STUDY OF THE FORMATION OF THIXOTROPIC STRUCTURED SYSTEMS*

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An analogy is established between phase transitions of the second kind and processes of thixotropic structure-formation in dispersed media.

It is well known that the whole rheological curve of thixotropic systems may be arbitrarily divided into three parts, characterized by different degrees of breakdown of the structure [1]. The existence of three states, corresponding to different mechanisms of the breakdown of structured systems, suggests that the description of these states requires corresponding mathematical expressions.

It is quite clear that the one- and two-term equations generally employed to describe such systems can only be regarded as approximate. Investigations show that, on subjection to certain external actions (temperature, vibration, etc.), there is a sharp change in the structural and mechanical properties of dispersed systems [2-5].

The problem here under consideration is that of establishing the physical laws governing the formation of thixotropic structured systems, using methods of hydrodynamics, rheology, information theory, and the mathematic apparatus of Markov processes.

It is well known [5] that for the laminar flow of a viscous liquid mass diffusion does not play any substantial part, and the momentum of the frictional forces can only be transmitted by molecular interactions.

For a uniform laminar plane-parallel flow, the rate of flow v depends on the distance from the stationary wall y, i.e.,

$$v = v_x = f(y), \ v_y = v_z = 0,$$

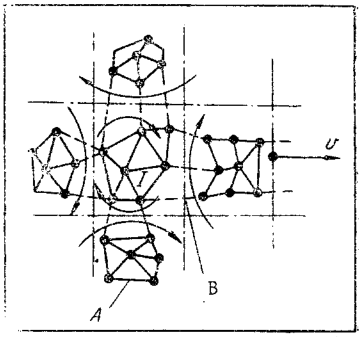

Fig. 1

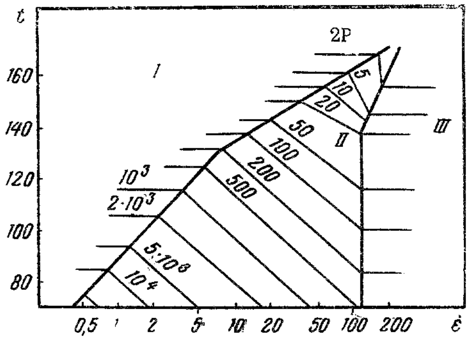

Fig. 2

Fig. 1. Schematic representation of the bonds between the aggregates: continuous curve A (unbroken bond); broken curve B (rupturing bond); the points represent particles of the dispersed phase.

Fig. 2. Temperature of BN-IV bitumen as a function of the velocity gradient, according to [7]; t, °C; ε, $\sec^{-1}$.

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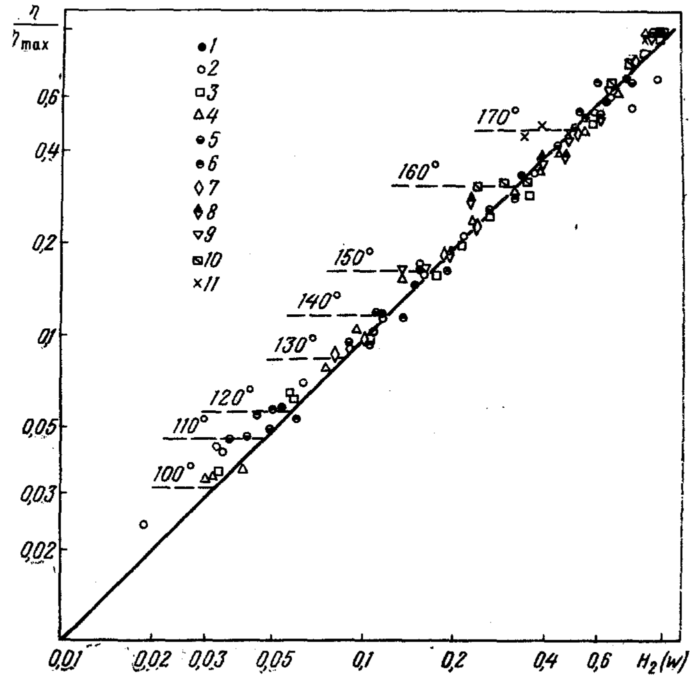

Fig. 3. Relative viscosity of the system at various temperatures, expressed as a function of its entropy: 1) at t = 70°C; 2) 80; 3) 90; 4) 100; 5) 110; 6) 120; 7) 130; 8) 140; 9) 150; 10) 160; 11) 170. Continuous line, calculated values based on Eq. (13); points and broken lines, experimental data [7].

while the particles of the medium rotate at an angular velocity ω equal to half the shear velocity, as well as executing translational motion.

