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THERMAL ACTIVITY OF SUPERCOOLED LIQUIDS

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An experimental procedure of studying the thermal activity of supercooled liquids using short-duration measurements in the stage of irregular thermal conditions is considered.

A metastable region bordering on a stable one contains matter in both a superheated and a supercooled state. The implementation of a supercooled state of a liquid and carrying out investigations of its thermophysical characteristics by stationary or nonstationary methods, when a nonstationary temperature field exists for a long time, is a rather complex problem. In particular, the liquid is to be thoroughly cleaned from artificial crystallization centers. On appreciable supercooling, it is impossible to carry out measurements because of the appearance of crystallization centers having a fluctuational origin, with the exception of some viscous fluids of the type of glycerin.

Promising possibilities for studying supercooled states exist through short-duration heating of ultrathin resistive elements that contact with the substance under study. Initially a thin layer of the substance is in a crystalline state. On passing a current pulse through the resistive element, the sample tested is heated, melted, and, consequently, a liquid in the vicinity of the resistive element is formed. On termination of the heat pulse, the liquid begins to cool off due to energy dissipation, and at a time τ^* its layer adjacent to the resistive element is cooled to the substance crystallization temperature. The subsequent instants of time $t > \tau^*$ correspond to the state of a supercooled liquid. When a certain degree of supercooling is attained, a short (measuring) voltage pulse is fed to the resistive element. The conditions of measurement are such that during the time of its passage the transformation in time and space of the temperature field initiated by the first (heating) pulse is insignificant, that is, the temperature field of the heating pulse seems to be "frozen" and virtually corresponds to a stationary temperature field.

The actual scheme of measurements presupposes the disposition of a plane layer of the substance investigated between two semi-infinite (thermally) media. The thickness of this layer is small, and its effect on heat transfer for high values of time can be neglected. Then, the model problem that allows one to determine the dynamics of the cooling-off of the system after its exposure to the heating pulse (q' = const) will be written as follows:

$$a_1 \frac{\partial^2 T_1}{\partial x^2} = \frac{\partial T_1}{\partial t} , \quad a_2 \frac{\partial^2 T_2}{\partial x^2} = \frac{\partial T_2}{\partial t} , \quad t \geq 0 ;$$

$$T_{1(t=0)} = \frac{2q' \tau^{1/2}}{\varepsilon_1 + \varepsilon_2} \operatorname{ierfc} \frac{|x|}{2\sqrt{a_1 \tau}} , \quad x \leq 0 ; \tag{1}$$

$$T_{2(t=0)} = \frac{2q' \tau^{1/2}}{\varepsilon_1 + \varepsilon_2} \operatorname{ierfc} \frac{|x|}{2\sqrt{a_2 \tau}} , \quad x \geq 0 ;$$

$$T_1 = 0 , \ T_2 = 0 \ \text{ for } \ |x| \to \infty ; \ T_1 = T_2 \ \text{ for } \ x = 0 .$$

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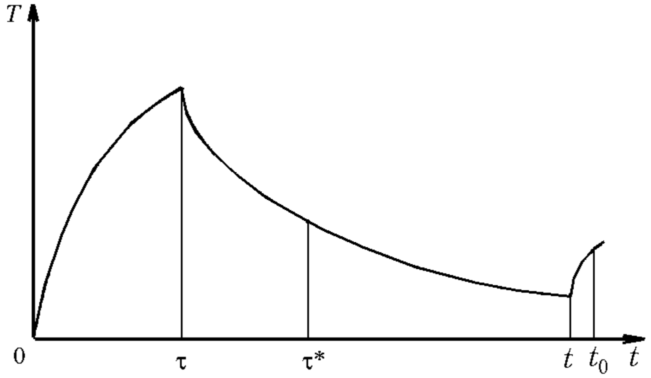

Fig. 1. Profile of the change in the temperature of the substance investigated. T, K; t, sec.

