International Journal of Thermophysics, Vol. 16, No. 2, 1995

Thermal Diffusivity and Thermal Conductivity of Toluene by Photon Correlation Spectroscopy: A Test of the Accuracy of the Method[1]

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Absolute measurements of the thermal diffusivity of liquid toluene were performed by photon correlation spectroscopy between 293 and 523 K near the saturation line. The experimental method is based on a time-resolved analysis of the laser light scattered from local equilibrium fluctuations in a transparent sample, enabling us to obtain the thermal diffusivity in macroscopic thermodynamic equilibrium. The experimental results are compared with previous data obtained with the same method, with the transient-hot-wire technique, and also with calculated values of thermal diffusivity from reference data for thermal conductivity, heat capacity, and density. They demonstrate an agreement of 2.5%, which is within the uncertainty of the reference data.

KEY WORDS: light scattering; photon correlation spectroscopy; thermal diffusivity; toluene.

1. INTRODUCTION

Photon correlation spectroscopy (PCS) is known as a method to obtain absolute measurements of the thermal diffusivity of fluids over wide ranges of pressure and temperature. With this technique, no macroscopic temperature gradients are applied to the sample, which greatly reduces systematic errors.

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[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

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For testing the accuracy of the PCS method, measurements on liquid toluene were performed. This fluid was selected since it has been recently recommended as a reference standard for thermal conductivity λ [1, 2]. From these values, together with density ρ and isobaric heat capacity C_p obtained from a widely accepted equation of state (EOS) proposed by Goodwin [3], the thermal diffusivity a can be calculated from

$$a = \lambda/(\rho c_p) \tag{1}$$

Equation (1) is used to verify the instrument performance within the mutual consistency of these different sets of data. Also, a comparison is made with data obtained by the same method in a different laboratory and with the transient-hot-wire technique.

2. METHOD

The principle of the PCS technique for the determination of thermal diffusivity is presented in much detail elsewhere (see, e.g., Refs. 4–6). The typical experimental setup is shown in Fig. 1 and described in detail in Ref. 7.

The most reliable way of performing light scattering measurements far away from the critical point is the heterodyne technique [6]. Here, strong reference light is superimposed on the Rayleigh-scattered light from the liquid by means of a second beam generated by a beam splitter (Fig. 1), or

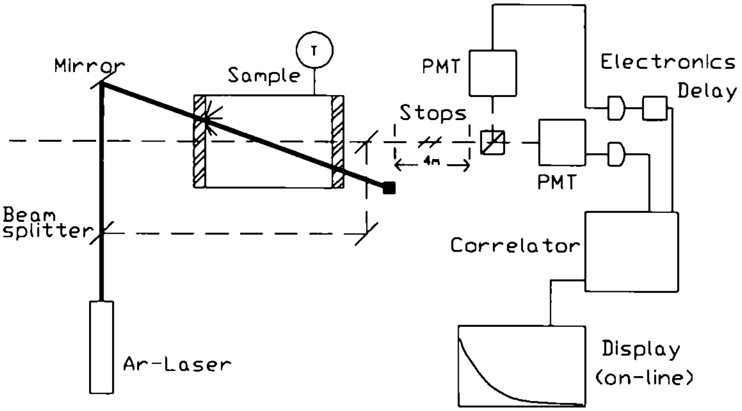

Fig. 1. Schematic of the experimental setup for the determination of thermal diffusivity by photon correlation spectroscopy.

by the scattering of reflections from the cell windows. In this case, the measured correlation function is a single, exponentially decaying function

$$G(\tau) = A + B^* \exp(-\tau/\tau_c) \tag{2}$$

with

$$\tau_c = \frac{1}{aq^2} \tag{3}$$

and

$$q = \frac{4\pi n}{\lambda_0} \sin \frac{\Theta_s}{2} \tag{4}$$

Here, q is the modulus of the scattering vector, which is determinated by the sample refractive index n, the laser wavelength λ_0 in vacuum, and the scattering angle Θ_s defined as the angle between the direction of observation and the incident laser beam within the sample. With these values taken from experiment, and with the decay time extracted from the measured correlation function, the thermal diffusivity a can be calculated from Eq. (4): $a = (\tau_c q^2)^{-1}$.

