

RHEOLOGY OF STRUCTURED LIQUIDS. FLOW REGIMES AND RHEOLOGICAL EQUATIONS

© 2025 V. N. Matveenko^a, * and E. A. Kirsanov^b

^a*Lomonosov Moscow State University, Moscow, Russia*

^b*State Social and Humanitarian University, Kolomna, Russia*

*e-mail: 13121946VNM@gmail.com

Received September 03, 2024

Revised October 17, 2024

Accepted October 17, 2024

Abstract. A system of rheological equations is presented, obtained on the basis of structural-kinetic representations, which describes viscous and elastic properties of structured liquids, namely concentrated suspensions, emulsions, micellar solutions, solutions and polymer melts. The structural model equations hold for equilibrium steady-state flow and for equilibrium oscillating flow. The equations are suitable for approximating rheological curves $\tau(\dot{\gamma})$, $N_1(\dot{\gamma})$, $G''(\omega)$, $G'(\omega)$, at individual intervals of shear rate or oscillation frequency. Each such interval corresponds to a certain state of the structure. As an example, the results of approximation of shear viscosity curves for polymer solution, micellar solution and emulsion are given.

Keywords: *rheological equations, structural rheological model, equilibrium stationary flow, equilibrium oscillating flow*

DOI: 10.31857/S00232912250105e8

INTRODUCTION

At present, there are no generally accepted views on the problem of non-Newtonian flow. Types of flow in suspensions, emulsions, micellar solutions, polymer solutions and melts are considered separately. Many local models and rheological equations have been proposed for each type of these structured systems [1–4].

Two main classes of rheological models can be distinguished, which consider fluid media either as homogeneous, homogeneous, or as heterogeneous, possessing some structure. In the first case, the methods of theoretical rheology based on continuum mechanics are used. Some physical justification of such rheological models is provided by mechanical models composed of springs, dampers, dry friction elements (Maxwell, Kelvin–Voigt, etc.).

In the second case, models describing aggregates of particles or associations of macromolecules that move in a viscous medium are used. The hydrodynamic approach is based on the laws of flow of particles and aggregates with viscous fluid and on the consideration of hydrodynamic forces that break the aggregates. The kinetic approach is based on kinetic equations describing the processes of formation and destruction of particle aggregates in shear flow.

The current state of the problem of non-Newtonian flow is described in various monographs, e.g., [5–7].

We have proposed a structural rheological model [8, 9] that allows us to describe the rheological behavior of various disperse and polymeric systems under steady-state and oscillatory flow.

The model is obtained by modifying and combining the well-known models of Casson [10] and Cross [11] (see Appendix 1).

In this paper, rheological equations derived from a unified structural approach will be fully summarized for both steady-state and oscillatory flow. These rheological equations are suitable for describing both viscous and elastic properties. As an example of using the rheological equations of the structural model, we have approximated the flow curves of some disperse systems.

STRUCTURED LIQUIDS

The structural rheological model describes shear flow of structured systems under equilibrium flow conditions. Such flow, the characteristics of which do not depend on time, is called steady-state or stationary flow. The structure of a system is the organization of particles by means of physical or chemical bonds into a unified whole. Concentrated suspensions, emulsions, micellar solutions, polymer solutions and melts, liquid crystals can be called structured liquids because they have some structure and shear flow.

In concentrated suspensions, particles combine into aggregates during collisions. In the process of shear flow, an individual aggregate moves for some time as a whole, i.e. as an independent flow unit. Aggregates are capable of disintegrating spontaneously, e.g. due to thermal motion, or forced, e.g. due to hydrodynamic breaking forces. Under certain conditions, particles form aggregates during collisions in shear flow (shear induced structure).

Aggregates and individual particles are elements of the structure. If a unit volume contains \tilde{N} particles, we denote the number of aggregated particles (included in all aggregates) as \tilde{N}_2 , and the number of individual particles as \tilde{N}_1 . In this way we can introduce an integral characteristic of a structured system, assuming that with increasing \tilde{N}_2 both the number of aggregates and their sizes increase.

In polymer melts and solutions, the role of particles is played by macromolecules, and the role of contacts is played by entanglements between macromolecules or direct interaction of chemical groups of neighboring macromolecules.

EQUATIONS OF THE STRUCTURAL RHEOLOGICAL MODEL

We can conditionally divide the full interval of shear velocities $\dot{\gamma}$ and the full interval of shear oscillation frequencies ω into four parts. In each separate interval there is a special structural state to which a certain flow regime corresponds. Measured rheological quantities: shear stress $\tau(\dot{\gamma})$, first normal stress difference $N_1(\dot{\gamma})$, loss modulus $G''(\omega)$, accumulation modulus $G'(\omega)$.

Here we briefly review the existing flow regimes, which are described in more detail in [9, 12–16]. Rheological curves $\tau(\dot{\gamma})$, $N_1(\dot{\gamma})$, $G''(\omega)$, $G'(\omega)$ can be conditionally divided into the following sections: low (II), high (III), very low (I), very high (IV) shear rates or oscillation frequencies.

Based on hydrodynamic considerations, a generalized flow equation [8, 9] was derived for the high shear rate interval (III) in the form:

$$\tau^{1/2} = \frac{\tau_c^{1/2} \dot{\gamma}^{1/2}}{\dot{\gamma}^{1/2} + \chi} + \eta_c^{1/2} \dot{\gamma}^{1/2}. \quad (1)$$

The shear viscosity can be written in the following form

$$\eta^{1/2} = \frac{\tau_c^{1/2}}{\dot{\gamma}^{1/2} + \chi} + \eta_c^{1/2}. \quad (2)$$

The physical meaning of the coefficients χ , $\tau_c^{1/2}$, $\eta_c^{1/2}$ is described in [8, 9], their values, in accordance with the hydrodynamic approach of Casson, have the following form:

$$\tau_c^{1/2} = \tau_{0c}^{1/2} \left[\left(\frac{1}{1 - k_2 \Phi} \right)^{A_2} - 1 \right],$$

$$\eta_c^{1/2} = \eta_0^{1/2} \cdot \left[\frac{1}{1 - k \Phi} \right]^{A_1}.$$

The coefficient χ reflects the compactness or friability of the aggregates and is zero if a continuous mesh of particles is formed.

