DEFORMATION AND STRENGTH PROPERTIES OF CONCENTRATED DISPERSE SYSTEMS (SURVEY)

M. P. Volarovich and N. I. Malinin

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In diverse branches of the national economy engineers and scientists are obliged to deal with the deformation and flow of various disperse systems—suspensions, colloidal solutions, and pastes—in which solid particles are distributed in a liquid medium. In examing specific problems of flow of such materials in various technological processes, it is important to know the law relating the stresses acting on the system to its rate of flow. This kind of problem is the subject of rheology [1]—the science of the flow of matter.

Dispersions of solids in liquids are complex two-or-more component systems, whose mechanical properties are determined by the molecular forces acting between the components. The study of the molecular interactions is one of the problems of physicochemical mechanics [2]—a new field of science formulated some ten or fifteen years ago at the interface of physics, chemistry, and materials science. Rheology, which is part of physicochemical mechanics, particularly in the mathematical description of the observed phenomena, usually restricts itself to purely phenomenological methods of description, or examines only the main, important interactions between components, neglecting second-order and less significant interactions.

Previous reviews have examined rheological studies of the plastico-viscous properties of disperse systems [3], as well as the general problems of rheology [4], connected with the study of structural-rheological parameters of colloidal-disperse systems. The present article is devoted to a more detailed examination of the properties of fluidity of dispersed solids in liquids, special attention being given to the effects of viscosity anomalies.

The presence of solid particles in a liquid medium inhibits flow of the system. The viscosity of dispersions of solid particles in a liquid is always greater than that of the dispersion medium. The increase of viscosity of the system with the addition of solid filler is due to two causes. First, the particles of the disperse phase play a purely passive role, occupying part of the volume of the medium, where there is no flow for this reason. At equal (macroscopic) shear rates, the actual shear rates in the microvolumes of the liquid phase of the disperse system are greater than for the pure liquid. To create higher velocity gradients, even higher stresses are required, for which reason the viscosity of suspensions or of a colloidal solution proves to be larger than that of the pure solvent. Second, the liquid has a hydrodynamic resistance to relative displacement of particles of the solid phase, leading to additional energy dissipation and to a still further increase in the viscosity of the system. This second effect is particularly manifest for elongated particles.

Investigation of phenomena of this kind is the province of a special section of rheology, called microrheology. The foundation of this field of knowledge was laid by A. Einstein in his doctoral thesis, the content of which has been published in [5]. He solved the problem of the influence of solid spherical inclusions on the viscosity of a liquid with small concentrations of solid phase.

To evaluate the influence of the "thickening action" of the solid phase, on the basis of the formula obtained by Einstein in the papers cited, use is now made of the so-called characteristic viscosity $[\eta]$, determined by the equation

$$[\eta] = (\eta - \eta_0)/\eta_0 c, \tag{1}$$

where η is the viscosity of the suspension, η_0 is the viscosity of the dispersion medium, and c is the volume concentration of solid phase. For low concentrations of solid phase, $a/b = 1$ does not depend on c, but only on the shape of the particles of the disperse phase.

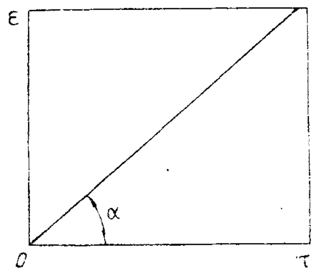

Fig. 1. Flow of a Newtonian liquid.

The problem of flow of a dispersion of ellipsoids of revolution with major axes a and b in a liquid medium, a problem similar to that of Einstein, was solved by Jeffrey, Eisenschitz, and Burgers [6]. They showed that if $a/b = 1$, then $[\eta] = 2.5$, as in Einstein's formula. With increase of the ratio a/b, the characteristic viscosity also increases. Thus, for example, when $a/b = 10$, $[\eta] = 3.50$; if $a/b = 100$, then $[\eta] = 10.1$; if $a/b = 1000$, then $[\eta] = 54$, etc. Thus, the more elongated the particle, the more it increases the viscosity of the liquid. The problems of Einstein and Jeffrey-Eisenschitz-Burgers were solved under the following assumptions.

