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Thermal diffusivity of transparent liquids by photon correlation spectroscopy—I. Results for toluene and methanol in an extended range of temperature and pressure

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Abstract—A modified photon correlation spectroscopy probe is described which allows the rapid determination of the thermal diffusivity of pure transparent liquids over a wide temperature and pressure range. The system uses Rayleigh scattering of laser light arising from local statistical fluctuations of the temperature in the liquid which itself is in thermodynamic equilibrium (no macroscopic temperature gradient is required). The technique produces absolute values and provides additionally a certain criterion for the recognition of systematical distortions in the measurement in the form of deviations from the expected single exponential decay of the measured correlation function. Results are presented for toluene and methanol in an extended temperature (20–150°C) and pressure (0.1–11 MPa) range.

1. INTRODUCTION

FOR MANY technical processes, the knowledge of the thermal conductivity λ or of the thermal diffusivity a ($\lambda = a\rho c_p$) of liquids involved in the process is of high importance. Exact data are however rare, in particular at high temperatures. The reason may be found in the difficulties of conventional measurement techniques working under thermal nonequilibrium conditions by making use of macroscopic temperature gradients. This usually gives rise to several disturbances of the measurement, for example, heat losses, convective and radiative contributions to the heat transfer in the liquid [1–5]. These disturbances are not easy to correct and tend to give an experimental value of λ or a which is larger than the true one [3, 6, 7]. Measurement accuracy is typically claimed to be of the order of ±1% (or even better) while a critical comparison of the data taken by different authors indicates deviations up to ±5% [6]. Such disturbances are extremely likely in the critical region of the liquid due to natural convection [8] and to difficulties in approaching the critical point when using temperature gradients [9]. Besides the high experimental and temporal efforts to be done in order to take into account the necessary corrections due to radiation and boundary effects (see, e.g. [2, 3, 10, 11]), it additionally takes a long time period, up to several days [10], to establish the required test conditions.

Photon correlation spectroscopy (PCS) is an alternative measurement technique which allows one to determine the transport coefficients of liquids by analysing the Rayleigh scattered light from the probe in the time domain working in macroscopic equilibrium. Thus it can be used for the measurement of the thermal diffusivity avoiding all the problems of the conventional techniques due to the employed temperature gradients. Additionally there are some other advantages of PCS over the conventional techniques. PCS produces absolute values without calibration procedures within a short adjustment and measurement time of less than 2 h in nearly all experimental situations. It provides a certain criterion for systematical inaccuracies in the measurement in the form of deviations from the expected single-exponential behaviour of the measured correlation function. On the other hand, there is one disadvantage which, however, is not of high importance for most technical liquids, e.g. working fluids for heat transfer processes: the liquid has to be transparent for optical wavelengths.

Besides the thermal diffusivity, also other diffusion processes can be investigated by PCS, e.g. the diffusion process of macroscopic particles or macromolecules [12–14] and the mass diffusion in liquid mixtures [15, 16] leading to the dynamic viscosity of the liquid and to the diffusion coefficient of the mixture, respectively. Compared with the measurement of these values and with the investigation near the critical point [17–19], the determination of the thermal diffusivity far away from the critical point is in some respect of extreme difficulty. The process is fast (a is about two orders of magnitude larger than the diffusion constants of the other process) and the signal arising from the local statistical fluctuations of the temperature in the liquid is weak. Because of these

NOMENCLATURE

a	thermal diffusivity
c_p	heat capacity for constant pressure
I'_0	irradiated laser intensity
I_0	intensity of reference light
I_s	intensity of Rayleigh scattered light
k_i	calibration constants
n_L	refractive index of the investigated liquid at wavelength λ_0
q	modulus of the scattering vector, $(4\pi n_L/\lambda_0)\sin\theta_s/2$
$\mathbf{r}$	position vector
T	temperature
t	time.

Greek symbols

$\Gamma(\tau)$	correlation function
δt	statistical temperature fluctuation
$\Delta\tau$	correlator sample time
θ_e	external scattering angle (irradiation angle)
θ_s	scattering angle
λ	thermal conductivity
λ_0	wavelength of laser radiation
ρ	density
τ	time
τ_c	characteristic decay time of the correlation function.

difficulties, only a few attempts were performed to measure the thermal diffusivity outside the critical region [15, 20, 21]. Comparing the results from different authors obtained by spectroscopic methods with those measured with conventional techniques, again deviations of more than ±5% are evident.

