RELAXATION KINETICS OF THE TEMPERATURE FIELD OF A SUBSTANCE AS A METHOD OF ANALYZING ITS STRUCTURE

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A method is proposed for studying the structure of a substance according to the relaxation kinetics data of an elementary thermal perturbation therein. Results are presented of experiments for glycerine and the oligomer PMS-400.

Arbitrary jumplike changes (pressure, temperature, potential, etc.) occurring in time and space are not instantaneously erased. The intensity of their damping is often described by the exponential law

$$p(t)=\sum_{i=1}^{n} p_0 \exp\left(-\frac{t}{\tau_{ri}}\right), \tag{1}$$

characteristic for one- and multistage relaxation processes.

Equilibration of the temperature during nonuniform heating of a body or dissipation of an artificially produced thermal perturbation in a medium by nonstationary heat conduction refers to such relaxation processes [1] and is characterized by a time, a relaxation rate, and a dimension of the domain of noticeable localization of the thermal perturbation in the lapse of the relaxation time.

In the general case relaxation of a temperature field perturbation is described by a homogeneous heat conduction differential equation

$$\frac{\partial T(r,\ t)}{\partial t}=a\Delta T(r,\ t). \tag{2}$$

Terms in the form of time exponents that reflect the relaxation nature of the evolution of the thermal perturbation parameters can be present in its solutions, of which there can be an infinite set.

Without going into a search for specific solutions of (2), let us try to describe the evolution of a thermal perturbation by relying on the formal experimental parameters of its profile: the height, area, or halfwidth. It should be noted that relaxation of a temperature perturbation was investigated earlier, but the quantitative data of these papers were not analyzed for the existence of polyrelaxation.

We selected the height of the temperature profile as the experimentally most accessible quantity in a nonstationary method of a thermal constant power probe as the characteristic macroscopic thermal perturbation parameter that varies during the relaxation process. This method is recommended as quite reliable in heat conduction measurements of rheologically complex media [2], and the extension of its possibilities because of using microwire cooling stages was of interest. A thin wire with small intrinsic specific heat located at the center of the thermal perturbation it creates fixes the dissipation (relaxation) kinetics of the thermal perturbation in the cooling stage precisely according to the decreasing magnitude of the temperature maximum. By analyzing the kinetic curve of the temperature maximum on the resolution of the relaxation times, useful information can be obtained about the relaxation times, the characteristic dimensions of localization of monorelaxation structures, and the rates of the relaxations proceeding therein [3]. It also seemed that a directed search of paths to increase the sensitivity and informativity of the nonstationary constant power thermal probe method permits later development of a spectral method of obtaining data on the structure of an isotropic medium as its response to thermal action.

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Outside its dependence on nature, an arbitrary relaxation process is an irreversible transition of a system from a nonequilibrium state into an equilibrium state described monotonically by a damping function that can, in principle, be approximated by an arbitrary descending function, including an exponential. However, only an exponential function or a function in the form of a sum of exponents has explicitly physical meaning associated with the relaxation time concept.

The relaxation time τ_r characterizes the duration of the existence of nonequilibrium by defining the proportionality of the rate of the system tendency to equilibrium the deviation from it in the kinetic equation

$$\frac{dp}{dt} = \frac{1}{\tau_r}[p_0 - p(t)], \tag{3}$$

where p_0 and $p(t)$ are the equilibrium and running macroscopic parameters of the system (the height of the thermal perturbation profile in our case). In the general case the relaxation time is a variable quantity dependent on not only the properties of the system itself but also on what initial nonequilibrium state the system was found, and how far from equilibrium. Evidently, the greater the thermal perturbation amplitude, the more probable the onset of different nonlinear thermo-hydrodynamic phenomena in the system (aggregate and phase transformations, initiation of motion of initially fixed pahse, development of anomalous mechanical stresses, localization of heating, etc.) that spoil the relaxation process criterion. Consequently, for uniqueness we give sufficiently small, i.e., elementary, perturbations that occur far from nonlinear phenomena.

The real shape of the radial profile of an elementary perturbation in the formation stage is approximated to an ideal narrow Π-shape, assuming a smooth descending shape with a maximum near the probe surface. The elementary perturbation being formed in the development (relaxation) stage is propagated in the isotropic medium being investigated with an initial uniform temperature that retains axial symmetry and cylindrical one-dimensionality. Since a linear source is superposed structurally with a thermal detector, the initial height of the radial perturbation profile

$$T_z(0, t_i) = \frac{q_L}{4\pi\lambda}\ln\frac{4at_i}{Cr_z^2} \tag{4}$$

is successfully recorded directly in experiment as is the height of the relaxing profile $T_z(0, t_i + t)$. In conformity with the theory of a linear constant power source the initial height depends on the heat conduction λ and the thermal diffusivity a of the medium, the power q_L and the time of linear source action t_i.