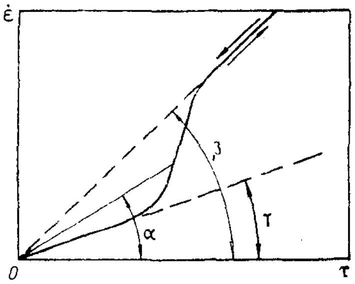

Fig. 2. Flow of a non-Newtonian liquid in the absence of viscous hysteresis (ctg $\alpha = \eta_{\mathrm{eff}}$, ctg $\beta = \eta_{\mathrm{m}}$, ctg $\gamma = \eta_0$).

The whole volume of the liquid phase close to some solid particle is artificially divided into two regions. Near the particle, in the macroscopically uniform shear rate field, the flow will be microscopically nonuniform because of the hydrodynamic interaction between the liquid and the particle. This "disturbed" region, together with the solid particle itself, forms, according to Reiner [7], a so-called complex element. If we neglect a certain small error, then inside the range of this "complex element," the particle has no influence on the flow. The solutions of Einstein and Jeffrey-Eisenschitz-Burgers are valid for the case when the volumes of the "complex elements" do not overlap. This requirement is satisfied only at very small concentrations c. At higher concentrations the whole volume of the liquid is disturbed by the solid particles, the volumes of the "complex elements" overlap, and the characteristic visocosity $[\eta]$ begins to increase with increase of c.

It is assumed also that the liquid is not bound by particles of the solid phase. Binding of the liquid by solid particles may occur due to the phenomena of sorption, osmotic absorption, and purely mechanical immobilization, if the particles have cavities or are coiled in spiral form.* When liquid is bound by particles of the solid material, the volume of the free liquid is reduced, the volume of the particles, on the other hand, is increased, and the characteristic viscosity increases in comparison with its theoretical value.

In accordance with what has been said about dispersions of solid particles in a liquid, a viscosity anomaly appears. By an anomaly we understand a change (decrease) in the numerical value of the viscosity with increase of shear rate. The viscosity anomaly is best seen on the fluidity curves, with the x-axis showing the shear stress τ, and the y-axis—the shear rate $\dot{\varepsilon}$ (Fig. 1). As is known, the viscosity $\eta = \operatorname{ctg} \alpha$, where α is the slope of the fluidity curve with respect to the x-axis. For a Newtonian viscous liquid the viscosity η does not depend on the stress and the shear rate.

Dispersions of solid particles in a liquid at not too high concentrations c have fluidity curves of the form shown in Fig. 2. Such systems have been called liquid-like [10, 11], i.e., they do not noticeably display any properties of a solid body. It may be seen from Fig. 2 that the effective viscosity, determined by the equation $\eta_{\mathrm{eff}} = \tau/\dot{\varepsilon} = \operatorname{ctg} \alpha$, depends on the stresses, as well as the shear rates. At very low shear rates ($\dot{\varepsilon} \to 0$), the initial viscosity has some maximum value η_0. With increase of shear rate the viscosity decreases, and finally, for high enough $\dot{\varepsilon}$, it takes a minimum value η_{m}, the effective viscosity being independent of $\dot{\varepsilon}$ and of τ in a certain range (up to transition to turbulence). The viscosity anomaly may be explained as follows.

As was shown by Burgers [6], the resistance of an elongated particle to a liquid flow depends on the angle φ between the direction of the principal shear rate and the major axis of the particle. If $\varphi = 0°$, the particle has minimum resistance. When $\varphi = 90°$, its resistance is a maximum. The liquid stream tends to align the elongated particle so that its major axis coincides with the principal shear rate. This tendency is opposed by the thermal (Brownian) motion, which tends to disorient the particles. In other words, the Brownian motion promotes the more uniform distribution of long particles as regards direction. At small flow rates the particles are distributed almost uniformly as regards directions in space, the forces of interaction between the liquid and the particles being insufficient for any noticeable orientation of particles along the stream direction. Therefore, at small shear rates the viscosity of the dispersion is relatively small. At higher flow rates the particles are oriented along the flow direction. Finally, at some critical velocity, the forces of hydrodynamic resistance increase to such an extent that they completely overwhelm the disorienting action of the Brownian motion, and all the elongated particles arrange themselves in the direction of the principal shear rate [12, 13].

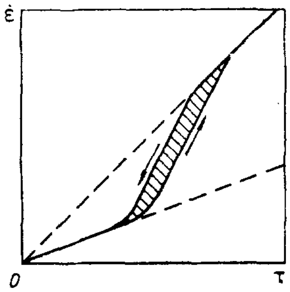

Fig. 3. Flow of a non-Newtonian liquid exhibiting viscous hysteresis.