In this paper, the PCS technique is described using heterodyne detection conditions in connection with two photomultiplier tubes (PMTs) in cross-correlation. The thermal diffusivity of toluene and methanol is presented being measured by this technique. Far away from the critical point, the data have been taken over a wide temperature (20–150°C) and pressure (0.1–11 MPa) range with an average in accuracy of about 1%.

2. MEASUREMENT TECHNIQUE

The basic principle of the measurement technique is shown schematically in Fig. 1. The beam of a continuous wave laser with intensity I'_0 passes a test cell which is filled with the liquid of interest. The local statistical temperature fluctuations δT cause local statistical fluctuations of the refractive index of the fluid, and by these statistical fluctuations Rayleigh scattering in all directions relative to the laser irradiation (in Fig. 1 just one direction is indicated) [22, 23]. Using the hypothesis of Onsager [24], the microscopic temperature fluctuations follow statistically the same rules which are found for macroscopic processes. That means, the dissipation of these fluctuations at a position $\mathbf{r}$ in the liquid obeys the Fourier heat equation

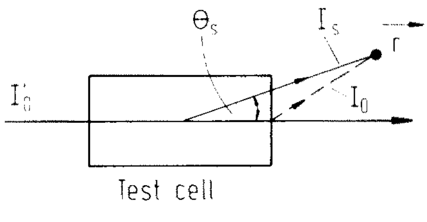

FIG. 1. Principle of the measurement technique.

$$\frac{\partial}{\partial t}\delta T(\mathbf{r},t) = a\nabla^2\delta T(\mathbf{r},t). \tag{1}$$

From the temporal behaviour of δT the value of a can be determined. For this procedure, the correlation function of δT

$$\Gamma_{\delta T}(\tau) \equiv \langle \delta T^*(t)\delta T(t+\tau)\rangle \tag{2}$$

is used, which gives the time average of the product (δT^* is the conjugate complex quantity of δT). The time dependence of the Rayleigh signal reflects the fluctuations of δT [23] and therefore can be used for the measurement of the thermal diffusivity a from the correlation function of the Rayleigh intensity.

In some cases it is advantageous to detect not only the intensity of the Rayleigh scattered light (homodyne detection), but simultaneously some of the original laser light ('reference light') which is scattered from, for example, the windows of the test cell (I_0) and is coherently superposing the light scattered from the liquid (I_s) (heterodyne detection) [25]. Taking the intensities with a scattering angle θ_s, the intensity correlation function can be expressed by [22]

$$\Gamma_I(\tau) = (I_0 + \langle I_s\rangle)^2 + 2k_1 I_0\langle I_s\rangle \exp(-\tau/\tau_c) + k_2\langle I_s\rangle^2 \exp(-2\tau/\tau_c). \tag{3}$$

The constants k_1 and k_2 are dependent on experimental parameters [26, 27]. For $I_0 \gg \langle I_s\rangle$, the homodyne term with decay time $\tau_c/2$ in equation (3) becomes negligible resulting in a single exponential correlation function decaying with decay time τ_c to a constant background $(I_0 + \langle I_s\rangle)^2$. As all time-dependent systematical disturbances will influence this single expon-

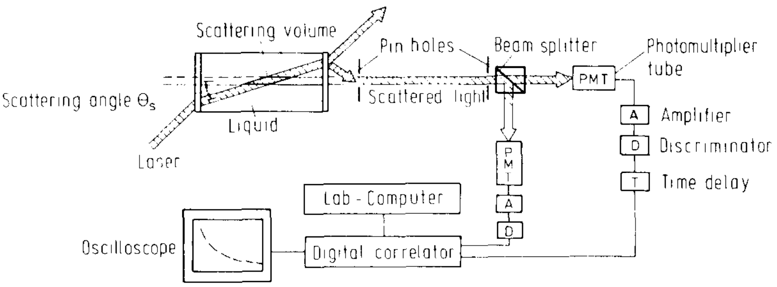

FIG. 2. Schematic of the experimental setup.

ential behaviour, this is a strong criterion for the quality of the measurement and its accuracy. A more detailed investigation of all important systematical disturbances and an extensive error discussion can be found elsewhere [6, 28, 29].