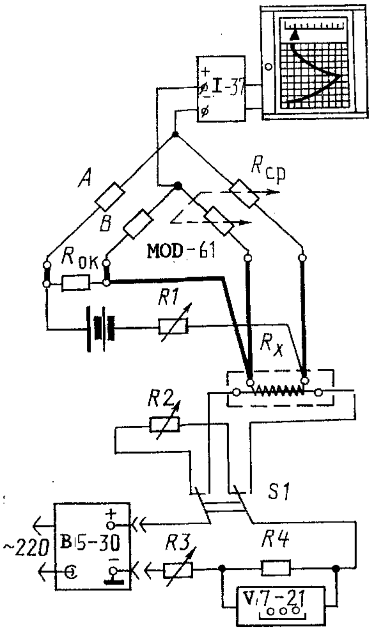

Fig. 1. Diagram of the laboratory set-up for investigating the thermophysical and thermorelaxation characteristics of substances.

Objects of Investigation. Chemically pure viscous fluids, the simplest triatomic alcohol, glycerine and a linear organosiloxane oligomer PMS-400, were selected as objects of investigation. The selection of these liquid media was dictated by the easy insertion of a wire probe in such media, by the elimination of a convective heat transport component in viscous media, by the importance of studying the kinetics of nonequilibrium processes in fluids for the investigation of their structure and physical properties.

Experimental Part. A laboratory set-up mounted on the base of the apparatus described in [2] was used in application to investigations of the kinetics of a change in heat conduction during solidification of epoxy compounds. The installation (Fig. 1) consists of a sensitive prob located at the center of the cell with the specimen, supply and probe temperature recording units and a thermostat apparatus.

The probe is in the form of two resistors: a 3Ω resistance linear thermal source (a manganin wire in a thermally stable enamel insulation with low TKS which assures the heating stability condition) and a 12Ω resistance thermal detector combined with it (a copper microwire in the same insulation with high TKS, which assures the necessary thermal sensitivity of the probe). The thermal source and the thermal detector are electrically mutually independent and interconnected just by a thermal contact: a copper microwire of 0.030 mm diameter wound in a compact monolayer on a 0.135 mm diameter and 5 mm long manganin. A 35 mm long winding is equally remote from the ends of the thermal source, which permits elimination of the influence of edge effect. By using portable wire support-current inputs the probe is mounted along the axis of the measuring cell.

A 55 mm long and 15 mm inner diameter measuring cell is fabricated from duraluminum. Externally it is a cylinder with a cavity that is placed compactly in the working zone of a tubular electric furnace supplied by using an automatic isodromic regulation servosystem. Stepwise thermostatting is realized with an accuracy no worse than 0.1°C in a 20-150°C range. The background temperature of the specimen is checked by a chromel—copel thermocouple connected to a V7-21 digital voltmeter.

A Kelvin—Thompson bridge circuit is used to measure the thermal detector resistance and the formation of the working signal proportional to the probe temeprature. The balancing comparison arms R_{co} of the bridge circuit are formed by duplex decade resistances of the serial bridge MOD-61 (accuracy class 0.05) and a hermally sensitive resistor R_x, and the reference arms of ratio A and B by constant 100Ω resistances of the same bridge and a standard resistance R_{ok} (accuracy class 0.02). The allowable magnitude of the measuring current is built up by using storage batteries and a limiter resistance R1. The probe signal in the form of a bridge circuit unbalance is amplified by a d.c. measuring amplifier and goes to a one-second self-recording milliammeter KSU-4 to assure its development in time at a 37.5 mm/sec rate.

The probe heating resistor is supplied electrically from a standard d.c. source with regulatable voltage. By using a fast-acting switch S1 the supply circuit is switched either to the thermal source or to the ballast matching resistor R2 simulating the resistance of this thermal source. This permits conservation of a constant load and improvement of the transient characteristic of the source the resistor R3 is a regulator of the input power of the probe heating loop. Together with the digital voltmeter V7-21 the standard resistor R4 assure measurement of the heating current to fourth decimal place accuracy.