Further increase of shear rate does not lead to any change of particle distribution as regards direction, and therefore does not lead to an increase in effective viscosity. Thus, for example, Volarovich and

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*See [8, 9] regarding the types of bond between the dispersion medium and particles of the solid phase.

Korchemkin [12] observed experimentally orientation of needle-shaped crystals of hematite suspended in an aegirine melt during flow of the melt in a tube. At the walls of the tube, where the velocity gradient was large enough, all the hematite crystals were oriented along the tube axis (and hence along the flow direction), while near the center of the tube, where $\varepsilon \approx 0$, no orientation was observed.

Certain long particles are broken up in a stream. The fragments are closer in shape to a sphere than the original particles, and therefore they have less resistance to the liquid motion. Therefore the effective viscosity diminishes with increase of velocity. If the flow of the system slows up or is curtailed altogether, recombination of "secondary" particles may occur. However, this process, if it does occur, proceeds slowly, and the system may exhibit decreased viscosity for a long time. Then the fluidity curves exhibit viscous hysteresis, as depicted in Fig. 3, the width of the hysteresis loop depending on the rate of increase of shear rate (i. e., on the magnitude of $\ddot{\varepsilon}$) and on its subsequent rate of decrease. Viscous hysteresis, as in Fig. 3, was observed in [14] for lubricating oils at low temperatures.

Liquid is partially adsorbed at the surface of lyophilic solid particles and is converted into bound liquid [8, 9]. Bound water, for example, possesses to some extent the properties of a solid, particularly mechanical strength, and a rather definite, measurable shear modulus, falling off with the distance of the layer examined from the surface of the solid [15, 16]. The strength of a bound liquid also rapidly drops with its distance from the adsorbing surface of a solid. At low flow rates the whole of the bound liquid behaves as a solid body and does not move relative to the surface of the solid particle. Thus, the volume of the liquid decreases, and the volume of the dispersed phase increases, which leads to an increase of viscosity in comparison with its theoretical value.

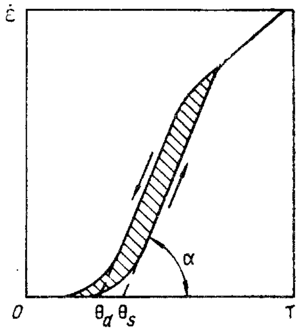

Fig. 4. Flow of a plastico-viscous (Bingham) body ($\operatorname{ctg} \alpha = \eta_p$).

With increase of shear rate, the stresses developing on the particle surface detach a certain amount of bound liquid and transform it to the free state. This phenomenon also leads to a reduction of effective viscosity.

Liquid immobilized by the internal cavities of particles of the solid phase (or by the coils of spiral-shaped formations) also does not participate in the flow, which leads to an increase in the viscosity of the system in comparison with the theoretical value.

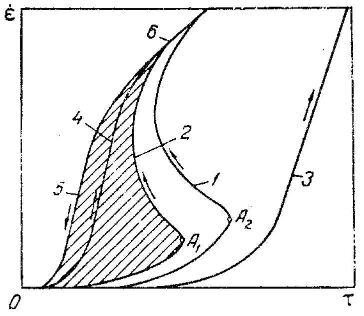

Fig. 5. Flow of a highly concentrated dispersion of solid particles in a liquid: 1) with $\ddot{\varepsilon}_1 = \text{const}$; 2—$\ddot{\varepsilon}_2 < \ddot{\varepsilon}_1$; 3—$\ddot{\varepsilon}_\infty \gg \ddot{\varepsilon}_2$; 4—$\ddot{\varepsilon}_0 \ll \ddot{\varepsilon}_1$; 5) under alternating acceleration; 6) with structure broken down to the limit.

Because of the action of stresses developing in the flow, particles of the dispersed phase are deformed or broken up. When particles are deformed, some part of the immobilized liquid is squeezed out of them, as if from a sponge, and goes over into the free state. Breakdown of the weakest particles usually occurs along the cavities; here again a certain amount of immobilized liquid is set free. These processes lead to reduction of the effective viscosity with increase of shear rate, some hysteresis again being observed.