3. EXPERIMENTS

The experimental setup is shown in Fig. 1. An argon ion laser is used with $\lambda_0 = 488$ nm in single mode. A typical power of 300 mW is used to irradiate the sample. More details are given in Ref. 7.

The temperature stability of the sample is better than 0.02 K over a measurement period. The temperature is measured with a resolution of 0.01 K by means of a calibrated 100-Ω platinum resistance thermometer. An accuracy of 0.05 K can be obtained in the calibration temperature range of 273–360 K. For higher temperatures the calibration curve has been extrapolated, which increases the uncertainty for the temperature range from 360 to 523 K.

For determining the scattering vector q, Eq. (4), the scattering angle Θ_s must be known, which can be substituted by the incident angle Θ_e (see Section 4.1.2). The measurement of this incident angle, defined as the angle between the incident beam at the entrance window and the direction of observation, is performed by beam autocollimation. The main measuring device is a rotary table, with an angle resolution of 0.01°, placed above the sample cell. With a mirror mounted on this table the laser beam can be reflected in the direction of the source of the laser beam. First the direction of observation is defined by centering the laser beam through the stops in the entrance of the photomultiplier tubes (PMTs). The laser is reflected with help of the mirror mounted on the rotary table to a target point at a distance of approximately 6 m. The corresponding angle value is measured with a reproducibility of ±0.01° when the beam is realigned repeatedly. Next the direction of the laser beam is adjusted for the measurement. After each measurement the laser beam is reflected again to that target point and the corresponding incident angle can be determined as the difference of the two directions.

The toluene sample was supplied by Merck with an analysis certificate specifying a purity of 99.9%. When filling the cell, the toluene was first filtered through Teflon membrane filters with 0.20 or 0.45 μm pore size to prevent dust or particles from entering the cell.

4. ERROR ANALYSIS

4.1. Primary Measured Variables

The primary measured variables can be found from Eqs. (3) and (4), with attention given to the considerations in Section 3. These variables are the decay time τ_c, the incident angle Θ_c, and the laser wavelength λ_0, with the last one giving a negligible contribution to the uncertainty.

4.1.1. Decay Time τ_c

There are two kinds of factors that will have a major influence on the accuracy of the evaluated decay time of a single measurement. These are systematic deviations from the expected single-exponential behavior of the correlation function and residual noise.

There are many experimental artefacts that may cause systematic uncertainties [7]. Any distortion of the ideal experiment will cause a departure from single-exponential behavior of the correlogram. Thus if a single-exponential behavior is reached, this is a clear indication for the absence of any distortions. For a long time this has been impossible [8]. As a consequence, terms had to be added to Eq. (2) allowing the determination of a decay time, but making the results uncertain to an unknown degree. Recently, the experimental setup and measurement procedure was improved such that we are now able to perform measurements showing the expected single-exponential behavior without any significant distortion.

Applying a sophisticated multifit evaluation procedure to the measured correlogram, the absence of systematic deviations can be proved with a high degree of confidence, showing that the experiment is running according to theory [9]. Correlograms exhibiting systematic deviations are rejected. In this way all measurements can be stated to be free of main systematic errors with respect to the evaluated decay time. Furthermore, the consistency of multiple measurements under different experimental conditions gives further confirmation of the performance of the experiment.

The effect of residual noise is estimated by evaluating a set of synthetic data, produced with stochastic noise and with known decay time. With our evaluation procedure, the relative standard deviation S_{τ_c} of the evaluated decay time can be estimated roughly from the relative standard deviation S_{Corr} of the fit of the correlogram according to the empirical correlation

$$S_{\tau_c} \approx 1.4 S_{\mathrm{Corr}} \tag{5}$$

A typical value for the noise level of the series of measurements presented in this paper is about 1%. This means, following Eq. (5), that the decay time of a single experiment is evaluated with a confidence of about 95%, with an uncertainty of 2.8%.

The noise level of the correlogram strongly depends on the optical setup and the scattering efficiency of the fluid under investigation. Compared to many fluids and in particular to most hydrochlorofluorocarbons (HCFC, HFC) used as alternative refrigerants and also measured with this same setup [7], toluene produces a rather poor signal with a high degree of noise.