For the laminar steady-state flow of a dispersed system, the frictional forces acting from the direction of the dispersion medium set the particles of the dispersed phase in translational and rotational motion, the components of the angular velocity (of the vortex) being expressed in the form

$$\omega_x = \omega_y = 0, \quad \omega_z = -\frac{1}{2}\frac{dv}{dy} = -\frac{1}{2}\dot{\varepsilon}, \ \text{sec}^{-1}, \tag{1}$$

where $\dot{\varepsilon}$ is the velocity gradient.

In the case of thixotropic structured systems, the elementary vortex may consist of a group of molecules or elements of the dispersed phase and the dispersion medium, rotating as a single aggregate. At a constant temperature and shear velocity these aggregates are (on the average) stable, i.e., their elements are united by unruptured bonds (Fig. 1). Furthermore, temporary bonds also exist between the aggregates; these are constantly being broken and reestablished; they serve to exchange the momenta of the viscous-frictional forces.

In order to elucidate the mechanism underlying the formation and rupture of thixotropic structures, we arbitrarily divide all the internal forces of interaction into three groups. The first group contains the forces which create stable bonds inside the aggregate; the second group is characterized by forces capable of creating "virtual" bonds (those alternately being broken and reformed); finally, the third group contains those forces which (under the conditions prevailing) play no part in bond formation.

In order to describe the mechanism underlying the formation and breakdown of the thixotropic structure, we express the number of virtual bonds N_v in the form of a sum of the number of actual bonds N_a existing at a specific instant of time under specified external conditions and the number N_{tb} of temporarily broken bonds still capable of being restored, i.e.

$$N_v = N_a + N_{tb} \tag{2}$$

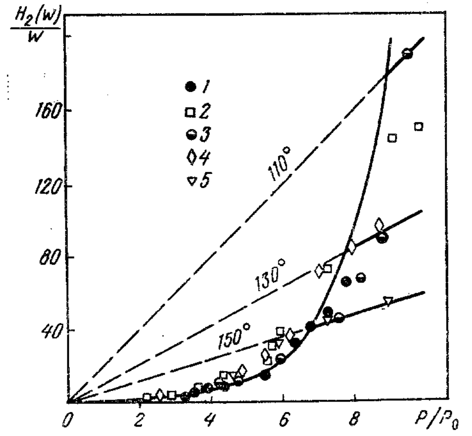

Fig. 4. The $H_2(w)/w = f(P/P_0)$ relationship: 1) at t = 70°C; 2) 90; 3) 110; 4) 130; 5) 150. Continuous lines, calculated values based on Eq. (17); points, experimental values [7].

It is reasonable to assume that, under steady-state conditions, at a specific instant of time, the breakdown-restoration process of the bonds in thixotropic structures, i.e., the transition of actual bonds into broken bonds and vice versa, is reproducible. Thus, on repeating the defining conditions, the numbers N_a, N_v, and N_{tb}, and also the number of transitions per unit time n_{tr}, should reproduce themselves. This may also be expected from the fact that the effective viscosity of the system depends solely on the temperature, t°, the velocity gradient, or the parameters of the vibratory actions (amplitude and frequency). Starting from this basis, it is convenient to take the Markov chain as a mathematical apparatus for describing the behavior of thixotropic structured systems.