The viscosity anomaly is small for negligible concentration of solid matter in the liquid, since then the viscosity of the system differs little from that of the solvent. The larger the concentration of solids, the greater the viscosity anomaly. At some intermediate concentrations the fluidity curves have the form shown in Fig. 4. There the fluidity in the initial section of the curve is only very small and often cannot be observed by coarse instruments. It is therefore assumed that the material does not flow at stresses below a certain value θ_s. For stresses greater than θ_s the fluidity becomes measurable, increasing rapidly with increase of stress. Bingham [16] considers that the fluidity at stresses above the fluidity limit θ_s varies in straight-line fashion, and for pure shear is described by the equation

$$\tau = \theta_s + \eta_p \dot{\varepsilon}, \tag{2}$$

where η_p is a parameter called the plastic viscosity of the material. Herschel and Bulkley [18] considered that for the materials investigated by them the fluidity curve is a parabola; they also proposed a corresponding rheological equation.

The composition of disperse systems exhibiting a fluidity limit differs from that of systems having no such limit. The properties of systems for which $\theta_s \neq 0$ are reminiscent of those of plastic solids. Therefore Rebinder [10, 11] called such systems solid-like, in distinction from liquid-like, for which $\theta_s = 0$. Solid-like disperse systems have the composition of a gel (or gelatin), and liquid-like systems—that of a sol. In sols the individual particles of the solid phase are separated by liquid phase and have no points of contact. There are no forces of molecular interaction between the solid particles of a sol. In gels the solid particles form a three-dimensional lattice structure. Neighboring particles have points of contact, where intermolecular (interparticle) forces act. These are usually secondary forces (Van der Waals). Thanks to its developed lattice structure, a gel possesses some fluidity limit.

As has been shown in the work of Volarovich and Gutkin [19], systems of the sol type, in which the solid particles represent electric dipoles regularly distributed in the dispersion medium, may also possess a fluidity limit.

For stresses below the fluidity limit, flow, even if it is observed, occurs with negligible velocity. Stresses high enough in comparison with the fluidity limit cause breakdown of the gel lattice structure, leading to increase of the fluidity of the system. Here we encounter so-called thixotropic phenomena.

Freundlich [20] understood thixotropy to be the isothermal transition of a gel to a sol in the presence of mechanical action on the sytem, and also the reverse transition, when the action is discontinued. At present by thixotropy we understand a reduction of the mechanical properties of the system upon mixing. Thus, if even as a result of mechanical action, the system still retains its plastic properties (i. e., is a gel), but its viscosity, strength, and fluidity limit decrease, it is considered that the decrease is connected with thixotropic phenomena.

Thixotropy is the chief cause of hysteresis loops in the fluidity curves of plastic disperse systems (Fig. 4). Because of thixotropic hysteresis two fluidity limits are observed: a static θ_s and a dynamic θ_d. The static fluidity limit (limiting shear stress) θ_s may be determined by extrapolation to $\dot{\varepsilon} = 0$ the straight-line part of the fluidity curve for the original material, without subjecting it to prior shear deformations (Fig. 4). The dynamic fluidity limit θ_d intersects on the x axis the extrapolated to $\dot{\varepsilon} = 0$ straight portion of the fluidity curve obtained for falling shear rates. As shown in [21], the static fluidity limit θ_s is always greater than the dynamic one θ_d.

The plastic viscosity is determined from the slope of the linear portion of the fluidity curve relative to the x-axis for stresses greater than θ_s (or θ_d).

Some substances, called pseudoplastic bodies in [14], have a static limiting shear stress (θ_s), but do not exhibit a dynamic limiting shear stress ($\theta_d = 0$).

With further increase of the solids content of the system, its deformation and strength properties become still more complex. Whereas the anomalous-viscous and plastico-viscous properties of disperse systems at small concentrations may be investigated with the aid of instruments of various kinds in which a nonuniform stress-strain field is set up [17, 21, 22], for concentrated systems it is preferable to use instruments where the stress field is practically uniform. The most suitable for this purpose are rotational instruments with a narrow gap between the inner and outer cylinders [23, 24].

In these instruments the outer cylinder is rotated by means of an electric motor. The inner cylinder is suspended on a wire [24], which serves as a torsion dynamometer. In the instrument described in [25], the "electric shaft" principle is used.

Before testing, the disperse system is kept in the working element of the instrument for some time, to acquire a structure. When the instrument is switched on, the outer cylinder of the viscometer begins to move, first accelerating, and then with constant velocity.