Taking into account the presence of square roots in equation (2), let us write the equation for shear viscosity, according to the kinetic approach of Cross:

$$\eta^{1/2} = \eta_\infty^{1/2} + B \tilde{N}_2, \quad (3)$$

where the coefficient $\eta_\infty^{1/2}$ describes the viscosity of all individual single particles, B is some positive constant independent of the shear rate.

Using the kinetic approach, let us write down the kinetic equation of formation and destruction of particle aggregates:

$$\frac{d\tilde{N}_2}{dt} = \tilde{k}_2 \tilde{N} - \tilde{k}_0 \tilde{N}_2 - \tilde{k}_1 \dot{\gamma}^{1/2} \tilde{N}_2 + \tilde{k}_3 \dot{\gamma}^{1/2} \tilde{N}_1. \quad (4)$$

Equation (4) contains the following coefficients: \tilde{k}_2 – rate constant of aggregate formation at particle collisions; \tilde{k}_0 – rate constant of spontaneous destruction of aggregates, for example, as a result of thermal motion; \tilde{k}_1 – rate constant of aggregate destruction under the action of tensile hydrodynamic forces, \tilde{k}_3 – rate constant of formation of particle aggregates from single particles under the action of shear. This kinetic equation does not consider the interaction of aggregates of different sizes with each other, nor does it introduce a specific form of aggregate as a duplex as, for example, in [17]. The integral characteristics of the system, namely the total number of aggregated particles and the total number of particles in a unit volume, are used to describe the process of destruction/aggregate formation. A comparison of the proposed kinetic equation with other similar equations reviewed in [18] is given in Appendix 1.

At the interval of high shear rates (III), shear-induced contact failure occurs, which leads to a decrease in the number of aggregated particles \tilde{N}_2 under the condition $(\tilde{k}_1 > 0, \tilde{k}_3 = 0)$. The equation of state under equilibrium conditions $d\tilde{N}_2/dt = 0$ takes the form:

$$\frac{\tilde{N}_2}{\tilde{N}} = \frac{\tilde{k}_2}{\tilde{k}_1 \dot{\gamma}^{1/2} + \tilde{k}_0}. \quad (5)$$

Substituting (5) into (3) we obtain a rheological equation similar to the generalized flow equation in the form (2):

$$\eta^{1/2} = \frac{B \tilde{N} \tilde{k}_2 / \tilde{k}_1}{\dot{\gamma}^{1/2} + \tilde{k}_0 / \tilde{k}_1} + \eta_\infty^{1/2}. \quad (6)$$

Thus, the coefficients of the generalized flow equation (1) or (2) can be expressed through the rate constants of the kinetic equation (4): $\tau_c^{1/2} = B\tilde{N}k_2 / k_1$, $\chi = k_0 / k_1$, $\eta_\infty^{1/2} = \eta_c^{1/2}$.

At interval (III), the shear viscosity decreases naturally with increasing shear rate, with the value of the structural viscosity $\tau_c^{1/2} / \chi$ or the value of the aggregation coefficient $\tau_c^{1/2}$ being much larger than the value of the coefficient $\eta_c^{1/2}$.

If shear results in strong contacts between particles under the condition ($k_1 > 0$, $k_3 > 0$), it is necessary to use equations (3) and (4) containing all four positive coefficients. Then one can obtain [9] an approximate expression for shear viscosity under the condition

$$\dot{\gamma} > \left(\frac{\tilde{k}_0}{\tilde{k}_3 + \tilde{k}_1} \right)^2 :$$

$$\eta^{1/2} \approx \left(\eta_\infty^{1/2} + B\tilde{N} \frac{\tilde{k}_3}{\tilde{k}_3 + \tilde{k}_1} \right) - B\tilde{N} \frac{(\tilde{k}_0 - \tilde{k}_2)}{(\tilde{k}_3 + \tilde{k}_1)\dot{\gamma}^{1/2}}. \quad (7)$$

Hence the rheological equation of the form

$$\tau^{1/2} = \eta_{cv}^{1/2} \dot{\gamma}^{1/2} - \tau_{cv}^{1/2}, \quad (8)$$

whose coefficients are equal to:

$$\eta_{cv}^{1/2} = \eta_\infty^{1/2} + B\tilde{N} \frac{\tilde{k}_3}{\tilde{k}_3 + \tilde{k}_1};$$

$$\tau_{cv}^{1/2} = B\tilde{N} \frac{(\tilde{k}_0 - \tilde{k}_2)}{(\tilde{k}_3 + \tilde{k}_1)}.$$

The coefficient $\tau_{cv}^{1/2}$ is positive if $\tilde{k}_0 > \tilde{k}_2$, and negative if $\tilde{k}_0 < \tilde{k}_2$. Therefore, three types of rheological behavior are possible in the interval (II). In the first case, the viscosity increases with increasing shear rate (shear solidification phenomenon). In the second case, the viscosity decreases with increasing shear rate, with the coefficient $\tau_{cv}^{1/2}$ being less than or comparable in magnitude to the coefficient $\eta_{cv}^{1/2}$. In the third case, the coefficient $\tau_{cv}^{1/2}$ is close to zero under the condition $\tilde{k}_0 \approx \tilde{k}_2$, then the rheological behavior is similar to "Newtonian" flow with an almost constant value of shear viscosity η_{cv} .

In the interval (IV) of very high shear rates, a significant decrease in shear stress τ is observed compared to the values calculated from equation (1). The value of τ decreases with increasing $\dot{\gamma}$ or remains constant over a large range of shear rates. This phenomenon is referred to as flow "stall"; it is possibly related to shear delamination of the sample or to a change in the flow velocity profile. In the interval (I) of very low shear rates, flow with constant shear viscosity is observed, possibly because the shear magnitude is not large enough to break existing particle aggregates or to create new strong contacts. Thus, the structure of the system remains constant. This "Newtonian" flow regime is usually observed at low velocities.

