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On the rheology of thixotropic and rheopexic suspensions

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Abstract

Semi-empirical equations are derived that describe the dependence of shear stress on shear rate during the flow of a one-component suspension. The suspension is considered as consisting of two fractions: single grains of the solid phase and their dimers, between which a reversible dimerization reaction occurs. In this case, the dimerization of single grains is considered as a reaction with an invariable rate constant, and the dissociation of dimers is considered as an inverse reaction with a rate constant that increases linearly with the shear rate. The equations are based on the Krieger-Doherty formula, generalized to the case of a multicomponent suspension.

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Introduction

In a previous work [1], equations were derived that describe the dependence of shear stress on shear rate during the flow of concentrated suspensions. The equations were based on the Krieger-Doherty formula [2, 3], generalized in our work [4] to the case of multicomponent suspensions:

$$\eta = \eta_0 \left(1 - \frac{\varphi}{\bar{\varphi}_0} \right)^{-[\bar{\eta}]\bar{\varphi}_0} \tag{1}$$

Here $[\bar{\eta}]$ and $\bar{\varphi}_0$ are the values of the parameters averaged over all solid components:

$$\begin{cases} [\bar{\eta}] = \dfrac{\sum [\eta_i]\varphi_i}{\varphi} \\ \bar{\varphi}_0 = \dfrac{\varphi}{\sum \varphi_i/\varphi_{0,i}} \end{cases}, \tag{2}$$

where φ is the total volume fraction of the dispersed phase, $[\eta_i]$ is the intrinsic viscosity of i-th component, φ_i and $\varphi_{0,i}$ – volume fraction and limiting concentration of the i-th component, respectively.

In that work, it was shown that the generalized Krieger formula (1–2) can be used to describe the dependence of the shear stress τ on the shear rate $\dot{\gamma}$ if the following assumptions are made:

1) A one-component suspension (i.e., a dispersion of one solid in a liquid) can be considered as a system consisting of two fractions: single grains ("singlets") of the solid phase and their dimers ("doublets"), moreover, single grains and their dimers correspond to different values of the parameters $[\eta]$ and φ_0;

2) Dimerization of singlets can be considered as a reaction with an invariable rate constant k_1, and dissociation of doublets as a reaction with a rate constant k, that increases linearly with the shear rate $\dot{\gamma}$: $k = k_2 + k_3\dot{\gamma}$. Here k_2 – dissociation rate constant in the absence of flow, k_3 – scan speed (change speed of rate constant with increasing of shear rate).

It was shown that the derived equations describe well the flow of both pseudoplastic and dilatant suspensions. However, it was tacitly assumed in [1] that the equilibrium between singlets and doublets is established instantly.

This work is a continuation and further development of the approach described in [1] and its generalization to the nonequilibrium case, when the achievement of equilibrium lags behind the change in the shear rate (i.e., there are relaxation effects - thixotropy or rheopexy).

Theory of calculations

So, let us consider a suspension as a system, the solid phase of which consists of two fractions: singlets (we denote their volume fraction as φ_1) and doublets (volume fraction φ_2).

Due to thermal motion, singlets (let's denote their number per suspension volume unit as n_1) collide with each other, after which they can be held together by cohesive forces, forming doublets (their number per suspension volume unit is n_2). Under the action of thermal motion, doublets can decay into singlets again, i.e. the reversible reaction $2n_1 \rightleftarrows n_2$ takes place. The application of shear stress should obviously promote the breakup of doublets, i.e. speed up the back reaction.

Let there be n_0 grains of the solid phase per unit volume of the suspension, and let the average grain volume be v. Then the volume fraction of the solid phase is $\varphi_0 = n_0 v$. At a given shear rate $\dot{\gamma}$ an equilibrium is established between singlets and doublets at a certain rate: $2n_1 \rightleftarrows n_2$ and $n_1 + 2n_2 = n_0$. Multiplying the left and right sides of the last equality by v, we get

$$\varphi_1 + \varphi_2 = \varphi_0. \tag{3}$$

Let the dimerization rate constant k_1 be invariable, and the reverse reaction rate constant k linearly depend on the shear rate $\dot{\gamma}$, which, in turn, is some function of time: $k = k_2 + k_3\dot{\gamma}(t)$. Further, we

will assume that $\dot{\gamma}$ changes linearly with time (which is usually implemented in practice in rotational viscometers). Thus, the reaction kinetics is described by the differential equation

$$\frac{d\varphi_1}{dt} = -k_1\varphi_1^2 + (k_2 + k_3\dot{\gamma})\varphi_2 \tag{4}$$