As a number of investigators [25–27] have shown, the start-up regime of the rotational instrument in operation has a considerable influence on the shape of the stress-time curves for concentrated disperse systems, since breakdown of the structure of the material very often occurs before the onset of steady-state flow. The stiffness of the dynamometer [25–27] also has some influence on the shape of the rheological curve, in conditions where there is no special provision for compensating the deformation of the dynamometer and for achieving a specified regime of deformation. Thus, the rate of growth of the shear rate, i. e., the quantity $\ddot{\varepsilon}$, has an influence on the shape of the rheological curve of concentrated disperse systems. Therefore, for drawing rheological curves, the most suitable regime of deformation, in our opinion, is $\ddot{\varepsilon} = \text{const} > 0$ during growth of the shear rate $\dot{\varepsilon}$ up to $\dot{\varepsilon} = \dot{\varepsilon}_{max}$, and during the subsequent decrease of $\dot{\varepsilon}$ to zero at constant acceleration $\ddot{\varepsilon} = \text{const} < 0$. It should be noted that such a regime is realized in the McKennell instrument [28].

It may be seen from Fig. 5 that at the origin the stresses τ are rapidly increasing, the rate of viscous deformation being completely insignificant. As the rate of deformation increases, the rate of growth of the stresses slows down. Starting with the point A_1, the stresses begin to fall, this being due to breakdown of the structure of the material. Then with further growth of shear rate, the stresses again begin to increase, due to the viscous resistance of the dispersion medium. The flow curve then reaches section 6, corresponding to limiting structure breakdown. This section is not usually observed, since either turbulence sets in beforehand, or breakdown of the continuity of the system occurs. There is no certainty that its continuation into the low $\dot{\varepsilon}$ region passes through the origin of coordinates (see Fig. 10 in [29]), just as it is not certain that the family of fluidity curves obtained at different $\ddot{\varepsilon}$ values merge into a single curve in section 6. At higher acceleration, for example, at $\ddot{\varepsilon}_2 < \dot{\varepsilon}_1$, the form of the flow curve changes as shown by curve 2 of Fig. 5. The abscissas of the extreme right points A_1 and A_2 may be taken as the limits of the strength of the system (see [30]), which prove to be dependent on time. The time dependence of the strength of concentrated dispersed systems was observed in [31, 33].

At very high accelerations $\ddot{\varepsilon}$ the fluidity curve apparently has the form shown in the figure by curve 3. At very low accelerations $\ddot{\varepsilon}$ the fluidity curve is represented in Fig. 5 by curve 4. At very low accelerations $\ddot{\varepsilon}$, and possibly also at very high $\ddot{\varepsilon}$, the stresses τ increase monotonically.

It should be noted that for highly concentrated systems, in order to obtain a monotonic character of the fluidity curve, it is necessary to use accelerations $\ddot{\varepsilon}$ or velocities $\dot{\varepsilon}$ so low that they are practically impossible to achieve [27]. In section 6 all the curves obtained at various values $\ddot{\varepsilon}$ merge into a single line. If the rate of deformation $\dot{\varepsilon}$ were to increase, and then begin to drop, the fluidity curve would have the form represented by curve 5 of Fig. 5. The shaded hysteresis loop is associated with energy loss in breaking down the structure of the material.

According to contemporary opinion [33, 34], the resistance of a concentrated disperse system to the action of external forces is equal to the sum of the viscous resistance of the dispersion medium and the resistance of the structure of the material. The resistance of the latter is the larger, the more developed the structure. When external forces act on the system, the gel structure begins to be broken down, the breakdown process proceeding with time. The rate of breakdown of the gel structure is the greater, the higher the stresses acting. The breakdown process, in the opinion of Billington [33, 34] and of the authors of [31, 32], conforms to the theory of absolute reaction rates [35, 36].

A somewhat different point of view is expressed in [37]. To describe the properties of disperse and high-molecular systems, similar to those represented in Fig. 5, use is made of a generalized Maxwell model containing a set of relaxation times. When large enough stresses act on an individual Maxwell element in this model, breakdown occurs, whereupon the load is redistributed among the undamaged elements.

It may be seen from Fig. 5 that the system behaves as a plastico-viscous body only in cases 3, 4, and 5. There the fluidity curves rise upwards so steeply that it is impossible to determine the plastic viscosity of the system. In any case it is many orders below the viscosity of the intact system, and many times below the viscosity of the limiting breakdown system. Therefore the idea of plastic viscosity becomes meaningless for concentrated disperse systems.

Fluidity curves similar in shape to those presented in Fig. 5 were also obtained for certain high-molecular compounds in [38].

With further increase in the content of solids in the disperse system, the entire liquid passes into the bound state. It is no longer a free liquid, and under the action of high stresses the system suffers brittle fracture [39].

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Institute of Mechanics,
Moscow