Separation of flow curves into separate intervals with different flow regimes can be done using root

coordinates $(\tau^{1/2} - \dot{\gamma}^{1/2})$, where rectilinear dependencies are clearly visible $(\tau^{1/2} \sim \dot{\gamma}^{1/2})$. Each section has a separate flow regime with its own values of the coefficients of the rheological equation. Therefore, it is impossible to describe the entire range of measurements with one rheological equation.

Note that individual particles can be solids, droplets, micelles, macromolecules. The role of aggregates of particles can be played by groupings of micelles, associations of macromolecules linked by entanglements.

The reasoning presented above can be applied to explain the elastic properties of matter under equilibrium shear flow. The elastic behavior at steady-state flow is described by the first normal stress difference $N_1 = \tau_{11} - \tau_{22}$. Let us introduce an expression for shear elasticity of the form $\eta_{ST} = N_1 / \dot{\gamma}$. Let us write the equation for shear elasticity in the form:

$$\eta_{ST}^{1/2} = n_\infty + B\tilde{N}_2. \quad (9)$$

If there are no aggregates, the shear elasticity is provided only by the elasticity of individual particles, i.e. it is related to the coefficient n_∞ .

Let us assume that the number of particles forming "elastic" aggregates is equal to \tilde{N}_2 . Let us write the kinetic equation of destruction and formation of "elastic" aggregates in the form similar to (4):

$$\frac{d\tilde{N}_2}{dt} = k_2\tilde{N} - k_0\tilde{N}_2 - k_1\dot{\gamma}^{1/2}\tilde{N}_2 + k_3\dot{\gamma}^{1/2}\tilde{N}_1. \quad (10)$$

The meaning of the rate constants remains the same, but their magnitude changes. Similar previous considerations lead to the rheological equation for the interval (III) of high velocities:

$$N_1^{1/2} = \frac{n_{ST}}{\dot{\gamma}^{1/2} + \chi_{ST}} \quad \dot{\gamma}^{1/2} + n_\infty \dot{\gamma}^{1/2}, \quad (11)$$

where $\chi_{ST} = k_0 / k_1$; $n_{ST} = B\tilde{N} k_2 / k_1$.

For the interval (II) of low shear rates, we obtain the equation:

$$N_1^{1/2} = n_0 \dot{\gamma}^{1/2} - \Delta N_1^{1/2}, \quad (12)$$

where

$$n_0 = n_\infty + B\tilde{N} \frac{k_3}{k_3 + k_1}; \quad \Delta N_1^{1/2} = B\tilde{N} \frac{(k_0 - k_2)}{(k_3 + k_1)}.$$

The coefficient $\Delta N_1^{1/2}$ is positive if $k_0 > k_2$, and negative if $k_0 < k_2$.

At the interval of very high shear rates, no anomalies similar to "stall" were observed on the curves $N_1(\dot{\gamma})$, considered by us [16].

In the interval (I) of very low shear rates, a power-law dependence of the following form is observed

$$N_1 \approx n_{00} \dot{\gamma}^n, \quad (13)$$

where $n \approx 2$. This kind of dependence does not follow from the mechanism of formation/destruction of particle aggregates. The structure of the system should probably be considered unchanged over the interval (I), and the elastic response should be attributed to the reaction of the entire system of bound particles. It is important to note that the boundaries of the flow regimes found for the dependence $\tau(\dot{\gamma})$ and for the dependence $N_1(\dot{\gamma})$ in the same structured fluid do not coincide completely.

We consider oscillating shear flow [9] as a type of shear flow whose magnitude and direction change according to a harmonic law. The amplitude of the shear velocity ($\gamma_0 \omega$) is some analog of the shear velocity $\dot{\gamma}$: $\dot{\gamma} = k_{\text{DIS}} \omega$, where k_{DIS} is the displacement factor. The model describing the dynamic moduli $G''(\omega)$ and $G'(\omega)$, is completely analogous to the model developed for steady-state flow [9]. The rheological equation describing viscous properties for the high frequency interval (III) has the following form:

$$G'^{1/2} = \frac{g' \omega^{1/2}}{\omega^{1/2} + \chi'} + \eta'_\infty^{1/2} \omega^{1/2}. \quad (14)$$

The aggregation coefficient g' indicates the degree of particle aggregation or the strength of macromolecule entanglements, the compactness coefficient χ' indicates the tendency to form loose aggregates of particles or associates of macromolecules, the ultimate viscosity coefficient $\eta'_\infty^{1/2}$ describes the viscosity resulting from the streamline of individual particles or macromolecules. The values of the coefficients present in equation (14) are: $\chi' = k'_0 / k'_1$; $g' = B \tilde{N} k'_2 / k'_1$.

The rheological equation for the low frequency interval (II) is as follows:

$$G''^{1/2} = g'_0 \omega^{1/2} - \Delta G'^{1/2}, \quad (15)$$

where $g'_0 = \eta'_\infty^{1/2} + B \tilde{N} k'_3 / (k'_3 + k'_1)$;
 $\Delta G'^{1/2} = B \tilde{N} (k'_0 - k'_2) / (k'_3 + k'_1)$.

The coefficient $\Delta G'^{1/2}$ is positive if $k'_0 > k'_2$, and negative if $k'_0 < k'_2$. If $\tilde{k}_0 \approx \tilde{k}_2$, the rheological behavior is similar to "Newtonian" with a nearly constant value of dynamic viscosity η' .

Quite similarly, we obtain the equations describing the elastic properties:

$$G'^{1/2} = \frac{g'' \omega^{1/2}}{\omega^{1/2} + \chi''} + \eta''_\infty^{1/2} \omega^{1/2}, \quad (16)$$

where $\chi'' = k''_0 / k''_1$; $g'' = B \tilde{N} k''_2 / k''_1$ and

$$G''^{1/2} = g''_0 \omega^{1/2} - \Delta G'^{1/2}, \quad (17)$$

where $g''_0 = \eta''_\infty^{1/2} + B \tilde{N} k''_3 / (k''_3 + k''_1)$;
 $\Delta G'^{1/2} = B \tilde{N} (k''_0 - k''_2) / (k''_3 + k''_1)$.

