination of thermophysical properties. Here, a fundamental advantage is given by the fact that DLS may be used in thermodynamic equilibrium.

The present contribution summarizes and reviews the activities performed at the Department of Chemical and Biological Engineering (CBI) and the Erlangen Graduate School in Advanced Optical Technologies (SAOT) of the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU) as well as by different research groups worldwide during the past five decades in the field of thermophysical property research and in particular of diffusion measurements in fluids by DLS. The continuous progress in this field is given in retrospect, covering the first steps since helium lasers became available in the 1960s until today. The representation of the methodological principles of DLS and its experimental realization includes light scattering from bulk of fluids on a molecular level as well as from particles and macromolecules in solution or, in general, from heterogeneous systems.



Measurement examples are presented for the variety of thermophysical properties accessible by DLS from the bulk of fluids focusing on mass and thermal diffusivities. Here, limitations of the method regarding the thermodynamic state and the accuracy will also be discussed in detail. Finally, examples for mass and thermal diffusivities for specific working fluids in chemical and energy engineering obtained by DLS at CBI and SAOT Erlangen are given. The objects of investigation cover refrigerants, organic Rankine cycle (ORC) fluids, biofuels, liquid organic hydrogen carriers (LOHCs), ionic liquids (ILs), and Fischer-Tropsch systems. Current research activities contribute significantly to a reliable database for different working fluids, see, e.g., Refs. [1-3], and provide also answers to fundamental questions regarding the theory behind the method with respect to multi-component mixtures [4].

References

- [1] S. Bi, T. M. Koller, M. H. Rausch, P. Wasserscheid, and A. P. Fröba, Dynamic Viscosity of Tetracyanoborate- and Tricyanomethanide-Based Ionic Liquids by Dynamic Light Scattering, *Ind. Eng. Chem. Res.* **54**, 3071-3081 (2015).
- [2] T. M. Koller, A. Heller, M. H. Rausch, P. Wasserscheid, I. G. Economou, and A. P. Fröba, Mutual and Self-Diffusivities in Binary Mixtures of [EMIM][B(CN)(4)] with Dissolved Gases by Using Dynamic Light Scattering and Molecular Dynamics Simulations, *J. Phys. Chem. B* **119**, 8583-8592 (2015).
- [3] A. Heller, M. H. Rausch, P. S. Schulz, P. Wasserscheid, and A. P. Fröba, Binary Diffusion Coefficients of the Liquid Organic Hydrogen Carrier System Dibenzyltoluene/Perhydrodibenzyltoluene, *J. Chem. Eng. Data* **61**, 504-511 (2015).
- [4] A. Heller, C. Giraudet, Z. A. Makrodimitri, M. S. H. Fleys, J. Q. Chen, G. P. van der Laan, I. G. Economou, M. H. Rausch, and A. P. Fröba, Diffusivities of Ternary Mixtures of *n*-Alkanes with Dissolved Gases by Dynamic Light Scattering, *J. Phys. Chem. B* **120**, 10808-10823 (2016).