The characteristic (1/e)-decay time τ_c contains the thermal diffusivity a ($\tau_c = 1/aq^2$) which can be used for the evaluation of a if q is known

$$a = q^2\tau_c. \tag{4}$$

The modulus of the scattering vector follows from

$$q = \frac{4\pi n}{\lambda_0}\sin(\theta_s/2). \tag{5a}$$

3. EXPERIMENTAL SETUP

The assembly of the photon correlation probe used for thermal diffusivity determination is shown schematically in its electro-optical part in Fig. 2. Monochromatic light ($\lambda_0 = 488$ nm) of an Ar^+ laser (300 mW) irradiates the transparent liquid to be investigated. The scattered light, which is observed at typical scattering angles θ_s of 3°–5°, is superposed coherently with laser light scattered from the windows of the test cell (in Fig. 2 indicated only for the rear window) to assure heterodyne detection conditions. Two pin holes in the collection optics fix the observation direction and the degree of spatial coherence in the registration of the scattered light.

In contrast to most of the other probes used for the spectroscopic determination of the thermal diffusivity of liquids (see, e.g. [14, 19–21]), here the signal registration is performed perpendicular to the rear window of the cell which is equipped with plane and parallel windows. This leads, for small scattering angles, to a simplified equation for the modulus of the scattering vector

$$q \simeq (2\pi/\lambda_0)\sin\theta_e \tag{5b}$$

containing the external scattering angle θ_e [30]. This irradiation angle is easier to measure than θ_s. Additionally, this approach has the advantage, that the refractive index of the liquid (n_L) has not to be known which may be difficult to obtain at high pressure and temperature. The accuracy in the evaluation of q is limited only by the measurement of θ_e which is found to be accurate within $\pm 0.02°$ using autocollimation techniques. This gives an inaccuracy of q of less than $\pm 1\%$.

The correlation function $\Gamma_I(\tau)$ is measured using a digital correlator (Malvern K 7023) in connection with two PTMs in cross-correlation. Two PTMs have been employed in order to avoid distortions of the correlation function from after-pulse and dead-time effects of the PTMs [31]. A time delay (coaxial cable) inserted in one of the signal lines allows one to measure the complete function including the first point $\Gamma_I(0)$ [31] and some values for negative times τ.

Due to the weak signal intensities, photon counting is the appropriate detection technique. The count interval (sample time $\Delta\tau$) has to be adjusted to be much shorter than the correlation time to be measured ($\Delta\tau \ll \tau_c$) in order to obtain sufficient resolution of the optical signal. During each sample time a number n of PTM pulses is received by the digital correlator, typically $n < 1$, which calculates the photon correlation function $\langle(0)\cdot n(\tau)\rangle$ being proportional to the intensity correlation function $\Gamma_I(\tau)$, equation (3). The way in which a digital correlator works is described elsewhere, see e.g. [32].

The test cell used is shown in Fig. 3 with its typical dimensions. Both windows (4) adjacent to the small sample volume (2) are relatively thick in order to limit the registered intensity of the reference light [6]. The optical surfaces are polished to $\lambda/10$ which avoids disturbances of the correlation function by spatial fluctuations of the laser beam [29]. The fluid temperature has been adjusted with a stability of better than 0.1 K and was measured with an accuracy better than 0.2 K.

4. RESULTS

Using heterodyne detection, deviation from the expected single exponential behaviour of the correlation function can be used to prove the presence of distortion sources and their significance. This usually is done by shifting the fit domain from the short-time

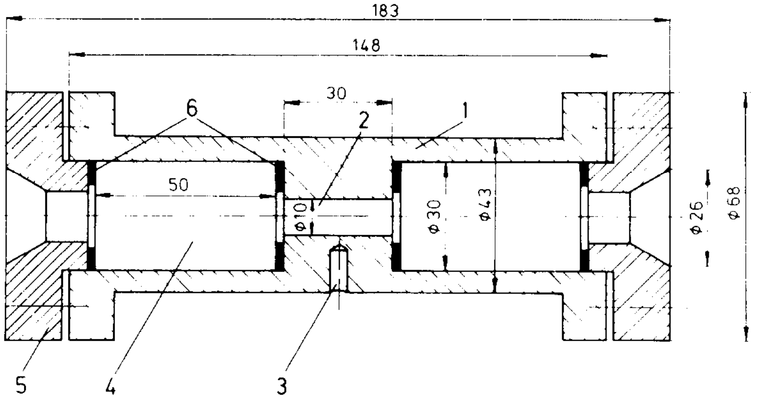

FIG. 3. Dimensions of the test cell (1, cylinder of refined steel; 2, liquid volume; 3, boring for the temperature sensor; 4, window; 5, mounting ring; 6, packing ring of PTFE/coal).