Substituting equality (3) into equation (4), we obtain:

$$\frac{d\varphi_1}{dt} = (k_2 + k_3\dot{\gamma})(\varphi_0 - \varphi_1) - k_1\varphi_1^2. \tag{5}$$

As initial conditions, we choose the concentration of singlets φ_1^{init} at equilibrium, which is established in the absence of flow, i.e. at $\dot{\gamma} = 0$ and $\frac{d\varphi_1}{dt} = 0$. Then $k_2(\varphi - \varphi_1) - k_1\varphi_1^2 = 0$, whence

$$\varphi_1^{init.} = \frac{\sqrt{k_2^2 + 4k_1k_2\varphi_0} - k_2}{2k_1} \tag{6}$$

Equation (5) is the well-known Riccati equation, which, unfortunately, in the general case cannot be integrated in quadratures [5, 6]. Therefore, it was solved numerically by the classical Runge-Kutta method of the fourth order [7]. The result of the numerical solution will be denoted as $\varphi_1(t)$.

The Krieger–Doherty formula for a two-component suspension according to (1) and (2) has the form

$$\tau = \tau_0 + \eta_0\dot{\gamma}\left(1 - \frac{\varphi_1}{\varphi_{10}} - \frac{\varphi_2}{\varphi_{20}}\right)^{-\frac{[\eta_1]\varphi_1 + [\eta_2]\varphi_2}{\varphi_1/\varphi_{10} + \varphi_2/\varphi_{20}}}, \tag{7}$$

with τ is shear stress, τ_0 is the yield stress, η_0 is the viscosity of the dispersion medium, $\dot{\gamma}$ – is the shear rate, φ_1 and φ_2 are the volume fractions of singlets and doublets (in accordance with (3) $\varphi_2 = \varphi_0 - \varphi_1$), φ_{10} and φ_{20} are the corresponding limiting concentrations, $[\eta_1]$ and $[\eta_2]$ – are the corresponding intrinsic viscosities.

Having a numerical solution $\varphi_1(t)$ of the differential equation (5), one can calculate the shear stress using formula (7). The results of the calculations thus depend on 7 parameters: the rate constants k_1, k_2 and k_3, the limiting concentrations φ_{10} and φ_{20}, as well as on the intrinsic viscosities $[\eta_1]$ and $[\eta_2]$.

Results and discussion

A study of the parametric sensitivity of the derived equations showed that the equations are capable of describing both the thixotropic and rheopex behaviour of suspensions (Fig. 1–6).
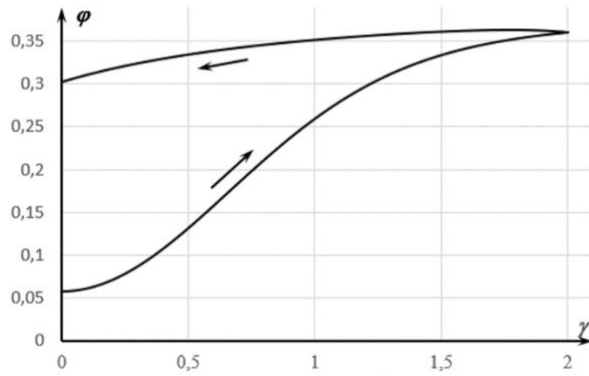
Fig.1. Dependence of the volume fraction of singlets on the shear rate. Parameter values: $k_1 = 10$; $k_2 = 0.1$; $k_3 = 10$; $\varphi_0 = 0.4$

From Fig. 1 can be seen that with an increase in the shear rate ("forward move"), the concentration of singlets increases (i.e., the suspension flow destroys doublets), and with a decrease in the shear rate ("reverse move"), their concentration is restored due to the flow of dimerization reactions, and due to the finite reaction rate, the change in concentration lags behind the change in shear rate, which leads to hysteresis in concentration and, as a result, to hysteresis in viscosity and shear stress.
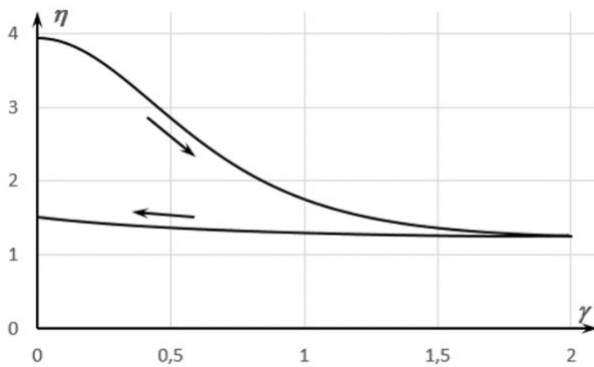

Fig. 2. Thixotropy: viscosity vs. shear rate. The rate constants are the same as in Fig. 1; values of other parameters: $\varphi_{10} = 0.5$; $\varphi_{20} = 0.45$; $\tau_0 = 0$; $\eta_0 = 0.1$; $[\eta_1] = 3$; $[\eta_2] = 4$.