The measurement procedure was reduced to obtaining probe heating and cooling thermograms in the medium under investigation (Fig. 2). Being assured of the adequate homogeneity

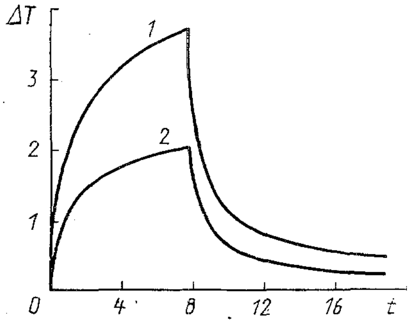

Fig. 2. Probe heating and cooling thermograms in PMS-400 (1) and glycerine (2). ΔT, K; t, c.

of the specimen temperature field (according to the kinetics of the change in the zero-th signal of the thermal detector), the electrical supply circuit with the ballast resistor was switched to the thermal source and the heating stage of probe operation was recorded. At a given time the circuit was returned to the initial position and the cooling stage or the relaxation of the perturbed zone was recorded. Taking account of the requirement of sufficient smallness of the thermal perturbation, the time of source action, and its power were given by what would permit elimination of nonlinear phenomena in the medium under investigation and the influence of its boundaries on the relaxation of the thermal perturbation.

Graphical-Analytic Computation of the Relaxation Time Spectra. The thermal relaxation behavior of the objects of investigation was described by discrete (DRTS) and continuous (CRTS) relaxation time spectra of the probe signal $T_z(t)$. The spectra were obtained from curves of the evolution of a thermal perturbation with 0.580 J energy by a Tobol'skii–Bartenev graphoanalytic method [4, 5].

The evolution of an elementary thermal perturbation is described most completely by using a continuous relaxation time spectrum that is a dependence, constructed in logarithmic coordinates, of the relaxation time distribution function on the relaxation time

$$H(\tau_r) = -\frac{dT_z(t)}{d(\ln t)}\Big|_{t=\tau_r}. \tag{5}$$

Here $H(\tau_r)d(\ln t) = |dTz(t)|$ is the partial elementary change in the maximum of the thermal perturbation during its dissipation in the medium under investiation because of those structural elements that have thermal relaxation times in the interval between $\ln\tau_r$ and $\ln\tau_r + d\ln\tau_r$. A third approximation of the distribution function

$$H_3(\tau_r) = -\frac{dT_z(t)}{d(\ln t)} + \frac{3}{2}\frac{d^2T_z(t)}{d(\ln t)^2} - \frac{1}{2}\frac{d^3T_z(t)}{d(\ln t)^3}\Big|_{t=3\tau_r} \tag{6}$$

was computed for a clearer resolution of the maximums in the CRTS.

The results of a computation processed in the CRTS form are represented in Fig. 3. The set of DRTS data of the objects of investigation is presented in Table 1. The relative error in approximation of the probe signal asymptotic by a sum of exponentials and the spectrum computations did not exceed 1.6%.

Analysis of the spectra shows:

1. Independently of their microstructure and the properties in the experimental 0.1-20 sec relaxation time "window", three CRTS bands are resolved in both the media under investigation that correspond to three temperature field relaxation components: fast, relaxing with small 0.27 and 0.35 sec time; intermediate, with 148 and 1.75 sec relaxation time, and slow, for which the relaxation time is 11.91 and 16.22 sec. The bands of the different media are similar to each other in shape.

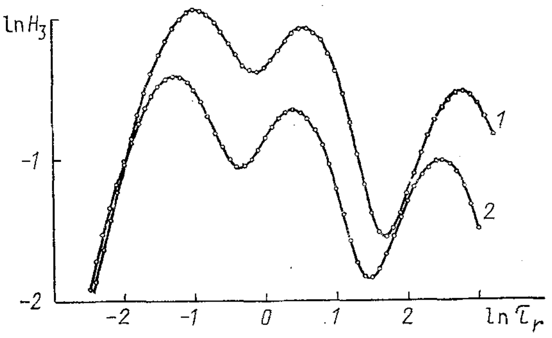

Fig. 3. Continuous relaxation time spectra of a thermal perturbation in PMS-400 (1) and glycerine (2) at 293 K in the time interval 0.1-20 sec. H_3, K/sec; τ_r, c.

TABLE 1. Thermophysical and Thermal Relaxation Characteristics of Viscous Fluids Obtained by the Nonstationary Method of a Constant-Power Thermal Probe at 20°C

Characteristics	Glycerine (η = 1.45 Pa·sec) (strongly associated fluid, H-bond network)	PMS-400 (η = 0.388 Pa·sec) (organosiloxane oligomer spiral-like struc.
Heat-conduction W/(m·K)	0,299	0,161
Thermal diffusivity, m^2/sec	$0{,}984\cdot 10^{-7}$	$0{,}869\cdot 10^{-7}$
Thermal relaxation time, sec		
τ_{r_1}	0,27	0,35
τ_{r_2}	1,48	1,75
τ_{r_3}	11,91	16,22
Mean thermal relaxation rate, m/sec		
$\langle v_1\rangle\cdot 10^3$	3,21	2,72
$\langle v_2\rangle\cdot 10^3$	1,20	1,08
$\langle v_3\rangle\cdot 10^3$	0,33	0,28
Dimensions (radii) of monothermal relaxation domains, m		
$r_1\cdot 10^3$	0,87	0,95
$r_2\cdot 10^3$	1,77	1,88
$r_3\cdot 10^3$	3,92	4,51