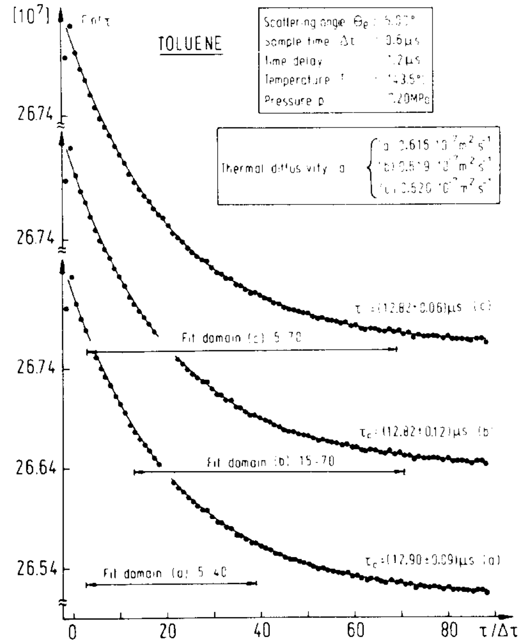

FIG. 4. Typical correlation function of toluene with different fit domains for calculating the thermal diffusivity.

to the long-time region. Figure 4 shows a typical example for toluene at a temperature of 143.5°C and a pressure of 7.2 MPa. For each fit domain a single exponential is fitted to the measurement points of the correlator channels used keeping free all three parameters of the exponential [baseline, decay time τ_c, and $\Gamma_n(0)$], and fitting by a weighted least-square algorithm. The agreement between the evaluated values of the three fit domains indicated is very good, the maximal deviation being 0.7%.

This accuracy can only be obtained by using $\Gamma_n(2\Delta\tau)$ as the first fitting point because of possible distortions by Brillouin scattering at shorter times [29, 33].

Figure 5 shows the thermal diffusivity of toluene (C_7H_8) in its dependence on temperature (20–150°C) for the pressure of 0.1 MPa and of 1.15 MPa. The results obtained by PCS are compared with the data which have been calculated with the λ, ρ and c_p values taken from different compilation works (c_p [34, 35]; ρ [35, 36]; λ [34, 37]). Using the λ data published recently by Leidenfrost [38] and Braun [3], the difference from our results is less than 3%, which is quite good taking into account the 4% inaccuracy for the c_p-values from ref. [34].

Due to the nonlinear behaviour of density with temperature, the theoretical curve is slightly bent. However, within the limited temperature range observed it may be approximated with good accuracy by a straight line. Assuming a linear temperature dependence of the thermal diffusivity

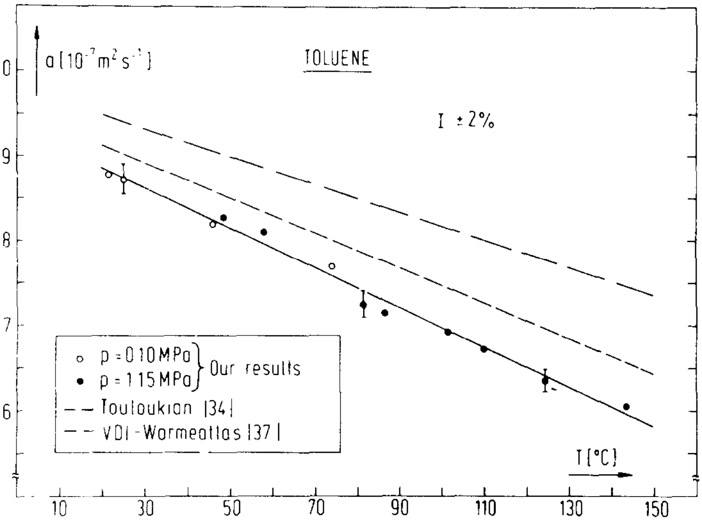

FIG. 5. Measured temperature dependence of the thermal diffusivity of toluene in comparison with data taken from compilation works.