The initial distributions of temperatures $T_{1(t=0)}$ and $T_{2(t=0)}$ correspond to heating of the media by a constant heat flux q' = const in a time τ [1]. Using the Laplace transformation and restricting ourselves to the first terms of the expansion, we have

$$T_{1(x=0)} = T_{2(x=0)} = T_0 = \frac{2q'\tau^{1/2}}{\sqrt{\pi}\,(\varepsilon_1 + \varepsilon_2)}\left(\sqrt{1 + \frac{t}{\tau}} - \sqrt{\frac{t}{\tau}}\right), \tag{2}$$

where ε_1 and ε_2 are the thermal activities of the media ($\varepsilon = \lambda\sqrt{a}$). Relation (2) determines the temperature of the thin resistive element located at the interface of the semi-infinite media. With the assumptions made, this temperature can be used to characterize the liquid under study.

Figure 1 demonstrates the profile of the temperature of the substance studied; it clarifies the experimental procedure. The interval 0–τ corresponds to its heating and subsequent melting; τ–t — to cooling-off; t–t_0 — to short heating of the liquid by a measuring pulse; τ^* is the time during which the substance crystallization temperature is attained.

The measuring pulse or, correspondingly, short heating of the resistive element by a constant heat flux q is a source of information on the thermal activity of the substance; this information is gained by applying the well-known method of measuring thermal activity [2] based on the relation

$$\Delta T = \frac{2q\sqrt{t_0}}{\sqrt{\pi}\,(\varepsilon_1 + \varepsilon_3)}, \tag{3}$$

where ΔT is the increment of the resistive element temperature during the time t_0 of exposure to the heat flux q; ε_1 and ε_3 are the thermal activities of semi-infinite media between which the resistive element is located. In the case considered, ε_1 is the thermal activity of the substrate on which the resistive element is located and ε_3 is the thermal activity of the liquid being studied.

Due to the short duration of measurement, the liquid layer may be considered as a semi-infinite medium. In the experiment considered, the above assumption is valid if the length of the temperature field diffusion in the substance under study is much less than the thickness of the substance layer l ($\sqrt{a_3 t_0} << l$, where a_3 is the thermal diffusivity of the liquid. In this case, thermally the layer of substance can be considered as a semi-infinite medium.

We will consider the experimental procedure. The schematic diagram of the setup is presented in Fig. 2. It contains the following basic elements: pulse generators G_1 and G_2, a delay unit (DU), and a measuring bridge circuit into which measuring (R_m) and compensation (R_c) cells were incorporated. The signal from the bridge was recorded by an S1-15 oscillograph.

The setup operates as follows. A rectangular voltage pulse of duration τ is fed from the generator G_1 to the bridge circuit and simultaneously, with the start of the pulse, a signal is supplied to the inlet of the delay unit. In time

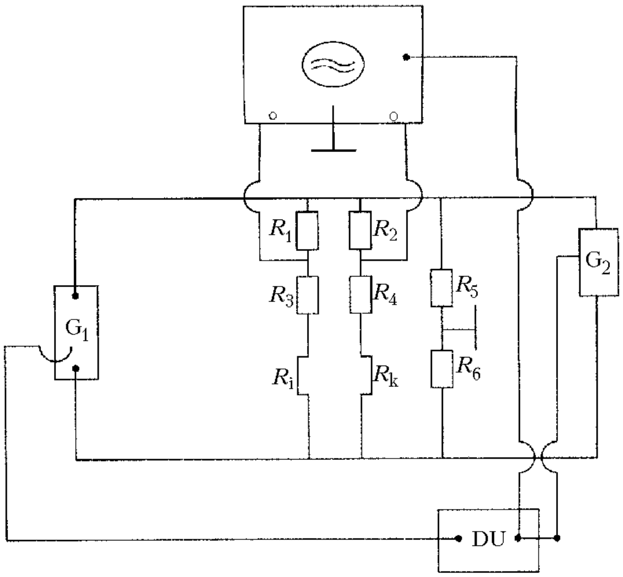

Fig. 2. Schematic diagram of the experimental setup.