The coefficient $\Delta G'^{1/2}$ is positive if $k''_0 > k''_2$, and negative if $k''_0 < k''_2$. The physical meaning of these rate constants is the same as described earlier in the case of steady-state flow.

At very low frequencies on the interval (I) there is a power-law dependence

$$G'^{1/2} = g''_{00} \omega^{n/2}, \quad (18)$$

where $n \approx 2$. It can be assumed that at this frequency interval the structure of the system does not change with increasing frequency. Then the frequency dependence (18) is due to the response of the entire elastic entanglement mesh to the action of oscillating shear flow.

At the interval (IV), an anomalous decrease of the dynamical moduli G'' and G' , is observed, and their value can even decrease with increasing frequency. We will call this phenomenon the "stall" of the oscillating flow or the "stall" of the moduli G'' and G' .

Examples of analyzing the frequency dependences of the loss modulus G'' and accumulation modulus G' from the viewpoint of the structural model are given in [13–15]. Here, some rheological curves obtained for steady-state flow of structured fluids of different nature will be shown and interpreted.

EXAMPLES OF STEADY-STATE FLOW REGIMES. VISCOSITY–STRUCTURE RELATIONSHIP

In [19], the viscosity curve of polymer aqueous solution of polyethylene oxide (PEO) is given, which has a section (II) of shear solidification at low shear rates ($\dot{\gamma} \leq 0.1 \text{ s}^{-1}$). The experimental data are shown in Table 2 (Appendix 2); the viscosity curve with approximation results is shown in Fig. 1. Shear solidification at low velocities was attempted by the authors [19] to be explained by a special intermolecular interaction. However, the uncharged, flexible and hydrophilic PEO chains are hardly capable of strong intermolecular interaction, although the formation of dimers is quite possible.

Plot (II) in Fig. 1 corresponds to the equilibrium flow, during which the processes of entanglement formation and destruction due to shear occur, but the formation process prevails ($\tilde{k}_1 > 0$, $\tilde{k}_3 > 0$, $\tilde{k}_0 > \tilde{k}_2$). Plot (III) corresponds to equilibrium flow, in which shear entanglement formation does not occur ($\tilde{k}_1 > 0$, $\tilde{k}_3 = 0$) and the process of entanglement destruction predominates.

At plot (IV), there is an abnormal decrease in viscosity, which gradually approaches the dependence $\eta \sim 1 / \dot{\gamma}$ (dashed line in Fig. 1). Such rheological behavior is called flow stall.

Fig. 2 shows the results of approximation by equations (1) and (8) in root coordinate plots.

According to the structural rheological model [9], the coefficient $\eta_c^{1/2}$ is the root of the minimum limiting viscosity, i.e., the viscosity of the non-aggregated system. This viscosity arises from the movement of individual macromolecules in aqueous solution and is quite small compared to the zero viscosity of a polymer solution with entanglements, which is described by the coefficient $\eta^{1/2}(0)$.

The coefficients of equation (8) are equal:

$$\eta_{cv}^{1/2} = \eta_\infty^{1/2} + B\tilde{N}\tilde{k}_3 / (\tilde{k}_3 + \tilde{k}_1), \quad (19)$$

$$\tau_{cv}^{1/2} = B\tilde{N}(\tilde{k}_0 - \tilde{k}_2) / (\tilde{k}_3 + \tilde{k}_1). \quad (20)$$

It follows from equation (19) that $\eta_{cv}^{1/2} > \eta_\infty^{1/2}$; the coefficient $\eta_{cv}^{1/2}$ can be comparable in magnitude to the coefficient $\eta^{1/2}(0)$. It follows from equation (20) that the value of $\tau_{cv}^{1/2}$ can be negative, positive and close to zero depending on the relationship between the rate constants \tilde{k}_0 and \tilde{k}_2 . These conclusions are confirmed by comparing the magnitudes of the coefficients in Table 1.

In [20], the rheological behavior of aqueous micellar solutions was considered. The cationic compound cetyltrimethylammonium bromide (CTAB) was used as a surface active agent, and the organic salt sodium salicylate (NaSal) was used as an additive. In such systems, cylindrical or worm-like micelles are formed. Shear solidification in micellar solutions is attributed to the formation of shear induced structure (SIS).

The experimental data are shown in Table 3 (Appendix 2), the viscosity curve with approximation results is shown in Fig. 3.

The graph (Fig. 3) shows three sections of the viscosity curve with three different flow regimes. At very low shear rates, the Newtonian flow regime is observed (plot I).

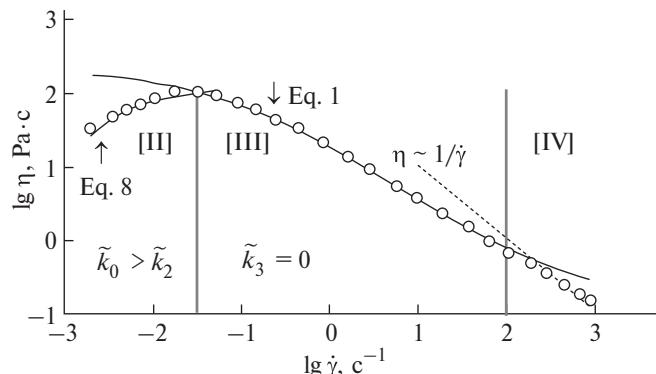


Fig. 1. Dependence of viscosity on shear rate in double logarithmic coordinates for aqueous solution of polyethylene oxide with a mass concentration of 2.5 %. Experimental data from [19].

Since the viscosity does not change, it can be assumed that the structure of the system also remains constant. Since the Newtonian viscosity η_N is less than the maximum viscosity but greater than the minimum viscosity present in the plot, it can be assumed that the constant structure at very low velocities contains both individual micelles and small micelle associations.

Fig. 4 shows the results of approximation by equations (1) and (8) in root coordinate plots.