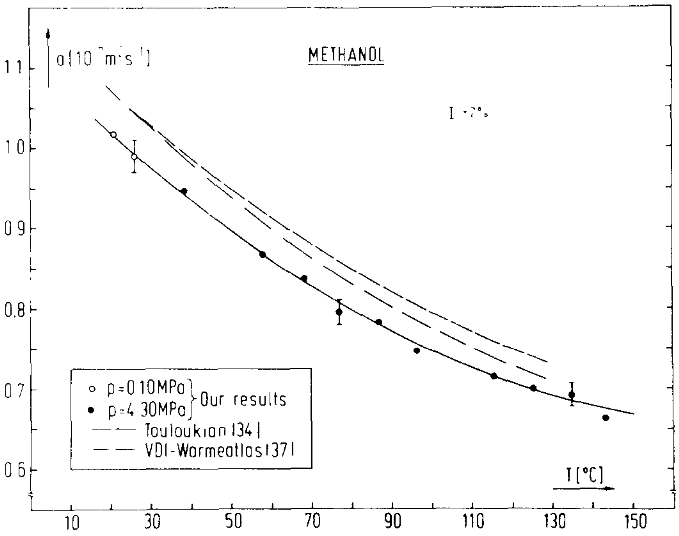

FIG. 6. Measured temperature dependence of the thermal diffusivity of methanol in comparison with data taken from compilation works.

$$a = a_0 - a_1 T, \qquad (6)$$

for the observed temperature range the constant a_0 (using the Kelvin temperature) and the temperature gradient a_1 are found to be $(1.57 \pm 0.03)10^{-7}\,m^2\,s^{-1}$ and $(2.35 \pm 0.08)10^{-10}\,m^2\,s^{-1}\,K^{-1}$, respectively.

Figure 6 shows for the same temperature range the results for methanol (CH_4O) taken for 0.1 MPa and for 4.3 MPa. Here, due to the more distinct nonlinear behaviour of the density [36] no linear fit is allowed. Assuming a quadratic temperature dependence

$$a = a_2 - a_3 T + a_4 T^2 \qquad (7)$$

the values a_2–a_4 are found to be: $a_2 = 3.58 \times 10^{-7}\,m^2 s^{-1}$, $a_3 = 12.91 \times 10^{-10}\,m^2 s^{-1} K^{-1}$, and $a_4 = 14.24 \times 10^{-13}\,m^2 s^{-1}\,K^{-2}$. Again the data calculated with the table works are shown for comparison. Here, the c_p values have been taken from Landolt–Börnstein [39]. Using instead the c_p values from Touloukian [34] or Vargaftik [35], the calculations would result in curves being totally different to our results in Fig. 6. More recent results obtained by conventional techniques are again within 3% of our data [4, 40] for the temperature range up to 50°C. For higher temperatures no comparable data have been found in the newer literature.

Finally, Fig. 7 shows the pressure dependence for two different temperatures of the thermal diffusivity of both liquids investigated. Within the accuracy of the PCS method, no pressure dependence could be recognized.

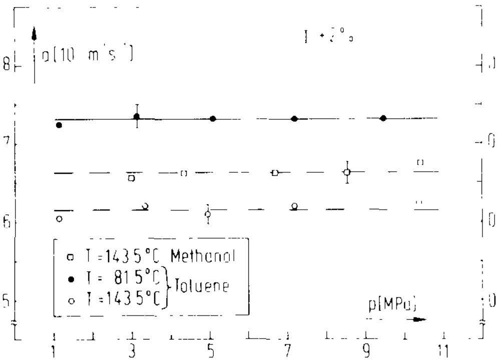

FIG. 7. Measured pressure dependence of the thermal diffusivity of methanol and toluene for two different temperatures.

5. CONCLUSIONS

Photon correlation spectroscopy (PCS) can be used for the fast and accurate determination of the thermal diffusivity of pure transparent liquids giving absolute values without any calibration procedure. No macroscopic temperature gradient is employed avoiding all the problems of conventional techniques with convective and radiative heat transfer. The results for toluene and methanol obtained by PCS indicate that an average inaccuracy of ±1% can be expected for a measurement time of about 30 min or for a total experiment duration of 1–1½ h (including setup adjustments, pressure/temperature variation and measurement time). The inaccuracy may increase to ±2% for single measurements (see Figs. 5 and 6). This is mainly caused by the inaccuracy in determining the scattering angle and by photon statistics which are dependent on the measurement time. An essential improvement of the measurement accuracy could be reached by using, instead of autocollimation procedures, the diffraction of the laser beam from injected acoustic waves of known direction and frequency (see, e.g. ref. [41]) or by using the Raman scattered light described in ref. [20]. The reproducibility of the results has been found to be within the limits indicated for the inaccuracies. Systematical distortions in the measurement can be recognized by deviations in the single exponential behaviour of the correlation function (see Fig. 4), providing thus a clear criterion for the measurement accuracy.

