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.

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MOLECULAR THERMAL CONDUCTIVITY OF ORGANIC LIQUIDS

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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

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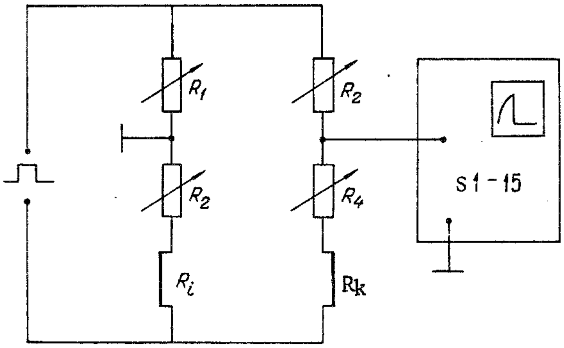

Fig. 1. Bridge measuring circuit.

method is the use of a compensation circuit [4]. When making temperature measurements one can only use a single reference value of the thermal conductivity of a standard liquid, i.e., the value of the thermal conductivity at only one temperature. As it applies to the problem of investigating molecular thermal conductivity, it is convenient to choose the reference value in the medium-temperature range, where the effect of the radiation is a minimum.

We will consider the possibility of using a compensation circuit to make temperature measurements. In this circuit (see Fig. 1) there are two sensors: the measuring sensor R_i and the compensation sensor R_k. (The sensor is a fine metal filament arranged between the current tappings.) The cell in which the measuring sensor is placed is in a thermostat whose temperature is varied during the measurements; the cell with the compensating sensor remains at a constant temperature throughout the measurements.

The measuring sensor is first placed in a standard liquid of thermal conductivity $\lambda_s(T_0)$, and when rectangular voltage pulses are periodically applied to the circuit (their frequency is chosen so that in the gap between pulses the temperature fields produced by them practically completely disappear) the bridge circuit is balanced, which means that not only are the constant components of the voltages compensated but also the variable components due to heating of the sensor filaments.

Since the law governing the increase in the filament temperature is the same for both [5]:

$$\Delta T(t) - \Delta T(t_0) = (q_l/4\pi\lambda)\ln\frac{t}{t_0}, \tag{1}$$

balance is possible in principle. The signal from t_0 to t is balanced by varying the resistances R_1 and R_3. To indicate the resulting signal from the bridge (e) an oscilloscope is used, which is triggered in synchronism with the time that the pulse is applied. At the instant when $e(t) = 0$ balance is obtained, and the values of $R_1(T_0)$ and $R_{0i}(T_0)$ are recorded.

As follows from [6], the condition for complete bridge balance occurs when the following equations are satisfied:

$$R_1(T_0)/(R_1(T_0) + R_3(T_0) + R_{0i}(T_0)) = R_2/(R_2 + R_4 + R_{0k}), \tag{2}$$

$$\frac{\Delta R_i(t,\ T_0) - \Delta R_i(t_0,\ T_0)}{R_1(T_0)} = \frac{\Delta R_k(t) - \Delta R_k(t_0)}{R_2}. \tag{3}$$

The measuring sensor is then transferred to the liquid being investigated at a temperature T and the circuit is again balanced. When this is accomplished the values $R_1(T)$ and $R_{0i}(T)$ are recorded.

The conditions for which the second balance is achieved have the form

$$R_1(T)/(R_1(T) + R_3(T) + R_{0i}(T)) = R_2/(R_2 + R_4 + R_{0k}), \tag{2a}$$

$$\frac{\Delta R_i(t,\ T) - \Delta R_i(t_0,\ T)}{R_1(T)} = \frac{\Delta R_k(t) - \Delta R_k(t_0)}{R_2}. \tag{3a}$$

Since the conditions in the compensation-element arm remain the same during the measurements, the right-hand sides of Eqs. (2), (2a) and (3) and (3a) are, respectively, equal. Hence

$$R_1(T)/(R_1(T)+R_3(T)+R_{0i}(T)) = R_1(T_0)/(R_1(T_0)+R_3(T_0)+R_{0i}(T_0)), \tag{4}$$

$$\frac{\Delta R_i(t,\ T)-\Delta R_i(t_0,\ T)}{R_1(T)} = \frac{\Delta R_i(t,\ T_0)-\Delta R_i(t_0,\ T_0)}{R_1(T_0)}. \tag{5}$$