Performance of multiple measurements at the same angle allows, in principle, an enhancement in the accuracy of the evaluated decay time to almost unlimited values.

4.1.2. Angle Measurement

One of the most crucial points of the measurements is the determination of the scattering angle Θ_s or the incident angle Θ_c. A small-angle approximation to the law of refraction can be used that allows the deterination of q without the knowledge of the refractive index n of the sample. This introduces an uncertainty of less than 0.1% in q for the range of angles used, from 2.5 to 5 deg. It leads to the following equation for q [10]:

$$q = \frac{2\pi \sin \theta_c}{\lambda_0 \cos\{\frac{1}{2} \arcsin[(\sin \theta_c)/n]\}} \cong 2\pi \frac{\sin \theta_c}{\lambda_0} \tag{6}$$

With the help of simple geometric considerations it can be shown that the effect of a nonperpendicularly oriented sample cell as well as effects from nonparallelity of the window surfaces can be neglected.

To prove the accuracy of the angle reading of the rotational table, a second measuring device was developed with which it is possible to obtain analytically an accuracy of 0.003° in the angle measurement. The comparison of the two devices in performing simultaneous autocollimation measurements indicated an agreement within ±0.01°, which is within the readout uncertainty of the previously used device (±0.01°), and confirms the precision of the autocollimation procedure described above. Finally, the accuracy of the determination of a single angle can be estimated, from the uncertainty in alignment and measurement, to be approximately ±0.014°. This will cause an uncertainty between 0.5 and 1% for the thermal diffusivity in the range of angles used.

After each measurement, however, the reference beam can be readjusted several times and multiple, independent measurements of the incident angle can be done. This allows a statistically significant decrease of uncertainty, depending on the number of independent measurements of angle and on the mechanical and thermal stability of the optical setup.

4.2. Temperature

From the typical variation of thermal diffusivity with temperature in the liquid phase of toluene, the uncertainty in the temperature measurement of 0.05 K will lead to a maximum uncertainty of 0.02% in the measured thermal diffusivity for the range of temperatures studied. Even outside the calibration range of the probe the uncertainty will not be larger. Only a temperature uncertainty as large as 2.5 K would cause an uncertainty of 1% in the thermal diffusivity.

4.3. Pressure

The setup used has no pressure measurement capabilities. For temperatures up to the normal boiling point, the pressure was kept at ambient. With increasing temperature, the valve of the test cell was closed and due to a finite volume of air in the top of the vessel, the pressure was slightly above vapor pressure. Given the very small pressure dependence of the thermal diffusivity [8], this effect can be neglected. All measurements can be considered to have been taken at saturation conditions.

4.4. Impurities

The presence of other components in the sample can produce a contribution to a itself, or influence the correlogram by the effect of mass diffusion. In the first case, if we assume that the entire 0.1% impurity level is water, than the error in a would be 0.2% assuming a linear mixing rule for the determination of the thermal diffusivity of the mixture from the thermal diffusivities of the pure components. This is a worst case, since the analysis certificate states a water content of only 0.01% and any other impurity will have a smaller thermal diffusivity compared to water. The influence of mass diffusion seems to be negligible, since there are no systematic deviations detected from the single-exponential decay of the correlation functions.

The presence of dust particles in the sample, which would strongly perturb the measurements, must be carefully avoided.

5. RESULTS AND DISCUSSION

The experimental results on the thermal diffusivity of liquid toluene are shown in Fig. 2 in comparison to experimental data obtained also by the PCS technique [5, 8] and by the transient-hot-wire method [11, 12], and to values calculated from density and isobaric heat capacity obtained from the equation of state (EOS) of Goodwin [3] and thermal conductivity data from Perkins et al. [12]. Our present results can be represented by a quadratic relation of the form

$$a = 2.179 - 5.899 \times 10^{-3} T + 5.098 \times 10^{-6} T^2 \qquad (7)$$

where a is in $10^{-7}\ \mathrm{m^2 \cdot s^{-1}}$ and T is in K. The relative deviation from Eq. (7) for the 115 single experimental points taken in our experiments was found to be about 2.5% in the range studied and is of the magnitude theoretically estimated in Section 4.1. A small decrease of deviation at