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DIFFUSIVITE THERMIQUE DES LIQUIDES TRANSPARENTS MESUREES PAR LA SPECTROSCOPIE A CORRELATION PHOTONIQUE—I. RESULTATS POUR LE TOLUENE ET LE METHANOL DANS UN LARGE DOMAINE DE TEMPERATURE ET DE PRESSION

Résumé—On décrit une sonde pour spectroscopie à corrélation photonique qui permet la détermination rapide de la diffusivité thermique des liquides transparents purs dans un domaine large de température et de pression. Le système utilise la diffusion Rayleigh d'une lumière laser en provenance des fluctuations locales statistiques de température dans le liquide qui est lui-même en équilibre thermodynamique (il n'y a pas de gradient macroscopique de température). La technique donne les valeurs absolues et fournit en plus un certain critère pour la reconnaissance de distortions systématiques dans la mesure sous la forme de déviation à la décroissance exponentielle de la fonction de corrélation mesurée. Des résultats sont présentés pour le toluène et le méthanol dans les domaines de température 20–150°C et de pression 0,1–11 MPa.

DIE TEMPERATURLEITFÄHIGKEIT EINER TRANSPARENTEN FLÜSSIGKEIT AUF BASIS DER PHOTONENKORRELATIONSSPEKTROSKOPIE—I. ERGEBNISSE FÜR TOLUOL UND METHANOL INNERHALB EINER WEITEN TEMPERATUR- UND DRUCKGEREICHES

Zusammenfassung—Der Aufbau einer modifizierten Streulicht-Sonde auf Basis der Photonenkorrelationsspektroskopie wird beschrieben, die eine schnelle und genaue Bestimmung der Temperaturleitfähigkeit einer transparenten Flüssigkeit innerhalb eines weiten Temperatur und Druckbereiches erlaubt. Das System nutzt die Rayleigh-Streuung von Laserlicht an lokalen statistischen Temperaturfluktuationen in der Flüssigkeit, die sich selbst im thermodynamischen Gleichgewicht befindet (kein markoskopischer Temperaturgradient wird angelegt). Die Technik erzeugt absolute Werte und besitzt ein sicheres Kriterium für das Auftreten systematischer Fehler in der Messung in Form von Abweichungen im erwarteten, einfach-exponentiellen Verhalten der gemessenen Korrelationsfuktion. Ergebnisse für Toluol und Methanol werden vorgestellt, die in einem weiten Temperatur- (20–150°C) und Druckbereich (0, 1–11 MPa) aufgenommen wurden.

ОПРЕДЕЛЕНИЕ ТЕМПЕРАТУРОПРОВОДНОСТИ ПРОЗРАЧНЫХ ЖИДКОСТЕЙ МЕТОДОМ КОРРЕЛЯЦИОННОЙ ФОТОННОЙ СПЕКТРОСКОПИИ—I. РЕЗУЛЬТАТЫ ДЛЯ ТОЛУОЛА И МЕТАНОЛА В ШИРОКИХ ДИАПАЗОНАХ ИЗМЕНЕНИЯ ТЕМПЕРАТУР И ДАВЛЕНИЙ

Аннотация—Предложен новый вариант датчика корреляционной спектроскопии, позволяющий быстро определять температуропроводность чистых прозрачных жидкостей в широком диапазоне температур и давлений. Схема основана на рэлеевском рассеянии лазерного света, происходящем на участках с локальными статистическими колебаниями температур в жидкости, которая сама находится в термодинамическом равновесии (не требуется создания макроскопического температурного градиента). Метод позволяет определять абсолютные значения и, кроме того, дает возможность получать определенный критерий появления систематических искажений в результатах измерений в виде отклонений от предполагаемого однократного экспоненциального затухания измеряемой корреляционной функции. Представлены результаты для толуола и метанола в широких диапазонах температур (20–150°C) и давлений (0,1–11 МПа).