The coefficients of the rheological equations are presented in Table 2. It can be seen that the value of $\eta_c^{1/2}$ is much smaller than $\eta^{1/2}(0)$; the value of $\eta^{1/2}(0)$ is comparable to the value of $\eta_{cv}^{1/2}$. The value of $\tau_{cv}^{1/2}$ is positive, which indicates the predominance of the process of formation over the process of destruction of contacts between micelles.

Fig. 5 shows the viscosity curve for the emulsion of Newtonian oil in aqueous solution given in the book [7]. The experimental data are presented in Table 4 (Appendix 2). The oil is a mixture of: tritolyl phosphate

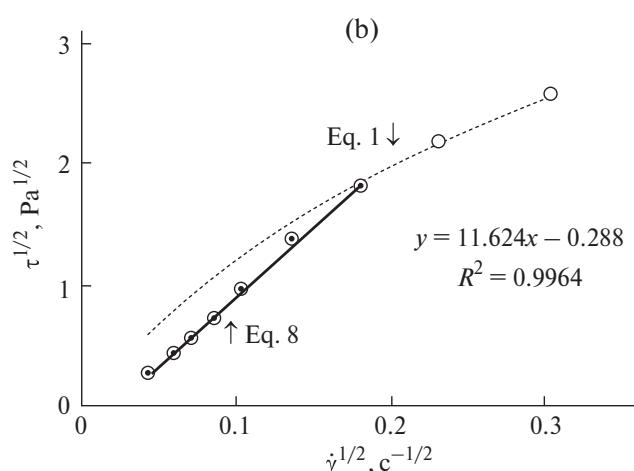
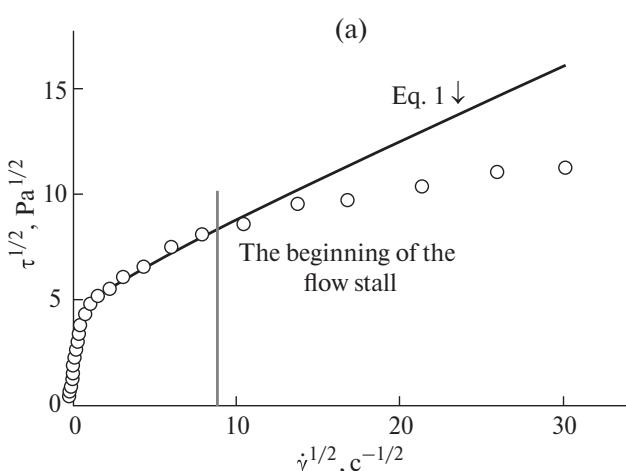


Fig. 2. Dependence of shear stress on shear rate in root coordinates for aqueous solution of polyethylene oxide with a mass concentration of 2.5%. a – on the full range of shear rates; b – on the range of low shear rates.

(24 wt%) and dioctyl phthalate (76 wt%). The aqueous solution has a viscosity of 0.00265 Pa·s and contains 20 wt. % of anionic surfactant. The ratio of the viscosity of the oil to the viscosity of the aqueous solution is 24.7.

Fig. 6 shows the results of approximation by equations (1) and (8) in root coordinate plots.

In Fig. 5. there are two flow regimes. Regime (II) corresponds to equilibrium flow, during which the processes of formation and destruction of contacts between drops due to shear occur, but the destruction process prevails ($\tilde{k}_1 > 0$, $\tilde{k}_3 > 0$, $\tilde{k}_0 < \tilde{k}_2$). Therefore, the value of $\tau_{cv}^{1/2}$ is less than zero. Plot (III) corresponds to the equilibrium flow, in which no contacts are formed due to shear, but only the destruction of contacts takes place ($\tilde{k}_1 > 0$, $\tilde{k}_3 = 0$).

The coefficients of the rheological equations are presented in Table 2. The value of $\eta_c^{1/2}$ is much smaller than $\eta^{1/2}(0)$; the value of $\eta^{1/2}(0)$ is comparable to the value of $\eta_{cv}^{1/2}$. The value of $\tau_{cv}^{1/2}$ is negative, which indicates the predominance of the process of destruction over the process of formation of contacts between the droplets.

The considered examples show that “experimental windows” demonstrate different flow regimes in the study of different structured fluids. Difficulties in data

interpretation can arise if the flow regimes are only partially represented in the plots. Therefore, it is important to perform measurements over as large an interval of shear rates as possible, as well as to choose a measurement time sufficient to reach the equilibrium flow state at each measurement.

It should be added that there is another structural approach to describe the viscosity of a structured fluid. The rheological model [21] describes the dependence of shear viscosity on the volume concentration $\eta(\Phi)$, with each viscosity curve obtained for a constant shear rate [22]. In the model proposed by us, the coefficients (parameters) of the rheological equation of the form $\eta(\dot{\gamma})$ depend on the concentration of the dispersed phase. The generalized flow equation is able to approximate the flow curves, which were previously described by the Herschel–Bulkley or Cross equations, for a variety of disperse systems, including polymer composites [23].

CONCLUSION

This paper presents the equations of the structural rheological model, which describe equilibrium steady-state and equilibrium oscillatory flow from a unified point of view. These equations are necessary and sufficient for analyzing rheological curves $\tau(\dot{\gamma})$, $N_1(\dot{\gamma})$, $G''(\omega)$, $G'(\omega)$. The equations provide an alternative to equations using the power law (Herschel–Bulkley, etc.) and equations based on mechanical models (spring, damper, dry friction element).

