diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Liquid Viscosity and Surface Tension by Surface 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

The application of dynamic light scattering (DLS) to a liquid surface, also called surface light scattering (SLS), can be used for the investigation of viscoelastic properties of fluids. Based on early theoretical and experimental work, renewed interest in SLS in recent years has resulted in a number of new applications. Objects of these investigations extend from simple fluids over polymer solutions, liquid crystals, surfactant monolayers, and supramolecular systems to high-temperature melts. The determination of the thermophysical properties surface tension and viscosity is of special interest for pure fluids and fluid mixtures. In this context the SLS-technique is well established for the investigation of the critical behavior of the surface tension, while, in general, for the viscosity, due to instrumental broadening effects and improper data evaluation procedures, a poor accuracy has been reported in the literature. In contrast, here it is demonstrated that the SLS-technique can be used for a reliable determination of surface tension and liquid viscosity - without any calibration procedure - with an accuracy comparable to or even better than that of conventional methods.

2. Basic Principles

Liquid surfaces in macroscopic thermal equilibrium exhibit surface waves which are caused by thermal movement of molecules and quantized in so-called "ripplons". In general, for the temporal decay of surface fluctuations, two cases may be distinguished. In the case of large viscosity and/or small surface tension, the amplitude of surface waves is damped exponentially, while in the case of small viscosity and/or large surface tension the amplitude decays in the form of a damped oscillation. SLS analyzes the light scattered by these surface waves. For a temporal analysis of the scattered light intensity using, e.g., photon correlation spectroscopy (PCS) under heterodyne conditions, where the scattered light is superimposed with stronger coherent reference light, the time dependent intensity correlation function is described by [1]

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

or

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

assuming that the decay of the surface waves' amplitude is oscillatory or overdamped, respectively. In the propagating case of surface fluctuations, the correlation function Eq. (1) can be used for the simultaneous evaluation of surface tension σ and kinematic viscosity ν. The correlation time τ_C and the frequency ω, which are identical to the mean life time of the "ripplons" and the frequency of propagation, respectively, are given in first order approximation by

$$\tau_C = 1/(2\,\nu q^2) \qquad\qquad \omega = (\sigma/\rho)^{1/2} q^{3/2}\,, \tag{3}$$

where the modulus of the scattering vector q is determined by the scattering geometry. In the overdamped case, if the fluid viscosity is large and/or the surface tension is very small, the lifetime of the "ripplons" in Eq. (2) is given in a first order approximation by

$$\tau_C = 2\,\eta/(\sigma q)\,, \tag{4}$$

where η is the dynamic viscosity. For a reliable determination of viscosity and surface tension a more detailed and rigorous consideration of the surface light scattering method than given by Eq. (1) to (4) has to be applied. Here, the reader is referred to literature, see, e.g., Refs. 1 and 2.

3. Results

The investigation of the important and, thus, well documented reference fluid toluene between 263 and 383 K under saturation conditions demonstrates for the SLS-technique an accuracy of better than 1 % for both properties of interest [3]. Beside toluene, we applied the SLS-technique to alternative pure refrigerants [4], their mixtures [5, 6], carbon dioxide [2], a silicone oil [2], and diisodecylphthalate (DIDP) [7]. All these data demonstrate the applicability of the technique to different fluids covering a wide range of viscosities ranging from about 10 μPas to 1 Pas. Yet, a value of 1 mPas does not seem to be the upper limit of the viscosity range that could be investigated by the SLS-technique. An estimation based on the time domain within a few nanoseconds to several hundred milliseconds, where photon correlation spectroscopy can be applied in a sensible way, indicates an order of magnitude of 1 kPas for the upper limit.

4. Conclusion

Within the scope of the measurement of thermophysical properties of fluids we applied the SLS technique until now especially to reference fluids including high-viscosity liquids and alternative refrigerants. The measurements demonstrate an excellent performance of the SLS-technique regarding both the achievable high accuracy and the application over a wide range of viscosities.

References

[1] D. Langevin, *Light Scattering by Liquid Surfaces and Complementary Techniques*, Marcel Dekker, New York 1992
[2] A. P. Fröba, Dr.-Ing. thesis, Universität Erlangen-Nürnberg 2001
[3] A. P. Fröba, A. Leipertz, Int. J. Thermophys. **24**, 895 (2003)
[4] A. P. Fröba, S. Will, A. Leipertz, Int. J. Thermophys. **21**, 1225 (2000)
[5] A. P. Fröba, S. Will, A. Leipertz, Int. J. Thermophys. **22**, 1349 (2001)
[6] A. P. Fröba, A. Leipertz, Int. J. Thermophys. **24**, 1185 (2003)
[7] A. P. Fröba, A. Leipertz, Int. J. Thermophys., submitted 2005