Fig. 2 shows the dependence of viscosity on shear rate at the same rate constants as in Fig. 1, and the values of the remaining parameters (limiting concentrations and intrinsic viscosities) were chosen so that the viscosity decreases with increasing shear rate, i.e. so that the suspension exhibits pseudoplastic behaviour. At the same time, it can be seen that the finiteness of the reaction rates leads to the fact that the recovery of viscosity occurs with a lag, and the viscosity with a decrease in $\dot{\gamma}$ remains less than the viscosity with an increase in $\dot{\gamma}$ (i.e., the suspension is thixotropic).

Such behaviour of viscosity can be explained by the fact that doublets make a greater contribution to the viscosity of the suspension than singlets, so the destruction of doublets leads to a decrease in viscosity, and the delay leads to the fact that during the experiment the viscosity does not have time to recover. Thus, pseudoplastic suspensions in the presence of relaxation effects demonstrate a thixotropic behaviour, which also can be seen from Fig. 3.
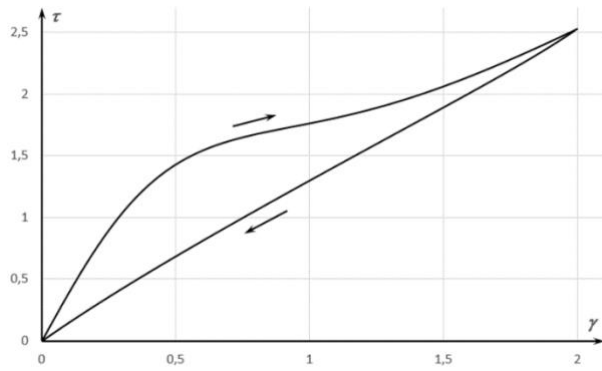
Fig. 3. Thixotropy: shear stress vs. shear rate. The parameter values are the same as in the previous figures.
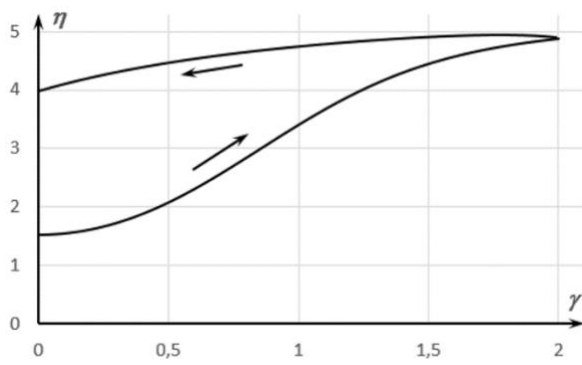

Fig. 4. Rheopexy: dependence of viscosity on shear rate. Parameter values: $[\eta_1] = 5$, $[\eta_2] = 2.5$; rest parameters have the same values.
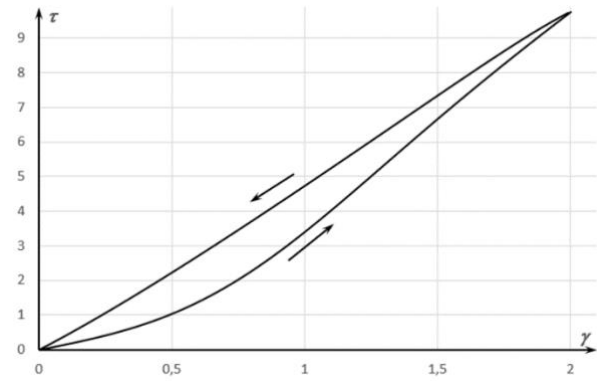

Fig. 5. Rheopexy: dependence of shear stress on shear rate. Parameter values are the same.

Fig. 4 and 5 show similar results for dilatancy and rheopexy. It is easy to see that in this case the doublets make a smaller contribution to the viscosity of the suspension, and their destruction leads to an increase in the viscosity, i.e. the suspension is dilatant, and the finiteness of the reaction rates leads to the fact that during the experiment, with a decrease in the shear rate, the viscosity does not have time to decrease to the previous value, and the suspension demonstrates rheopex behaviour. Thus, dilatant suspensions become rheopex in the presence of relaxation effects.

