19. H. Ziebland, "Thermal conductivity of toluene," Int. J. Heat Mass Transfer, 2, 275-279 (1961).
20. G. S. Yanin, "Experimental investigation of isobaric heat capacity of organic liquids and mixtures," Candidate's Thesis, Groznyi (1977).
21. T. S. Akhundov, "Investigation of the thermophysical properties of hydrocarbons of the aromatic series," Doctor's Thesis, Baku (1974).

MEASUREMENT OF THE VISCOSITY OF LIQUIDS AND THE DIMENSIONS OF SUSPENDED PARTICLES BY THE METHOD OF CORRELATION OPTICAL-MIXING SPECTROSCOPY

M. A. Anisimov, Yu. F. Kiyachenko,
G. L. Nikolaenko, and I. K. Yudin

UDC 530.162:535.36

The Brownian motion of spherical particles in water is investigated using optical-mixing spectroscopy. The diameters of the particles and the viscosity of the liquid are measured. Multiple scattering was found to affect the results.

One of the most promising applications of optical-mixing spectroscopy is the measurement of the shear viscosity of transparent liquids. In this method small spherical particles are introduced into the liquid being investigated and their diffusion coefficient is measured.

The diffusion coefficient is defined using the results of measurements of the width of the unbiased (central) component in the spectrum of the scattered light using an optical-mixing spectrometer [1]

$$\Gamma = DK^2. \tag{1}$$

Further, using the Einstein–Stokes formula, which describes the Brownian motion of spherical particles [2], one of two quantities is determined, viz., the viscosity of the liquid or the radius of the particles (if the second quantity is known)

$$D = \frac{k_B T}{6\pi\eta r_0}. \tag{2}$$

To determine the experimentally attainable measurement accuracy and possible limitations of the method, we investigated the diffusion of spherical particles of polystyrene latex in water. The experimental arrangement employed is shown in Fig. 1.

The radiation of an LG-36A He–Ne laser ($\lambda = 0.633$ μm) is focused by a lens L of long focal length onto the center of a cuvette containing the specimen. The cuvette is placed in a thermostat which keeps the temperature constant to within ±0.02°K. The temperature of the specimen is measured with a TSPN-2V platinum thermometer with an error of 1 mK. The light scattered at an angle ϑ is received by an FÉU-79 photomultiplier, operating as a photon counter. The output signal of the photomultiplier is applied to a 72-channel digital correlator [3] which measures the autocorrelation function of the scattered light $G(\tau)$. The value of Γ was found by processing the measured autocorrelation function on an ES-1022 computer using the least-squares method [4]. The experimental data were approximated by an exponential function, which corresponds to the scattering of light for the case of monodisperse spherical particles

$$G(\tau) = A \exp \Gamma\tau + B, \tag{3}$$

where Γ, A, and B are the varied parameters in the least-squares method.

A more detailed description of the equipment, the method of measurement, and the method of processing the results can be found in [5].

All-Union Scientific-Research Institute of Physicotechnical and Radio Measurements, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 38, No. 4, pp. 651-655, April, 1980. Original article submitted July 6, 1979.

0022-0841/80/3804-0387$07.50

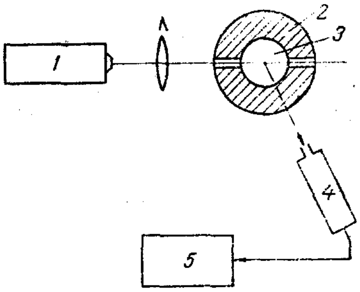

Fig. 1

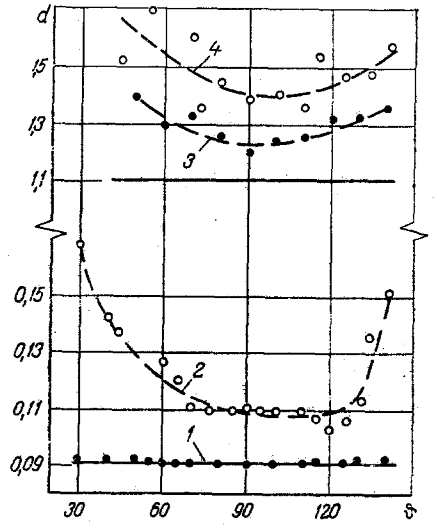

Fig. 2

Fig. 1. Sketch of the experimental arrangement: 1) laser; 2) thermostat; 3) cuvette; 4) photomultiplier; 5) correlator.

Fig. 2. Dependence of the measured particle diameter d, µm, on the scattering angle, ϑ, deg.