Four flow regimes are distinguished on the full interval of shear rates (or oscillation frequency). In the interval (I) the structure of the system is practically constant, which corresponds to the “Newtonian” behavior. In the interval (II) there is simultaneous formation and destruction of contacts between particles (entanglements between macromolecules), which is described by a rheological equation with two coefficients. If the formation process prevails, the shear viscosity η increases; if the destruction process prevails, the viscosity η decreases with increasing shear rate $\dot{\gamma}$. The same applies to shear elasticity η_{ST} ($= N_1 / \dot{\gamma}$), dynamic viscosity η' and dynamic elasticity η'' . In the interval (III), only shear-induced contact failure

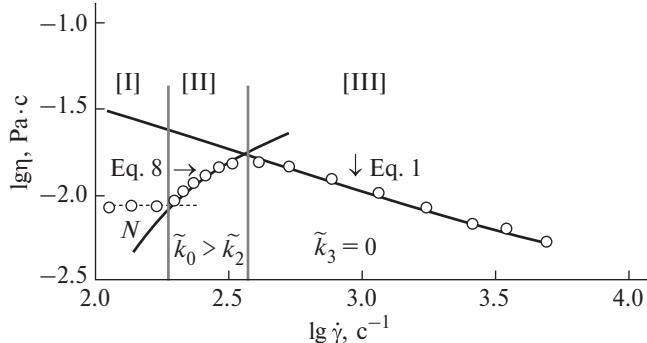


Fig. 3. Dependence of viscosity on shear rate in double logarithmic coordinates for CTAB/NaSal micellar solution with surfactant concentration $C_D(M) = 0.08$. Experimental data from [20].

Table 1. Rheological characteristics of polymer solution, micellar solution, and emulsion: coefficients of rheological equations 1 and 8 (SI system)

Structured fluid	$\tau_c^{1/2}$	$\eta_c^{1/2}$	χ	$\eta^{1/2}(0)$	$\eta_{cv}^{1/2}$	$\tau_{cv}^{1/2}$
Polyethylene oxide solution	5.29	0.364	0.362	14.98	11.62	0.288
CTAB/NaSal micellar solution	2.36	0.042	7.32	0.364	0.232	1.924
Oil emulsion in aqueous solution	5.35	0.306	0.676	8.211	2.30	-1.04

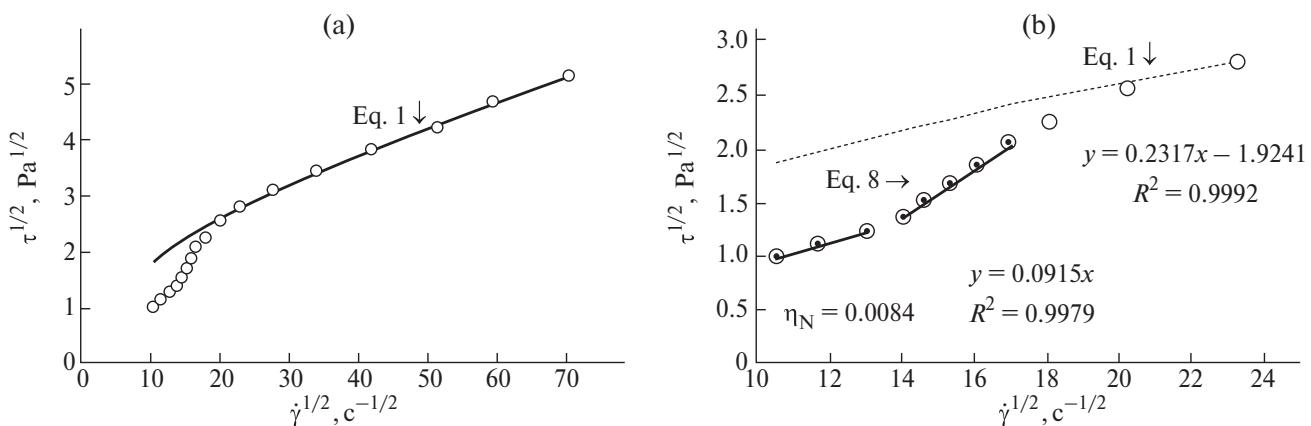


Fig. 4. Dependence of shear stress on shear rate in root coordinates for CTAB/NaSal micellar solution with surfactant concentration $C_D(M) = 0.08$. a – at full shear rate interval; b – at low shear rate interval.

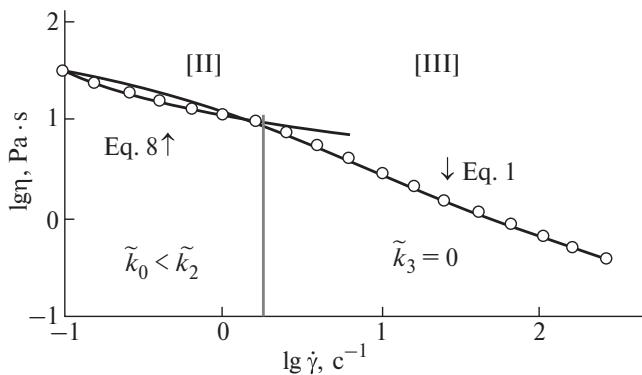


Fig. 5. Dependence of viscosity on shear rate in double logarithmic coordinates for aqueous oil emulsion with volume concentration $\varphi = 0.8$. Experimental data from [7].

(entanglement rupture) occurs, which is described by a rheological equation with three coefficients. As the shear rate (or frequency) increases, the rheological quantities η , η_{ST} , η' , η'' decrease.

At interval (IV), there is an anomalous decrease in rheological values τ , G'' and G' , which is possibly due to shear stratification and change in flow velocity profile.

Examples of the use of the equations at selected shear rate intervals in describing the flow curves of some disperse systems (polymer solution, micellar solution, emulsion) are given.

FUNDING

The research was carried out under the budgetary funding of Lomonosov Moscow State University, Faculty of Chemistry, CiT&S No. 121031300084-1.

ETHICS DECLARATION

There are no human or animal studies in this paper.

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

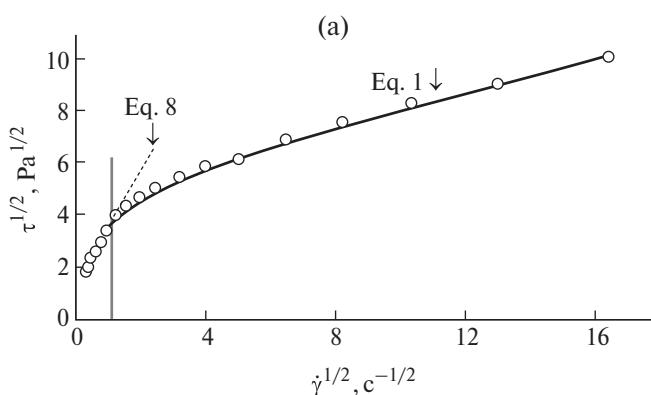


Fig. 6. Dependence of shear stress on shear rate in root coordinates for aqueous oil emulsion with volume concentration $\varphi = 0.8$: a – at the full range of shear rates; b – at the interval of low shear rates.

