

## Diffusivities accessible from dynamic light scattering across the two-phase boundary of an equimolar propane-methane mixture

**Maximilian Piszko\***, Michael H. Rausch, Cédric Giraudet, Andreas P. Fröba

Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP),  
Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany

\*maximilian.piszko@fau.de

Dynamic light scattering (DLS) is a well-established contactless technique for studying diffusive processes for a large variety of systems and thermodynamic states. In fluids and fluid mixtures at macroscopic thermodynamic equilibrium, spontaneous microscopic fluctuations give rise to a Rayleigh-Brillouin spectrum analyzed by DLS. In the case of a binary fluid mixture, the Rayleigh component of the spectrum consists of two contributions or hydrodynamic modes associated with thermal and mutual diffusivity. The intensity ratio of the mode associated with the mutual diffusivity to that one associated with the thermal diffusivity is called Rayleigh ratio and depends on the given thermodynamic state. Although the applicability of DLS for the simultaneous measurement of thermal and mutual diffusivity has been demonstrated for various binary mixtures, experimental situations occur where only one hydrodynamic mode is observable, e.g., if both diffusivities match. In the case of different diffusivities, also only a single mode can be resolved if the intensity of one mode is much larger than that of the other mode. Here, the type of diffusivity behind the single hydrodynamic mode observable in the experiments depends on the Rayleigh ratio. While for Rayleigh ratios much larger than one the detectable mode is associated with the mutual diffusivity, Rayleigh ratios much smaller than one indicate that the observed mode is connected with the thermal diffusivity.

In order to identify which diffusivity is accessible by DLS near a phase boundary, heterodyne DLS experiments and theoretical calculations for the Rayleigh ratio were performed for an equimolar propane-methane mixture at various states across the two-phase boundary. In total, the mixture was studied at 125 different thermodynamic state points including the gaseous, supercritical, and compressed liquid regions. The present measurements document that in the compressed liquid phase and along the vapor-liquid equilibrium, both diffusivities can be determined simultaneously. In the compressed liquid phase far from phase transitions, calculated and experimental Rayleigh ratios agree within combined uncertainties. Only one hydrodynamic mode could be observed in the supercritical, near-critical, and gaseous regions. At pressures and temperatures above or close to the critical isochore, the theoretically calculated intensity of the mode associated with the mutual diffusivity was found to be two orders of magnitude larger than the one related to the thermal diffusivity. Furthermore, the behavior of the detectable diffusivity along different isobars crossing the compressed liquid and supercritical states follows the expected trend for the mutual diffusivity. In the low-density gas region, however, the hydrodynamic mode is attributable to the thermal diffusivity. Between the gas regions with low and high density, no remarkable differences in the intensities of the two modes as well as in the thermal and the mutual diffusivity can be found. Here, an effective diffusivity describing both transport properties at the same time is determined by DLS.