Expressions (1) and (2) cannot be used to describe the behavior of the actual specimen because of: 1) the polydisperse nature of the specimen, mainly due to the presence of dust and coagulants, and also because of the finite width of the distribution of the dimensions of the particles; 2) multiple scattering, due to the very high particle density; 3) the non-Gaussian nature of the photocurrent statistics, due to the small number of particles in the scattering volume (the very small particle density); and 4) the possible dependence of the width of the spectral line on the product Kr_0 (for $Kr_0 \gg 1$), as is observed in the region of the critical point [1].

In addition to these reasons, laser noise, equipment vibration, and other distorting factors may have a considerable effect on the results obtained.

We had four types of monodispersion polystyrene latex specimens at our disposal with particle diameters of 0.091 ± 0.0058, 0.234 ± 0.0026, 0.527 ± 0.0125, and 1.099 ± 0.0059 µm with an initial 10% concentration. The latexes were diluted with distilled water to the required concentration (10^{-5}–10^{-6} by weight of polystyrene) and were filtered to remove particles of dust and coagulants.

Figure 2 shows the results obtained from measurements of the particle dimensions for the 0.091 and 1.099 µm latexes as a function of the scattering angle. The temperature of the specimen was maintained at 20°C. When calculating the radius of the particles using Eq. (3) we used the most reliable values for the viscosity of water given in [6]. The error in determining the particle diameter is 0.3–1%. It can be seen from Fig. 2 that the results of measurements for the 0.091 µm latex agree quite well with the Einstein–Stokes theory, viz., over the whole experimental range of scattering angles the measured value of the diameter agrees with the certified value (curve 1). It can also be seen how strongly the results are distorted when dust and coagulants are present in the specimen, which were not filtered out after preparation (curve 2). The form of this curve is typical for a specimen containing extraneous large particles. The measured value of the particle diameter considerably exceeds the true value. The rise in the curve in the region of small and large angles is obviously due to considerable asymmetry of the indicatrix of the light scattered by the extraneous particles. This effect can also be partially seen on curve 1. A similar result is also obtained for the 0.234 µm latex.

For latex with a particle diameter of 1.099 µm it was not possible to obtain good agreement with theory (curves 3 and 4). Although filtering reduces disagreement between the measured and theoretical results (3), it does not eliminate it completely. For the 0.527 µm latex the measurement data was also not completely satisfactory.

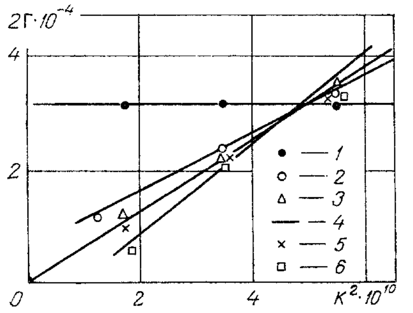

Fig. 3

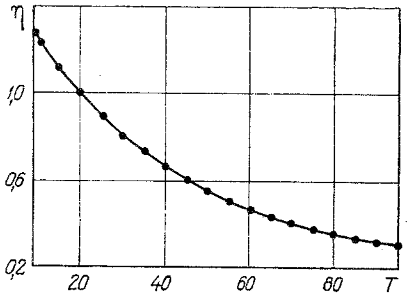

Fig. 4

Fig. 3. Effect of multiple scattering and non-Gaussian statistics: 1) $c = 1.6 \times 10^{-4}$; 2) 8×10^{-5}; 3) 4×10^{-5}; 4) 10^{-5}; 5) 2.7×10^{-6}; 6) 6×10^{-7}. $2\Gamma \cdot 10^{-4}$, μsec^{-1}, $K^2 \times 10^{10}$, cm^{-2}.

Fig. 4. Temperature dependence of the viscosity of water. η, cP, T, °C.

The values obtained can obviously be explained by the fact that to filter the 0.091 and 0.234 μm latexes we used "millipore" filters with hole diameters of 0.22 μm and 0.45 μm, respectively. For the 0.527 and 1.099 μm latexes there were no such filters, so we used ordinary fiber filters, which, possibly, allowed much larger particles to pass through.

To explain the effect of particle scattering and the nature of the statistics we measured the width of the spectral line of the scattered light over a wide range of latex concentrations. We chose 1.099 μm latex as the specimen, for which regions of multiple scattering and non-Gaussian statistics are most easily achieved experimentally. The results of measurements of the linewidth for three scattering angles and for different concentrations are shown in Fig. 3. For concentrations of 3×10^{-6} and 4×10^{-5} they are described by the Einstein—Stokes theory no worse than curve 3 in Fig. 2. The disagreement with theory for small concentrations (6×10^{-7}) is due to the non-Gaussian nature of the statistics of the signal at the output of the photomultiplier, since the number of latex particles in the scattering volume does not exceed 10.