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APPENDIX 1

Casson rheological model [10]. The model considers fluid systems possessing a limiting dynamic shear stress. The plastic behavior of such systems is well described by the equation $\tau^{1/2} = \tau_c^{1/2} + \eta_c^{1/2} \dot{\gamma}^{1/2}$, where the Casson coefficients $\tau_c^{1/2}$ and $\eta_c^{1/2}$ correspond to the limiting dynamic shear stress and viscosity coefficient at infinitely large shear rate. Experimental points in the root coordinates $\tau^{1/2} - \dot{\gamma}^{1/2}$ in this case are located on the same straight line, which is well confirmed by experimental data for dye dispersions, blood and many structured fluids.

Casson derived this equation based on the microrheological theory, in which aggregates-chains of two or more particles arise under the action of some cohesive forces F_s . Since hydrodynamic calculations to describe the chain breakage and energy dissipation during chain flow proved to be too complicated, Casson replaced chains with long model cylinders, assuming that their hydrodynamic behavior in simple shear flow is identical to that of rigid chains of particles. When flowing around opposite parts of the cylinder, a hydrodynamic force F_h along the axis arises, which at a certain orientation of the cylinder contributes to its rupture. The cylinder breaks into two parts if the tensile hydrodynamic force F_h exceeds the cohesive force F_s , which prevents the cylinder from breaking. Long cylinders rupture in shear flow, and short cylinders spontaneously unite upon collision into longer cylinders. This replacement of chains by cylinders made it possible to use Kuhn's model to calculate the hydrodynamic rupturing force and the magnitude of energy dissipation.

Omitting Casson's calculations given by us in published monographs [8, 9], let us write down the expression for the viscosity of the "diluted" suspension of model cylinders:

$$\eta = \eta_0 (1 - \Phi) + \eta_0 \bar{\alpha} \Phi \left(\alpha + \beta / (\eta_0 \dot{\gamma})^{1/2} \right),$$

where η_0 – is the viscosity of the dispersion (liquid) medium, the coefficient $\bar{\alpha} \approx 0.7$ assuming random initial orientation of model cylinders. The parameter α can be interpreted as an extremely low axial ratio at infinite shear rate. The root of the shear rate appears in the equation. The mean-field method (approximation of Brinkman and Roscoe, 1952) was used to account for the hydrodynamic interaction of the particles. As a result of the calculation, the root of the viscosity value appears in the equation:

$$\eta^{1/2} = \frac{\tau_c^{1/2}}{\dot{\gamma}^{1/2}} + \eta_c^{1/2}.$$

As a result of modification of the Casson model, we obtained a generalized flow equation

$$\tau^{1/2} = \frac{\tau_c^{1/2}}{\dot{\gamma}^{1/2} + \chi} \dot{\gamma}^{1/2} + \eta_c^{1/2} \dot{\gamma}^{1/2}, \text{ and the calculated values}$$

of coefficients slightly differ from those obtained in the Casson model.

Cross rheological model [11]. The processes of destruction and recovery of aggregates during shear flow can be described using kinetic equations. This approach was used by Cross, who replaced the concentration of a substance used in chemical kinetics by the number of bonds between particles (L). Cross assumed that a suspension consists of chains of particles with an average number L of bonds between particles, introduced a rate constant for bond formation (\tilde{k}_2), a rate constant for spontaneous bond breaking (\tilde{k}_0) and a rate constant for bond breaking due to shear flow ($\tilde{k}_1 \dot{\gamma}^n$). The rate of change of the number of bonds between particles is assumed to $\frac{dL}{dt} = \tilde{k}_2 N - (\tilde{k}_0 + \tilde{k}_1 \dot{\gamma}^n) L$, where

N is the total number of initial particles in a unit volume, L is the number of bonds between particles.

Cross used an empirical expression from polymer theory: $\eta = \eta_\infty + BL$, where η_∞ is the viscosity of the system at $\dot{\gamma} \rightarrow \infty$, when all bonds are broken, B is some coefficient. Omitting here Cross's calculations, let us write down the final equation of Cross in the form:

$$\frac{\eta - \eta_\infty}{\eta(0) - \eta_\infty} = \frac{1}{1 + (\tilde{k}_1 / \tilde{k}_0) \dot{\gamma}^n}.$$

Commenting on the derivation of the Cross equation, Hunter noted that there is no theoretical justification for the choice of the constant as $\tilde{k}_1 \dot{\gamma}^n$. The Cross equation is widely used to describe dispersed and polymeric systems.

As a result of the modification of the Cross model, we obtained an equation similar to the generalized flow equation, where the coefficients are expressed through the rate constants of fracture/aggregate formation, the number of bonds is replaced by the number of aggregated particles, and the viscosity root and shear rate root are introduced by analogy with the Casson model.

Coagulation and aggregation of particles. Let us consider the relationship between the equations of the structural model and the classical theory of coagulation. Let us assume that there is no spontaneous detachment of particles from aggregates ($\tilde{k}_0 = 0$) and no flow ($\tilde{k}_1 \dot{\gamma}^{1/2} = 0$). Then the process of particle aggregation formally occurs up to the formation of a continuous mesh

$$(N_2 = N): \frac{dN_2}{dt} = \tilde{k}_2 N; \int_0^N dN_2 = \int_0^{t_g} \tilde{k}_2 N dt; N = \tilde{k}_2 N t_g;$$

i.e., the time of formation of a continuous mesh is equal to $t_g = 1 / \tilde{k}_2$.

