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Thermal Diffusivity of Fluids by Dynamic Light Scattering

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1. Introduction

The thermal diffusivity a is the transport property for which the development of dynamic light scattering (DLS) is probably most advanced and where measurements can be carried out routinely over a wide range of temperatures and pressures for the liquid phase and, due to the lower signal levels, in an extended vicinity of the critical point for the vapor phase. What makes the measurement of a particularly interesting is the fact that it is hardly possible by any other than light scattering techniques to measure this property directly, with a comparable accuracy, and in macroscopic thermodynamic equilibrium. Other methods access the thermal conductivity $\lambda = a\,\rho\,c_\mathrm{p}$, which is related to a by density ρ and isobaric heat capacity c_p, and are subject to the use of macroscopic gradients.

2. Method

When a fluid sample in macroscopic thermodynamic equilibrium is irradiated by coherent laser light, light scattered from the sample can be observed in all directions. The underlying scattering process is governed by microscopic fluctuations of temperature, pressure, and of species concentration in mixtures. The relaxations of these statistical fluctuations follow the same rules that are valid for the relaxation of macroscopic systems. Thus, the decay of temperature fluctuations is governed by a. In light scattering experiments the above-mentioned equalization processes result in a temporal modulation of the scattered light intensity. Information about these processes can be derived from a temporal analysis of the scattered light intensity using photon correlation spectroscopy (PCS). For a pure fluid under heterodyne conditions, where the scattering light is superimposed with stronger coherent reference light, the time-dependent intensity correlation function for the analysis of the temperature fluctuations is described by [1]

$$G^{(2)}(\tau) = A + B\exp(-\tau / \tau_\mathrm{C})\,, \qquad (1)$$

where A and B are experimental constants, which are essentially determined by the total number of counts registered, the ratio of scattered light to reference light, and the coherence properties of the optical system. From the correlation time τ_C, which is equivalent to the mean lifetime of the temperature fluctuations observed, a can be calculated by

$$a = 1/(\tau_{\mathrm{C}_\mathrm{t}}\, q^2)\,, \qquad (2)$$

where the modulus of the scattering vector q is determined beside by the laser wavelength in *vacuo*, by the scattering geometry.

3. Results

There have been ample applications on the determination of a for a wide range of fluids. By the determination of a for the important, and thus well documented reference fluid toluene, the accuracy of the DLS-technique could be successfully assessed [2, 3]. For a comparison with data for the thermal conductivity λ, these have been converted with values for the specific heat at constant pressure c_p and density ρ into a according to $a = \lambda/(\rho\, c_p)$. At moderate temperatures away from the critical point, agreement has been found within the combined uncertainty of the different methods. At high temperatures, approaching the critical point, systematic deviations could be observed, which may be attributed to the fact that conventional methods are subject to the use of macroscopic gradients.

Especially over the last years, DLS has contributed to an improvement in the data situation for fluids of technical interest. Measurements were carried out on pure refrigerants as well as on refrigerant mixtures with low environmental impact [4, 5]. While the measurement of a in pure fluids is basically a straightforward task, this is clearly more difficult in fluid mixtures. The situation becomes easier if the refractive indices of the two components nearly match, as the signal from the concentration fluctuations may then be treated as a low-amplitude perturbation. The results for a of a refrigerant mixture of R125 (pentafluoroethane) and R143a (1,1,1-trifluoroethane) measured in this way were used for the validation of a prediction method which can be applied in a straight forward way to obtain accurate information on different thermo-physical properties of multicomponent mixtures over a wide temperature range in the two-phase region up to the critical point [6].

4. Conclusion

DLS can be applied successfully to investigate a of pure fluids and fluid mixtures over a wide range of states up to the critical region. For the latter, however, an accurate determination of a is restricted to the case where the pure components have similar refractive indices. Apart from being used as a mean for testing the DLS-technique itself, the determination of a has been performed during the last thirty years with the aim of extending the data basis for fluids of technical and fundamental interest as well as for the validation and development of theoretical models for the prediction of thermophysical properties.

References

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