For concentrations greater than 5×10^{-5} the data are distorted by multiple scattering. The dependence of the linewidth on the scattering angle also begins to decrease, and for concentrations of 6×10^{-4}, in general, disappears. In this case the scattering becomes completely multiple. This is the first interesting result that follows from Fig. 3. Another is that there is a value of the scattering angle $\vartheta \approx 115°$ for which the "correct" value of the linewidth is obtained (the point of intersection of the straight lines in Fig. 3). These results are interesting both from the point of view of the physics of the phenomenon and from the point of view of practical applications of the method.

To measure the viscosity we took as the Brownian particles a latex of 0.234 μm. When calculating the temperature dependence of the viscosity we used the reference value of this viscosity for 20°C [6]. The variation in the dimensions of the particles due to thermal expansion was ignored since it was less than the measurement error. The results of measurements of the temperature dependence of the viscosity of water are shown in Fig. 4. A typical measurement error is ±0.5%. Within the limits of the error the results agree with the values for the viscosity of water given in [6].

The method of measuring the viscosity described has a number of advantages over other methods: the absence of macroscopic disturbances of the object (it is possible to measure the viscosity of liquids close to the critical points), the possibility of contact-free and continuous monitoring of the viscosity, e.g., during a technological process, the small measurement time (30-60 sec), and the small value of the systematic errors.

Particular attention was given to the problem of processing the data. The processing program for the computer enabled us not only to approximate the experimental curves by a model with the required number of varied parameters, but also enabled us to determine how adequately the model employed describes these curves [4]. It turns out that the single-exponential model (4) adequately describes the experimental data not only for monodisperse particles (curve 1, Fig. 2), but also in the case of polydisperse specimens and multiple scattering where we would not expect the single-exponential correlation functions to apply. When determining the dimensions of the particles this leads to measured values of the diameter that are too high, but when measuring the viscosity this difficulty can be eliminated if one can make a calibration at one temperature and use the average value of the particle diameter obtained for further measurements.

NOTATION

Γ, half-width of the spectral line; D, diffusion coefficient of the Brownian particles; K, wave number of the fluctuations; n, refractive index of the medium; λ, wavelength of the incident light; ϑ, scattering angle; k, Boltzmann's constant; T, temperature; η, shear viscosity of the liquid; r_0, radius of the particle; $G(\tau)$, autocorrelation function; τ, time; and c, concentration.

LITERATURE CITED

1. H. Z. Cummins and E. R. Pike (editors), Photon Correlation and Light Beating Spectroscopy, Plenum Publ. (1974).
2. R. B. Bird, V. Stuart, and B. Lightfoot, Transport Phenomena, Wiley (1960).
3. Yu. F. Kiyachenko and I. K. Yudin, "A multichannel correlator for optical-mixing spectroscopy," Prib. Tekh. Eksp., No. 4, 218-220 (1978).
4. A. T. Berestov and V. M. Malyshev, "The use of statistical methods for processing experimental data," Tr. VNIIFTRI, No. 32(62), 122-128 (1977).
5. I. K. Yudin, "Development of a method and apparatus for correlation optical-mixing spectroscopy for measuring kinetic viscosity coefficients," Candidate's Dissertation, VNIIFTRI, Moscow (1978).
6. A. A. Aleksandrov and M. S. Trakhengerts, "The viscosity of water at temperatures of 20-150°C," Inzh.-Fiz. Zh., 27, 660-666 (1974).

MOLECULAR THERMAL CONDUCTIVITY OF ORGANIC LIQUIDS

G. G. Spirin

UDC 536.22

The molecular thermal conductivity of a number of organic liquids is measured using a nonstationary method in an optically thin layer.

There is a wide range of liquids whose thermal conductivity has not been studied in sufficient detail. The results obtained have been generalized in [1]. In addition, there is an ambiguity in the values of thermal conductivity obtained due to the phenomenon of radiation. This is due to the fact that the result of an experimental investigation of semitransparent liquids is, as a rule, the effective thermal conductivity, which takes into account both the molecular heat transfer and the radiation heat transfer. In metrological measurements the radiation transfer mechanism emerges as a "distorting" factor, which makes it difficult to interpret the results in terms of the true or molecular thermal conductivity.

It therefore seems advisable to develop direct experimental methods of determining the molecular thermal conductivity. Such methods require the thermal conductivity to be measured in a small spatial volume, which satisfies the reqirement of an optically thin layer [2,3].

Since the efficiency of radiation transfer increases considerably with the temperature, its effect as a "distorting" factor is most appreciable at high temperatures. Correspondingly it is here that the treatment of the experimental results is most ambiguous.

It is of interest to investigate the temperature dependence of the molecular thermal conductivity of organic liquids. For this purpose we developed a relative version of the short-term measurement method at the stage of the irregular thermal mode. The basis of this

---

Sergo Ordzhonikidze Moscow Aviation Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 38, No. 4, pp. 656-661, April, 1980. Original article submitted July 4, 1979.

0022-0841/80/3804-0390$07.50