Mutual Diffusion Coefficient in Fluids
by Dynamic Light Scattering

Andreas P. Fröba, Cristina Botero, Heiko Kremer, and Alfred Leipertz

Lehrstuhl für Technische Thermodynamik (LTT), Universität Erlangen-Nürnberg,
Am Weichselgarten 8, D-91058 Erlangen, Germany,
E-Mail: sek@ltt.uni-erlangen.de

1. Introduction

An overview of dynamic light scattering (DLS) is given, as a valuable tool for the measurement of the mutual diffusion coefficient D_{12} of transparent fluids. First, the basic principles of the method and its experimental realization are presented in some detail. The measurement of D_{12} in binary fluid mixtures, however, is also treated with the simultaneous determination of the thermal diffusivity a which can be realized under certain conditions. In this context beside results for fluids of technical interest, typical measurements within the critical region are highlighted for a binary fluid mixture along the critical isochor and for a critical separation system.

2. Basic Principles

In binary fluid mixtures, one can basically simultaneously determine D_{12} and a from the linewidth of the Rayleigh line, governed by microscopic fluctuations of temperature and concentration [1]. The relaxation of the two hydrodynamic modes present in binary fluid mixtures follow the same laws which are valid for the relaxation of macroscopic systems. Thus, the decay of temperature and concentration fluctuations is governed by a and D_{12}, respectively. Information about these equilibration processes can be derived through the temporal analysis of the scattered light intensity using photon correlation spectroscopy (PCS). For heterodyne conditions, where the scattered light is superimposed with stronger coherent reference light, the time-dependent intensity correlation function for the analysis of temperature and concentration fluctuations is described by [2]

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

where A, B, and C are experimental constants, which are essentially determined by total number of counts registered, the ratio of scattered light to reference light, and the coherence properties of the optical system. The decay time τ_{C_c}, which is equivalent to the mean lifetime of the concentration fluctuation observed, is related to D_{12} by

$$D_{12} = 1/(\tau_{C_c} q^2).\qquad(2)$$

Similarly, from the characteristic decay time τ_{C_t}, which is equivalent to the mean lifetime of the temperature fluctuations observed, a can be determined by

$$a = 1/(\tau_{C_t} q^2).\qquad(3)$$

In Eqs. (2) and (3), q is the modulus of the scattering vector, which is defined beside by the laser wavelength in *vacuo*, by the scattering geometry.

Since D_{12} is in general one order of magnitude smaller than a, the two hydrodynamic modes present in binary fluid mixtures should be observable on different time scales. Whether it is possible to resolve both signals of the correlation function is mainly restricted by the ratio of the scattering intensities I_c / I_t, where the subscripts t and c denote the contributions from temperature and concentration fluctuations. The ratio I_c / I_t depends on the relative difference of the refraction indices of the two components and their concentration [2]. Generally, it is easier to simultaneously determine both signals in binary mixtures if the refractive indices of the two components have comparable values than in the case of a large difference, where the scattering intensity from concentration fluctuations dominates the correlation function.

3. Results

As an example for the simultaneous determination of D_{12} and a, results of investigations of an equimolar methane-ethane mixture are renewed [3]. Measurements were performed over a wide temperature range between the plait critical point (binary mixture liquid-vapor critical point) at 263.55 K and 310 K along the critical isochore. Due to the small signal amplitude of the fast mode, a could be obtained only with a relatively large measurement uncertainty. For the system methane-ethane, however, a seems to remain finite when asymptotically approaching the plait critical point, while D_{12} reflects the critical slowing down of the order-parameter fluctuations and vanishes.

In most instances, especially when the difference of refractive indices is large, the determination of D_{12} may be performed by standard experiments. For this case, results for the temperature dependence of D_{12} of a separation system of n-hexane and nitrobenzene near the consolute point (binary liquid-liquid mixture critical point) are shown [4]. Additionally, measurements of D_{12} are presented for selected binary fluid mixtures of technical interest, e.g., systems from chemical engineering and medical technology.

4. Conclusion

DLS has been applied successfully for the accurate measurement of D_{12} of transparent fluid mixtures over a wide range of temperature and pressure. The technique provides absolute values of D_{12} without the need of any calibration procedure. The determination of D_{12} is proceeded in macroscopic thermodynamic equilibrium without employing a macroscopic gradient in concentration. Moreover, in some instances DLS can be applied to simultaneously measure the two hydrodynamic diffusion modes, mass and thermal diffusion, present in binary fluid mixtures.

References

[1] R. D. Mountain, J. M. Deutch, J. Chem. Phys. **50**, 1103 (1969)
[2]   J. N. Shaumeyer, R. W. Gammon, J. V. Sengers, in *Measurement of the Transport Properties of Fluids*, eds. W. A. Wakeham, A. Nagashima, J. V. Sengers, Blackwell Scientific, Oxford 1991, pp. 197-213
[3] A. P. Fröba, S. Will, A. Leipertz, Int. J. Thermophys. **21**, 603 (2000)
[4] G. Wu, M. Fiebig, A. Leipertz, Wärme- Stoffübertr. **22**, 365 (1988)