At high rates of dimerization and decay of dimers, the derived equations degenerate into the limiting case of instantaneous establishment of equilibrium. This limiting case is described in the previous work [1], where it is shown that the equations describe pseudoplasticity and/or dilatancy well (depending on the ratio of the parameters φ_{10}, φ_{20}, $[\eta_1]$ and $[\eta_2]$).

For experimental verification of in this work derived equations, the data published in the literature [8–10] were used. The results of comparing theory with experiment are shown in the following figures.
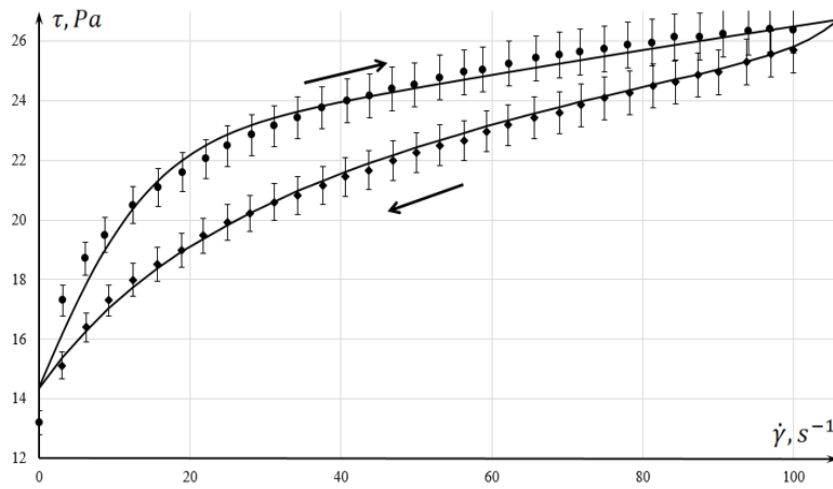
Fig. 6. Aqueous suspension of nanodiamonds according to [8]. Parameter values: $k_1 \approx 56.81$, $k_2 \approx 2.287$, $k_3 \approx 1.035$, $\varphi_0 \approx 0.370$, $\varphi_{10} \approx 0.582$, $\varphi_{20} \approx 0.358$, $\tau_0 \approx 14.4$, $\eta_0 \approx 0.0492\ Pa \cdot s$, $[\eta_1] \approx 2.948\ \text{Па} \cdot \text{с}$, $[\eta_2] \approx 5.370\ Pa \cdot s$. The standard deviation of the curves from the points is 0.3 Pa (1.3% of the mean value of the shear stress). The error indicator shows a spread of 3%.

Fig. 6 shows the dependence of the shear stress on the shear rate for an aqueous suspension of nanodiamonds according to the data of [8]. The dots represent the experiment; the solid curves represent the calculation by the derived equations. It is easy to see that the derived equations are in good agreement with the experiment, and the parameters of the equations take realistic values. The calculated dependences of the volume fraction of singlets, as well as the viscosity on the shear rate, corresponding to the results presented in Fig. 6 are shown in Figs. 7 and 8, respectively. It is easy to see that the suspension is pseudoplastic and, as expected, the presence of a relaxation effect leads to thixotropy.
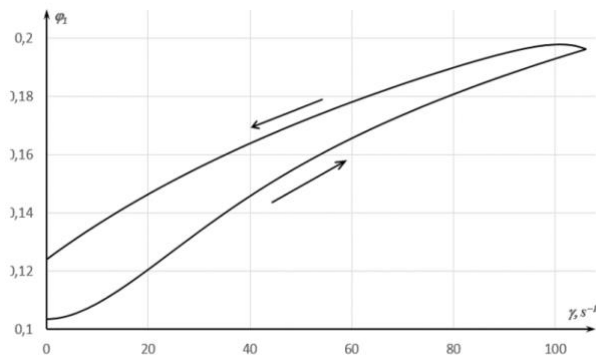

Fig. 7. Aqueous suspension of nanodiamonds. Calculated dependence of the volume fraction of singlets on the shear rate.
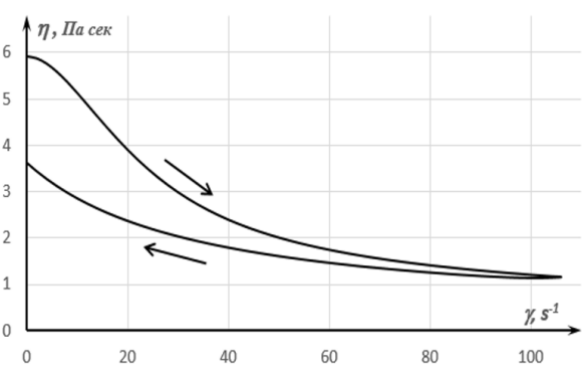

Fig. 8. Aqueous suspension of nanodiamonds. Calculated dependence of viscosity on shear rate.