The last condition can be written as

$$\left(\frac{dR_i}{dT}\right)_T \frac{(\Delta T_i(t,\ T)-\Delta T_i(t_0,\ T))}{R_1(T)} = \left(\frac{dR_i}{dT}\right)_{T_0} \frac{(\Delta T_i(t,\ T_0)-\Delta T_i(t_0,\ T_0))}{R_1(T_0)}. \tag{6}$$

Assuming $R_i(T)$ to have the form

$$R_i(T) = R_i(T_0)[1+\alpha(T-T_0)+\beta(T-T_0)^2],$$

we have

$$\frac{dR_i}{dT} = R_i(T_0)\alpha + 2R_i(T_0)\beta(T-T_0).$$

Hence we have

$$\left(\frac{dR_i}{dT}\right)_{T_0} = R_i(T_0)\alpha,\quad \left(\frac{dR_i}{dT}\right)_T = R_i(T_0)[\alpha+2\beta(T-T_0)]. \tag{7}$$

Substituting (7) into (6), we obtain

$$\frac{\left[1+\frac{2\beta(T-T_0)}{\alpha}\right](\Delta T_i(t,\ T)-\Delta T_i(t_0,\ T))}{R_1(T)} = \frac{\Delta T_i(t,\ T_0)-\Delta T_i(t_0,\ T_0)}{R_1(T_0)}. \tag{8}$$

Using (1) we have

$$\frac{\left[1+\frac{2\beta(T-T_0)}{\alpha}\right]q_i(T)}{R_1(T)\lambda(T)} = \frac{q_i(T_0)}{R_1(T_0)\lambda_s(T_0)}. \tag{9}$$

Substituting the expressions for the thermal fluxes and using (4) we can convert (9) to the form

$$\frac{\left[1+\frac{2\beta(T-T_0)}{\alpha}\right]R_{0i}(T)}{R_1^3(T)\lambda(T)} = \frac{R_{0i}(T_0)}{R_1^3(T_0)\lambda_s(T_0)} \tag{10}$$

(the length of filament is assumed to be independent of the temperature; this assumption is justified for metals when heated to several hundred degrees).

Hence, the theoretical relation which gives the required thermal conductivity has the form

$$\lambda(T) = \lambda_s(T_0)\left(\frac{R_1(T_0)}{R_1(T)}\right)^3 \frac{R_{0i}(T)\left[1+\frac{2\beta(T-T_0)}{\alpha}\right]}{R_{0i}(T_0)}. \tag{11}$$

Experimental investigations were made using the equipment described in [4]. To produce short-term temperature fields we used platinum filaments of radius 1 µm and length 20-30 mm. The length of the pulses applied to the bridge circuit was 10^{-3} sec, and the frequency at which they were applied was 1 Hz. The maximum heating of the filament when the pulse passed through it did not exceed 2°C. Complete balance was achieved on the "tail" of the temperature signal from $t_0 = 0.3 \times 10^{-3}$ to $t = 10^{-3}$ sec.

The compensation sensor was placed in toluene and kept at constant temperature in a bath of melting ice. To eliminate temperature drift the resistances R_2 and R_4 were stabilized in the same way.

The liquid being investigated was placed in the cylindrical cavity of a vessel of constant volume. A metal plug with insulated current tappings in which the platinum filament (R_i) was placed was screwed into the cavity. The temperature of the liquid was measured from the resistance of the filament using the $T(R_i)$ calibration relation.

When using this method the most important thing is to choose the reference value of the standard liquid. It is necessary that this value should continuously represent the molecular