The proposed structural model may be formulated in the following way: the thixotropic system is, in effect, a space of random singularities (virtual bonds) which may appear in one of two states: The first (1) makes the assertion "a bond exists", with a probability P_{11}, and the second (2), makes the assertion "there is no bond", with a probability P_{22}. The transition of the first state into the second, i.e., the breakdown of the bonds of the thixotropic structures, is effected with a probability P_{12}, the transition from the second state to the first (restoration of the bonds of the thixotropic structures) with a probability P_{21}. The following conditions have here to be satisfied [6]:

$$P_{11} + P_{12} = 1 \text{ and } P_{21} + P_{22} = 1. \tag{2'}$$

Clearly in the steady-state condition we have a dynamic equilibrium, i.e., the number of transitions n_{tr} from the first state to the second equals the number of transitions in the opposite direction, i.e.,

$$n_{tr} = N_a P_{12} = N_{tb} P_{21}. \tag{3}$$

Since $N_{tb} = N_v - N_a$, from Eq. (3) we obtain

$$N_a = N_b \frac{P_{21}}{P_{12} + P_{21}}. \tag{4}$$

For large values of N_v the proportion of virtual bonds w existing in the first state (for a specific steady-state mode of flow of the thixotropic system) is expressed in the form

$$w = \frac{N_a}{N_v} = \frac{P_{21}}{P_{12} + P_{21}}. \tag{5}$$

Allowing for (4) and (5), Eq. (3) takes the form

$$n_{tr} = N_v \frac{P_{21}}{P_{12} + P_{21}} P_{12} = N_v w P_{12}. \tag{6}$$

For constant external actions (temperature, vibration parameters), as the rate of rotation of the aggregate (ω) increases, the probability of the restoration of broken bonds P_{21} diminishes, since the molecular restoring forces have to overcome the rotational kinetic energy, which increases with increasing rate of rotation. The probability of the breakdown of the thixotropic structure P_{12} then increases also.

According to (2'), $P_{12} < 1$; hence

$$n_{\mathrm{tr}} = N_{\text{в}} \frac{P_{12}P_{21}}{P_{12}+P_{21}} < N_{\mathrm{V}} \frac{1P_{21}}{1+P_{21}} = N_{\mathrm{V}} f\left(\frac{1}{\dot{\varepsilon}}\right). \tag{7}$$

Thus with increasing velocity gradient $\dot{\varepsilon}$ the structure breaks down, and the number of actual bonds N_a declines. The probability of finding virtual bonds in the first state and the number of transitions from the first state into the second also diminish, and this leads to a reduction in the effective viscosity of the system. This justifies us in considering that the effective viscosity of the thixotropic structures is a function of the probability of the first state, i.e.,

$$w = N_a/N_{\mathrm{V}} = \varphi\left(\frac{1}{\dot{\varepsilon}}\right). \tag{8}$$

Let us establish a relationship between the effective viscosity of the system η and the probability of finding actual bonds of the thixotropic structure in the first state (w). It is already known from information theory that a system consisting of elements (singularities) capable of existing in one of two states is characterized by a degree of indeterminacy, namely, the information entropy $H_2(w)$, expressed in the form [6-9]:

$$H_2(w) = -[w \log_2 w + (1-w)\log_2(1-w)], \text{ bit}, \tag{9}$$

where (1—w) is the proportion of virtual bonds in the second state.

It follows from (7) that

$$(n_{\mathrm{tr}})_{\max_{t^\circ}} \sim \eta_{\max_{t^\circ}}. \tag{10}$$

Allowing for (7), (9), and (10) we may consider that for t° = const

$$\eta/\eta_{\max} = f_1(n_{\mathrm{tr}})_{t^\circ} = f_2\left(\frac{1}{\dot{\varepsilon}}\right)_{t^\circ} = f_3\left(\frac{\dot{\varepsilon}_0}{\dot{\varepsilon}}\right)_{t^\circ} = f_4(w) = \varphi[H_2(w)]t^\circ. \tag{11}$$

Taking account of (8), we accept that $w = \dot{\varepsilon}_0/\dot{\varepsilon}$, where $\dot{\varepsilon}_0$, $\sec^{-1}$ is an experimental coefficient depending on the temperature.