However, in the literature [9, 10] there are also experimental data, according to which a pseudoplastic suspension demonstrates a rheopex character [9], (the dependence of shear stress on shear rate for such a suspension according to the data of [9] is shown in Fig. 9), as well as

suspensions with a variable flow character [10] (i.e., at some shear rates, thixotropy is observed, and at others, rheopexy). These data are presented in fig. 10.
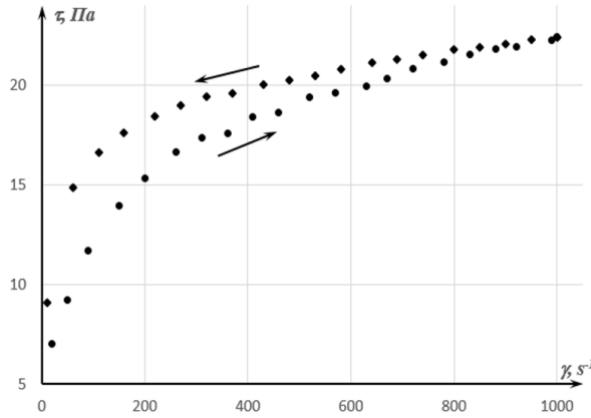

Fig. 9. Aqueous suspension of palygorskite. Dependence of shear stress on shear rate according to [9].
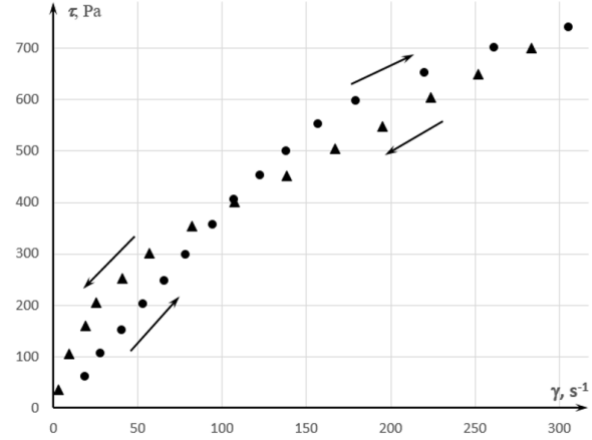
Fig. 10. Polymer suspension filled with ceramic nanoparticles. Dependence of shear stress on shear rate according to [10].

As it turned out, the derived equations do not describe these results. The reason is that these equations predict the following behaviour:

The convex dependence $\tau(\dot{\gamma})$, shown in Figs. 9, means a decrease in viscosity during the forward move, i.e. pseudoplasticity. During the subsequent reverse move, the viscosity should recover (increase) with a delay, i.e. the curve $\tau(\dot{\gamma})$ for the reverse move should lie below the curve $\tau(\dot{\gamma})$ for the forward move, which contradicts the experimental data presented in Fig. 9.

The data in Fig. 10 represent a system with a variable nature of the flow: with a forward move, the dependence $\tau(\dot{\gamma})$ is first concave (dilatancy), then convex (pseudoplasticity); the same for the reverse. As was shown in previous works [1, 11], to describe the variable nature of the flow, it is necessary to take into account the formation of trimers. Therefore, it is natural to assume that taking into account the formation of trimers, together with taking into account the finiteness of the reaction rate, will also make it possible to describe both the data presented as in Fig. 10 and in Fig. 9. The next work will be devoted to the study of this possibility.

Conclusions

1. A one-component suspension can be considered as a system consisting of two fractions: single grains and their dimers, between which an equilibrium is established at a certain final rate, depending on the shear rate. This model describes uniformly and naturally 4 types of rheological behaviour of suspensions: pseudoplasticity, dilatancy, thixotropy and rheopexy.

2. The application of shear stress leads in all cases to the destruction of dimers and a shift of equilibrium towards single grains.

3. The type of rheological behaviour of the suspension depends on the ratio of four parameters: the limiting concentrations of the components φ_{10} and φ_{20}, their characteristic viscosities $[\eta_1]$ and $[\eta_2]$, as well as on the time to reach equilibrium. If this time is small compared with the time of experiment, the equations degenerate into the limiting (equilibrium) case and describe pseudoplasticity and/or dilatancy. If this time is comparable with the time of the experiment, relaxation effects appear – thixotropy and/or rheopexy.

4. An assumption was made (already confirmed by further studies) that taking into account the formation of trimers will also make it possible to describe the cases when the suspension, depending on the shear rate, exhibits both thixotropic and rheopex behaviour.

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