TABLE 1. Molecular Thermal Conductivity of a Number of Liquids

T, °C	Liquid	$\lambda_m \cdot 10^3$ W/m·deg K	$\lambda_{eff} \cdot 10^3$ W/m·K	$\frac{\lambda_m - \lambda_{eff}}{\lambda_m}$, %
20	Toluene	131,5	134,7	—2,4
40		125,0	129,9	—3,9
60		118,0	125,1	—6,0
80		112,5	120,4	—7,0
100		106,0	115,7	—9,1
120		101,5	111,0	—9,4
140		96,0	106,2	—10,6
160		91,0	101,6	—11,5
180		86,0	96,8	—12,6
20	Benzene	144,5	147,0	—1,7
40		137,5	139,5	—1,5
60		129,5	133,0	—2,7
80		123,0	128,0	—3,8
100		115,0	121,5	—5,6
120		108,0	116,0	—6,7
20	Dichloroethane	132,0	134,5	—1,8
40		126,0	130,0	—3,2
60		119,5	125,5	—5,0
80		113,5	121,0	—6,6
100		107,0	—	—
120		100,5	—	—
140		94,5	—	—

thermal conductivity. We therefore carried out absolute measurements of the thermal conductivity of toluene, which is recommended as a standard for studying thermal conductivity. Measurements were made using the procedure described in [5], which enabled us to investigate the values of molecular conductivity directly. When investigating the thermal conductivity of toluene platinum, filaments of radius about 1 μm were used; filaments of radius less than that used in [5] reduced the error due to the natural thermal capacity of the filament (for the same measurement time), while the increase in the resistance (for the same length) enabled the increase in its temperature during pulsed heating to be measured more accurately [6].

Particular errors in the experiments were: when measuring the voltage, 0.2%, the length of the filament, 0.5%, the temperature coefficient of resistance of its material, 0.2%, and the rate of heating, 0.5%. Neglect of the natural heat capacity of the filament affected the results of measurements of its temperature by not more than 0.1%. Hence, the maximum measurement error is 1.5%. The spread in the experimental values did not exceed 1.3% of the mean. For toluene at 20°C, $\lambda_{20°C} = 0.1315$ W/m·deg K.

The results of an investigation of the temperature dependence of the thermal conductivity of toluene (20-180°C), benzene (20-120°C), and dichlorethane (20-140°) are given in Table 1. Table 1 also gives values of the effective thermal conductivity of these liquids from the results obtained in [1] and the relative values of their disagreement.

Analysis of the error of the relative measurements shows that their main source is due to the effect of the natural thermal capacity of the filament, apparatus errors when measuring R_1 and R_i, and uncertainty in indicating when the bridge is balanced. The effect of the natural thermal capacity was estimated as described in [7]; in this case we also took into account the results of the use of the compensation circuit. In [5] it was pointed out that the logarithmic law of increase in filament temperature (1), which reflects the correspondence between the physical model of the measurement and the idealized model, the solution of which was used in calculating the thermal conductivity, is strictly valid. In the compensation-measurement method the necessary condition for this correspondence is compensation of the variable signals due to heating of the filament. In fact, distortion of the logarithmic law of increase of temperature of one of the filaments, e.g., due to incorrect specification of the boundary conditions, made it impossible to obtain time-compensation. In the experiments the latter was found to be of good quality. In particular, the results of measurements of the thermal conductivity when there was compensation over the section 0.3-0.6 msec and 0.6-1 msec did not differ by more than 0.2%.

According to our estimates the resulting error of the relative measurements of thermal conductivity did not exceed 1%. The spread in the experimental data and their reproducibility confirm this estimate.

Comparison of the values of the molecular and effective thermal conductivity of the semitransparent liquids investigated shows that whereas they are fairly comparable at room temperature, as the temperature increases the molecular thermal conductivity becomes much less than the effective value (for toluene, e.g., at 180°C by 12.6%).

In conclusion, we note that the considerable disagreement between the molecular and effective thermal conductivities at high temperatures shows that it is necessary to develop experimental investigations for the direct determination of molecular thermal conductivity in order to explain the effect of radiation on the results. The most appropriate methods here are short-term measurements at the stage of the irregular thermal mode and methods based on probing the liquid with high-frequency temperature fields.

NOTATION

t, time, sec; $\Delta R(t)$, increase in the temperature of the filaments up to the instant of time t, °K; q_l, specific thermal flux, W/m; R, bridge resistance, Ω; $R(T)$, bridge resistance corresponding to the temperature of the liquid investigated, T; $\Delta R(t, T)$, increment in the resistance of the filament corresponding to the instant of time t and to the temperature of the liquid investigated, T. The indices used are as follows: i, measured quantity; k, compensated quantity; m, molecular; eff, effective; and 0, initial level at which the resistance or temperature is read.

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