2. The PMS-400 characteristic relaxation time is higher than for glycerine, i.e., an increase in the heat conduction of the medium causes a diminution in the relaxation time of all three observable relaxation processes, where the relative dimunution in the relaxation time is not proportional to the times themselves: the increase in heat conduction exerts the greatest influence on the diminution of the large relaxation times. This means that the heat conduction exerts the greatest influence in the relaxation time "window" being observed because of mobility of the structural elements of large size.

3. The partial elementary contributions of the thermal relaxing elements of the less heat conductive medium PMS-400 are higher than for the more heat conductive medium, glycerine.

4. Utilization of two stages of the probe experiment permits computation of the effective dimensions of the monorelaxation structures surrounding the wire probe and the mean thermal relaxation rate therein. The dimensions of the first are computed as radial coordinates of the relaxing thermal perturbation front by formal application of the solution of the heat conduction differential equation for an instantaneous heat source in an unlimited medium with the allowable absolute error in measuring the temperature ±0.10°C taken into account

$$r = 2\sqrt{a\tau_r \ln\left(\frac{7{,}96W_L}{\lambda\tau_r}\right)}, \tag{7}$$

where W_L is the energy liberated by unit source length, J/m.

The mean thermal relaxation rate is found from the formula

$$\langle v\rangle = \frac{r}{\tau_r}. \tag{8}$$

The thermophysical and thermal relaxation characteristics of the objects of investigation are presented in Table 1.

Model representations of the structure of the media under investigation and the thermal perturbation relaxation mechanism are constructed on the basis of the data obtained.

An arbitrarily taken condensed medium can be considered as a system in which several (closed, mutually-penetrating, or combined) weakly interacting subsystems enter. For instance, network structures of H-bonds, different in size; compounds from several macromolecules, individual macromolecules, atomic groups, different in size, etc. Their definite values of the physical quantities describing the kinetic processes including the characteristic of the duration of a local thermal perturbation, its relaxation time, are characteristic for each of the mentioned subsystems. Discontinuous excitation of such a system by the Joulean heat of a heated thin wire produces a boundary domain of elevated mobility of nonselectively excited system components, which then relax into an open infinite system of the same components during mutual interaction because of the different radial energy transport mechanisms, the "relaxation channels". The different "relaxation channels" cause DRTS of the components in the boundary domain and radial energy fluxes in a definite sequence: 1) high-speed in the particles of small size and mass, and 2) slow over the whole array of particles, for example, over the spatial network of molecular bonds or its coarse fragments. The former are apparently elusive because of the superposition of activation times on the relaxation time (high-speed apparatus is required for their investigation). The latter appear in the domains of large relaxation times indicating activity of subsystems with large sizes and masses.

Therefore, the proposed approach to the study of heat conduction by a nonstationary thermal probe method permits obtaining additional information about the structure of a substance and the thermal process proceeding therein.

The question naturally occurs of whether media exist with a monorelaxation damping process of an elementary thermal perturbation whose kinetics is described by one relaxation time. The mechanism of such a model process is evidently due to the high homogeneity of the structure and the mobility of the thermal motion carriers which it is actually impossible to reproduce. Real, even quite homogeneous media are deeply micro- and macroheterogeneous, consequently, the process of local thermal perturbation dissipation therein is described by the sum of exponentials and the relaxation time spectrum that is associated with the properties of the components of the medium (mass, dimensions, mobility, etc.) their interaction (valence, H-bonds, van-der-Vaals), the heat transmission mechanism (heat conduction, covnection, radiation).

It seems that the method being developed further can be utilized to solve problems of clarification of the structure of mixtures and composite materials according to the known spectra of the temperature field relaxation time therein.

Notation. $p(t)$, p_0 are the running and equilibrium macroscopic parameters of the relaxing system; τ_r is the relaxation time, sec; t, t_i are the running time and the time of source action, sec; T, T_z is the temperature and height of the relaxing temperature field profile (probe signal), °C; W_L, q_L are the energy and power liberated by unit source length, J/m and W/m; $H_3(\tau_r)$ is the thermal relaxation time distribution function in a third approximation; λ, a is the heat conduction, W(m·K), and thermal diffusivity m^2/sec; $\langle v \rangle$ is the mean thermal relaxation rate, m/sec; η is the dynamic viscosity, Pa·sec; r, r_z is the radial coordinate and the probe radius, m; TKS is the temperature coefficient of resistance (TCR).

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