In coagulation theory, the initial equation contains some number of "conditional" particles v , which represent both individual particles and aggregates of particles: $\frac{dv}{dt} = -k v^2$. The solution has the form: $v(t) = \frac{v_0}{1 + kv_0 t}$. The formation of a continuous mesh of particles is formally equivalent to the formation of one large "particle" i.e.

$\frac{v_0}{1 + k v_0 t_g} = 1$. Hence, the time of “complete” coagulation is formally equal to $t_g = \frac{1}{k} (1 - \frac{1}{v_0}) \approx \frac{1}{k}$. Thus, there is no direct contradiction between the description of the aggregation process (in the Cross equation) and the description of the coagulation process, although both kinetic equations actually no longer work when large aggregates of particles appear.

Kinetic equations for aggregate formation/destruction processes

We have proposed the expression

$$\frac{d\tilde{N}_2}{dt} = \tilde{k}_2 \tilde{N} - \tilde{k}_0 \tilde{N}_2 - \tilde{k}_1 \dot{\gamma}^{1/2} \tilde{N}_2 + \tilde{k}_3 \dot{\gamma}^{1/2} \tilde{N}_1.$$

In [17], a kinetic equation is presented, which we present here in the form necessary for comparison, replacing the volume concentration by the number of \tilde{N}_1 singlet or \tilde{N}_2 duplets in a unit volume and substituting indices for the rate constants:

$$\frac{d\tilde{N}_1}{dt} = -\tilde{k}_2 \tilde{N}_1^2 + \tilde{k}_0 \tilde{N}_2 + \tilde{k}_1 \dot{\gamma} \tilde{N}_2 \text{ or}$$

$$\frac{d\tilde{N}_2}{dt} = \tilde{k}_2 \tilde{N}_1^2 - \tilde{k}_0 \tilde{N}_2 - \tilde{k}_1 \dot{\gamma} \tilde{N}_2.$$

The difference is the lack of square root, the change of the system to singlet and duplets, and the use of classical coagulation theory for the particle aggregation process.

In [18], a kinetic equation for thixotropic dispersion of the form $d\Lambda / dt = -k_1 \Lambda \dot{\gamma}^\beta + k_3 (1 - \Lambda) \dot{\gamma}^{1/2} + k_0 (1 - \Lambda)$, where Λ is a structural parameter that describes the change in internal structure with changing shear rate, is used. If we write the structural parameter as the relative number of aggregated particles ($\Lambda = \tilde{N}_2 / \tilde{N}$), we obtain an equation of the form $d\tilde{N}_2 / dt = k_0 \tilde{N} - k_0 \tilde{N}_2 - k_1 \dot{\gamma}^\beta \tilde{N}_2 + k_3 \dot{\gamma}^{1/2} \tilde{N}_1$.

The difference is that the rate constants $\tilde{k}_0 = \tilde{k}_2$ are equated and the degree exponent β has an arbitrary value. It is important to note that the terms of the equations describing the formation of aggregates under the action of shear completely coincide.

APPENDIX 2

Table 2. Dependence of viscosity on shear rate of aqueous solution of polyethylene oxide with mass concentration of 2.5%

$\lg \dot{\gamma}, \text{ c}^{-1}$	-2.686	-2.425	-2.273	-2.116	-1.954	-1.724	-1.473
$\lg \eta, \text{ Pa}\cdot\text{s}$	1.479	1.661	1.739	1.818	1.909	2.000	1.987
$\lg \dot{\gamma}, \text{ c}^{-1}$	-1.028	-0.824	-0.594	-0.343	-0.061	0.211	0.462
$\lg \eta, \text{ Pa}\cdot\text{s}$	1.844	1.739	1.609	1.479	1.297	1.115	0.945
$\lg \dot{\gamma}, \text{ c}^{-1}$	0.755	1.001	1.283	1.582	1.822	2.042	2.293
$\lg \eta, \text{ Pa}\cdot\text{s}$	0.698	0.548	0.333	0.151	-0.018	-0.188	-0.344
$\lg \dot{\gamma}, \text{ c}^{-1}$	2.460	2.669	2.837	2.962	—	—	—
$\lg \eta, \text{ Pa}\cdot\text{s}$	-0.487	-0.643	-0.760	-0.865	—	—	—

Table 3. Dependence of viscosity on shear rate of CTAB/NaSal micellar solution with concentration of surface active substance $C_D (M) = 0.08$ at the ratio of $C_D / C_{\text{NaSal}} = 4.21$

$\lg \dot{\gamma}, \text{ c}^{-1}$	2.050	2.142	2.233	2.300	2.333	2.375
$\lg \eta, \text{ Pa}\cdot\text{s}$	-2.082	-2.078	-2.074	-2.047	-1.990	-1.941
$\lg \dot{\gamma}, \text{ c}^{-1}$	2.417	2.463	2.517	2.617	2.733	2.892
$\lg \eta, \text{ Pa}\cdot\text{s}$	-1.897	-1.853	-1.826	-1.818	-1.849	-1.924
$\lg \dot{\gamma}, \text{ c}^{-1}$	3.067	3.250	3.425	3.550	3.700	—
$\lg \eta, \text{ Pa}\cdot\text{s}$	-2.003	-2.091	-2.179	-2.215	-2.281	—

Table 4. Dependence of viscosity on shear rate of oil emulsion in aqueous solution with volume concentration $\varphi = 0.8$ and average droplet radius 7.7 μm

$\lg \dot{\gamma}, \text{ c}^{-1}$	-1.000	-0.795	-0.577	-0.385	-0.179	0.013
$\lg \eta, \text{ Pa}\cdot\text{s}$	1.484	1.369	1.280	1.204	1.102	1.038
$\lg \dot{\gamma}, \text{ c}^{-1}$	0.218	0.410	0.615	0.808	1.026	1.218
$\lg \eta, \text{ Pa}\cdot\text{s}$	0.975	0.847	0.720	0.579	0.439	0.312
$\lg \dot{\gamma}, \text{ c}^{-1}$	1.410	1.628	1.833	2.038	2.230	2.436
$\lg \eta, \text{ Pa}\cdot\text{s}$	0.166	0.045	-0.076	-0.197	-0.312	-0.427