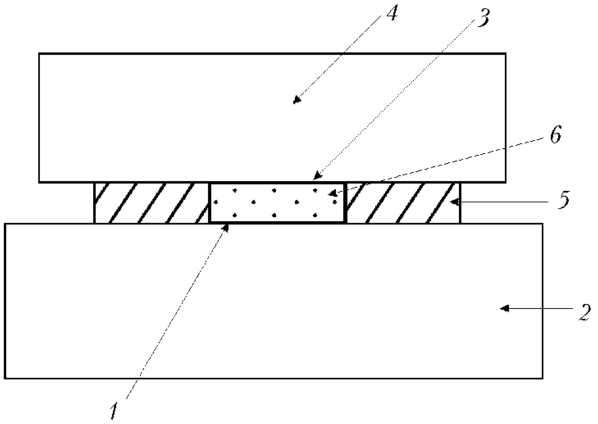

Fig. 3. Scheme of the measuring cell: 1) position of the heater; 2, 4) round glasses; 3) position of the resistance thermometer; 5) washer; 6) test substance.

t the delayed pulse triggers the other generator G_2, from which a rectangular short voltage pulse t_0 is supplied to the bridge circuit. To raise the accuracy of relative measurements the compensation bridge circuit of [3] was used in the present work.

A compensation cell is a vessel (test tube) with vaseline oil into which a resistive element (20 × 1 mm) is placed; the latter is nickel sprayed onto a Sitall backing to a thickness about 400 Å. The compensation cell was thermostated at 0^{o}C.

The measuring cell (Fig. 3) consists of a heater and a resistive element analogous to that used in the compensation cell, but sprayed onto a round glass. The heater was formed by parallel resistive tracks made by a razor blade on a round glass surface spray-coated with aluminum. Contact areas were spray-coated with copper. By means of stop washers made from polyethylene terephthalate film a gap of $\sim 10^{-5}$ m was made between the glasses into which a test liquid or a test substance was placed. Prior to measurements, the gap was filled with a standard fluid (toluene) and was thermostated at 0^{o}C. As soon as the pulses operated (their parameters were not changed), a complete balance of the bridge circuit was made (i.e., the balance of both the constant and variable components of temperature signals) for the time range corresponding to the duration of the measuring pulse. On achieving the balance, the resistance R_1 was

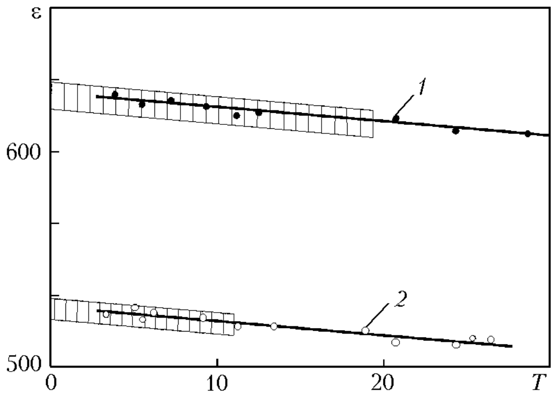

Fig. 4. Thermal activity of the test liquids: 1) PEG-600; 2) dioxane. Dashed regions, overcooled state. ε, W·sec$^{1/2}$/(m^2·K); T, K.

recorded. The resistance of the resistance element of the measuring cell R_m and, correspondingly, the liquid temperature were measured following the scheme of determining the instantaneous values of resistance [4].

The above-noted operations were carried out for different delay times. From the results obtained $R_{1(t)\text{st}}$ and $R_{\text{m}(t)\text{st}}$ were found. Thereafter, the gap was filled with the substance being investigated, which crystallized at a thermostat temperature of 0°C. The procedure of measurements of $R_{1(t)\text{in}}$ and $R_{\text{m}(t)\text{in}}$ is analogous to that described above.

The unknown value of the thermal activity was calculated with the aid of the relation

$$\varepsilon_{(T_2)} = \left(\varepsilon_{1(T_1)} + \varepsilon_{\text{st}(T_1)}\right)\left(\frac{R_{1(t)\text{st}}}{R_{1(t)\text{in}}}\right)^3 \frac{R_{\text{m}(t)\text{in}}}{R_{\text{m}(t)\text{st}}} - \varepsilon_{1(T_2)} , \tag{4}$$

which is similar to that given in [5]. Here, $\varepsilon_{1(T_1)}$ is the thermal activity of the substrate (glass) at the temperature attained at delay time t and on contact with a standard liquid; $\varepsilon_{1(T_2)}$ is the same but for contact with the substance being investigated; $\varepsilon_{\text{st}(T_1)}$ is the thermal activity of toluene at the temperature attained at delay time t.