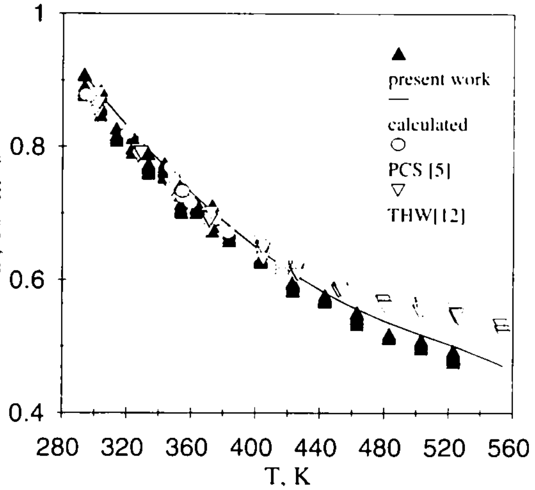

Fig. 2. The thermal diffusivity of liquid toluene near the saturation line. The solid line represents the values calculated from the thermal conductivity data correlation of Ramires et al. [14] and from the density and isobaric heat capacity obtained from the equation of state of Goodwin [3].

higher temperatures is found as expected, since with increasing temperatures the signal-to-noise ratio of the correlograms improves. This is due to the fact that with increasing temperature the range of correlation between fluctuations will extend upon approaching the critical point and the intensity of the scattered radiation will increase. On the other hand, thermal diffusivity becomes smaller. Together, these effects will produce for toluene in the present experimental conditions an almost constant percent deviation, with 95% of the points in a 2.5% band from Eq. (7), the maximum deviation from Eq. (7) being 3.8%. We shall consider the value of 2.5% as a measure of the precision of the method for this series of measurements. This precision is defined as a measure of the uncertainty interval for a new independent single measurement. Since the existence of any systematic deviation is reduced to a level lower than this value, and is not apparent in the evaluation procedure, we state that the accuracy of the method is governed by precision and has a value of 2.5%.

Figure 3 presents the experimental data in the form of deviations from the calculated values for thermal conductivity. For comparison, also included in this figure, besides the above referred data, is the calculated

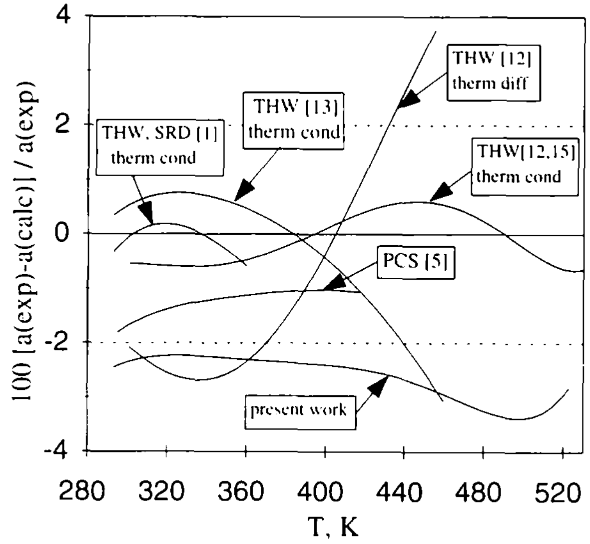

Fig. 3. Comparison between directly measured and calculated thermal diffusivity. For the sets calculated from experimental thermal conductivity data, the density and isobaric heat capacity were obtained from the equation of state of Goodwin [3]. The zero line corresponds to the calculation for thermal conductivity of Ramires et al. [14].

thermal diffusivity using the standard reference data (SRD) for the thermal conductivity of toluene [1] and the more recent thermal conductivity data from Yamada et al. [13]. Covering the complete temperature range we have measured, we choose to use as baseline the values derived from the correlation for the thermal conductivity proposed by Ramires et al. [14], which represents the primary experimental data for toluene of several authors. For temperatures above 380 K only the data from Ref. 12 are used to build this correlation.