Thus

$$\eta/\eta_{\max} = \varphi\left[H_2\left(\frac{\dot{\varepsilon}_0}{\dot{\varepsilon}}\right)\right]_{t^\circ}. \tag{12}$$

It follows from Eq. (12) that a correlational relationship should exist between the effective viscosity of the system and the information entropy. If the results of our analysis of the experimental data are expressed in the form of a relationship $t^\circ = f(\dot{\varepsilon})$, the boundaries of the three parts of the rheological curve

$$[\eta_0 = f_1(t^\circ),\ \eta = f_2(t^\circ,\ \dot{\varepsilon}),\ \eta_{\min} = f_3(t^\circ)]$$

may be most readily appreciated. This is confirmed by Fig. 2, which are constructed with due allowance for the results of the investigations described in [7]. Analysis of these data shows that in the first region (I) the number of virtual bonds is a maximum and is constant for a specified temperature; this corresponds to the greatest effective viscosity of the system. In the second region (II) the number of these bonds declines with increasing velocity gradient or temperature, which leads to a reduction in the effective viscosity of the system. Finally, in the third region (III) the number of virtual bonds falls to a minimum, while the viscosity is equal to the minimum viscosity of the system at the temperature in question.

On the basis of the foregoing discussion, the entropy of the system should also diminish. An analysis of earlier arguments also leads to the conclusion that, if we arbitrarily assume that the regions under consideration constitute phase states of the dynamic system, the transition from one region into another may, by analogy, be considered as a phase transformation of the second kind [8]. This is explained by the fact that the information entropy of the system, which characterizes its effective viscosity, varies continuously. In addition to this, the first derivative of the information entropy with respect to the temperature or velocity gradient only changes discontinuously at the transition point (Fig. 2).

As a result of an analysis of the experimental data of [7] it was established that, on varying the temperature of BN-IV bitumen from 70 to 170°C, the temperature dependence of the experimental coefficient $\dot{\varepsilon}_0$ was linear. Hence in this case we have

$$\eta/\eta_{\max} = H_2(w), \text{ bit}. \tag{13}$$

Figure 3 shows the dependence of the relative viscosity on the entropy of the system, i.e. $\eta/\eta_{\max} = f[H_2(w)]$. This figure illustrates the satisfactory agreement between the experimental and calculated data. An analysis of the results of these investigations shows that for every temperature there is a specific value of the entropy at which the thixotropic system starts behaving as a Newtonian liquid with a minimum viscosity (broken lines in Fig. 3); with increasing ε_{t° or $H_2(w)_{t^\circ}$ the ratio $\eta/\eta_{\max}$ diminishes and tends toward a constant value, equal to $\eta_{\min}/\eta_{\max}$. The investigations also show that with increasing bitumen temperature the fall in $\eta_{\max}$ takes more rapidly than $\eta_{\min}$, leading to an increase in the ratio $\eta/\eta_{\max} = f \cdot [H_2(w)]$, as may be seen from Fig. 3.

Since the shear stress $P = \eta\dot{\varepsilon}$, we have

$$P = \eta_{\max}\frac{\eta}{\eta_{\max}}\dot{\varepsilon}_0\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} = \eta_{\max}\dot{\varepsilon}_0\frac{H_2(w)}{w}. \qquad (14)$$

Denoting

$$P_0 = \eta_{\max}\dot{\varepsilon}_0 = f(t^\circ), \qquad (15)$$

we obtain

$$P = P_0\frac{H_2(w)}{w}. \qquad (16)$$

Figure 4 illustrates the relationship

$$\frac{H_2(w)}{w} = f(P/P_0). \qquad (17)$$

This figure also shows satisfactory agreement between the experimental and calculated data.

Thus the use of the methods described in this paper is very effective when studying the behavior of thixotropic structured systems subject to various external actions.

NOTATION

v, rate of flow; y, distance from stationary wall; v_x, v_y, v_z, projections of flow velocity; f-(y), function of coordinate y; ω, angular frequency; ω_x, ω_y, ω_z, projections of angular frequency; $\dot{\varepsilon}$, velocity gradient; N_v, number of virtual bonds; N_a, number of actual bonds; N_{tb}, number of temporarily broken bonds; n_{tr}, number of transitions-per-unit-time; t°, temperature; P_{11}, probability of effecting the first state ("a bond exists"); P_{22}, probability of effecting the second state ("there is no bond"); P_{12}, probability of a transition from the first state into the second; P_{21}, probability of a transition from the second state into the first; w, proportion of virtual bonds in the first state; η, effective viscosity of the system; H_2, information entropy of the system; $\eta_{\max}$, maximum effective viscosity of the system; η_0, viscosity of an almost unbroken structure; $\eta_{\min}$, minimum viscosity of almost completely broken structure; P, shear stress.

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