The procedure considered was applied for studying the thermal activity of dioxane and polyethylene glycol (PEG-600). The lengths of the heating and measuring pulses were τ = 50 msec and t_0 = 100 μsec. The warming-up of the resistive element on action of the measuring pulse did not exceed 5°C.

The pause between the sequences "heating pulse–liquid cooling-off–measuring pulse" was 3–5 sec. In this time, due to energy dissipation, the system had time to virtually restore the initial level (0°C).

In estimating uncertainties [6], both errors associated with the difference of the real model of measurement from the idealized one (the intrinsic heat capacity of the element, edge effects, nonlinearity of the thermal problem) and instrumental errors were taken into account. An additional source of errors is the nonstationary temperature field created by the heating pulse. Its effect manifests itself as follows: first, it brings distortions into the recorded temperature of the element occurring due to the action of the measuring pulse and, second, owing to the evolution of heat from the edges of the element the error in the determination of the instantaneous temperature should be taken into account. In estimating the uncertainty, it should be taken into consideration that the presence of the compensation circuit reduces the influence of all the factors enumerated. The net error of relative measurements is estimated to be 3%. The scatter of experimental data and reproducibility of the results agree with such an estimation.

Experimental investigations (Fig. 4) have shown that at the attained depths of penetration into the metastable region for the liquids investigated the points corresponding to the experimental values of the coefficients of thermal activity lie on a straight line extrapolated from the stable region. This means that at the attained degrees of supercooling of the liquids no noticeable crystallization centers appeared, the presence of which could have caused conversion of the homogeneous liquid layer into a two-phase system with volumetrically distributed heat sources. Such a conversion could have an effect on the results of measurement of the thermal activity by distorting [7] them.

Thus, the technique described allows one to experimentally investigate the thermal activity of overcooled liquid. It seems there are no physical prerequisites for doubting the validity of extrapolation of experimental data from a stable region into a metastable one (overcooled state). It should also be noted that in conducting experiments no effects associated with the appearance of solid phase nuclei in the overcooled liquid were recorded.

NOTATION

a, thermal diffusivity, m^2/sec; *q*, heat flux, W/m; *R*, bridge circuit resistance, Ω; *T*, temperature, K; *t*, time, sec; *x*, coordinate, m; ε, thermal activity, $W \cdot sec^{1/2}/(m^2 \cdot K)$; λ, thermal conductivity, W/(m·K); τ, duration of the heating pulse, sec. Subscripts: in, investigated; st, standard; m, measuring; c, compensation.

REFERENCES

1. B. I. Il'in, A. V. Gurskaya, V. F. Salokhin, and G. G. Spirin, Measurement of the thermal activity of liquids in the metastable region, *Inzh.-Fiz. Zh.*, **29**, No. 4, 595–599 (1975).
2. B. I. Il'in, V. F. Salokhin, and G. G. Spirin, Experimental study of the thermal conductivity of weakly absorbing liquids in layers transparent to infrared radiation, *Inzh.-Fiz. Zh.*, **30**, No. 6, 972–978 (1976).
3. A. V. Luikov, *Heat Conduction Theory* [in Russian], Vysshaya Shkola, Moscow (1967).
4. Yu. A. Polyakov and G. G. Spirin, The pulse method of determining the coefficient of thermal activity in matter, *Inzh.-Fiz. Zh.*, **16**, No. 2, 330–333 (1969).
5. G. G. Spirin, Yu. A. Polyakov, and S. D. Solomonov, A pulse method for studying the thermoactivity of dielectric liquids, *Inzh.-Fiz. Zh.*, **18**, No. 2, 253–258 (1970).
6. G. G. Spirin, Methodical characteristic features of short-time measurements in the stage of irregular thermal regime, *Inzh.-Fiz. Zh.*, **38**, No. 3, 403–410 (1980).
7. G. G. Spirin, E. A. Nakashidze, and L. N. Kudryavtseva, Brief measurements of thermal activity in the melting range of a substance, *Inzh.-Fiz. Zh.*, **49**, No. 1, 77–82 (1985).