The comparison with this data sets shows that we are within 2% of the SRD [1] and also in agreement within 1.5% with results obtained by PCS with another instrument [5]. It has to be mentioned that these former measurements were subject to a long-time decay in the correlation function, which was accounted for by an additional exponential term in the evaluation function, Eq. (2) [8]. If the statement of the absence of systematic errors in our measurements is true, Eq. (7), which represents a statistical average of more than 100 independently measured results, should have a much better accuracy than the referred method accuracy of 2.5% for a single measurement.

However, the only possible strong statement based on the current data comparison is that all the data sets, with exception of the thermal diffusivity data measured directly with the transient-hot-wire (THW) method [12], are consistent within a band of 3%. It should be stressed that this consistency is between sets of data for four different properties from different sources including EOS.

The deviation of the line representing the thermal diffusivity measured with the THW method increases up to 10% in the extreme of the temperature range. This behavior was already shown by the authors [12] and may be due to a wrong estimate of the radiation correction and not to an error in heat capacity by EOS. This is supported by the fact that all the other sets follow a very close trend in the ranges where they are defined.

6. CONCLUSION

The comparison of the different data sets for liquid toluene presented in this paper shows that the accuracy of the method stays well within the accumulated uncertainty for the data on thermal conductivity, heat capacity, and density used to calculate the thermal diffusivity.

It is shown that for the PCS technique one of the main factors defining the obtainable single-point accuracy is the quality of the signal. The stated 2.5% accuracy for the thermal diffusivity is only an indication on the quality of the single measurements and is, in general, a function of measurement duration, fluid investigated, thermodynamic state of the fluid, and experimental setup. The accuracy of the method can be enhanced for fluids with larger scattering cross section than toluene or by simply performing multiple measurements, thus partly averaging out the random errors from angle measurement and from the evaluation procedure.

In the present state of development of the technique, to the best of our knowledge, there is no possible systematic perturbation known in performing the measurements. With a sophisticated experimental setup and evaluation procedure, significant deviations from the ideal experiment can be avoided and their absence can be proved with a high degree of confidence. Based on this knowledge, the application of this method should allow measurements of the thermal diffusivity with an accuracy limited only by the number of experiments which can be performed.

ACKNOWLEDGMENTS

Partial support of a postdoctoral fellowship of M.M.L. in Germany was provided by the Portugese national science board, Junta Nacional de Investigação Cientifica e Tecnológica. The development of the PCS technique and its application to the investigation of many different fluids, including toluene, has received support from the Deutsche Forschungsgemeinschaft for several years.

REFERENCES

1. C. A. Nieto de Castro, S. F. Y. Li, A. Nagashima, and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **15**:1073 (1986).
2. M. L. V. Ramires, C. A. Nieto de Castro, and R. A. Perkins, *High Temp. High Press.* **25**, in press (1993).
3. R. Goodwin, *J. Chem. Phys. Ref. Data* **18**:1565 (1989).
4. B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).
5. M. Hendrix, A. Leipertz, M. Fiebig, and G. Simonsohn, *Int. J. Heat Mass Transfer* **30**:333 (1987).
6. A. Leipertz, *Int. J. Thermophys.* **9**:897 (1988).
7. K. Kraft and A. Leipertz, *Int. J. Thermophys.* **15**:387 (1994).
8. M. Hendrix, Ph.D. Thesis, Ruhr-Universität, Bochum (1984).
9. S. Will and A. Leipertz, *Appl. Opt.* **32**:3813 (1993).
10. G. Simonsohn and F. Wagner, *J. Phys. D Appl. Phys.* **22**:1179 (1989).
11. C. A. Nieto de Castro, B. Taxis, H. M. Roder, and W. A. Wakeham, *Int. J. Thermophys.* **9**:293 (1988).
12. R. A. Perkins, H. M. Roder, and C. A. Nieto de Castro, *J. Res. Natl. Inst. Stand. Technol.* **96**:247 (1991).
13. T. Yamada, T. Yaguchi, Y. Nagasaka, and A. Nagashima, *High Temp. High Press.*, in press (1993).
14. M. L. V. Ramires, C. A. Nieto de Castro, and R. A. Perkins, *High Temp. High Press.* **25**, in press (1993).
15. C. A. Nieto de Castro, R. A. Perkins, and H. M. Roder, *Int. J. Thermophys.* **12**:985 (1991).