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Structure and rheology of highly concentrated emulsions: a modern look

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The review concerns modern physicochemical, chemical and physical approaches to research into structural features that determine the rheological properties of highly concentrated emulsions. The structures and properties of various systems (suspensions, emulsions as well as transient forms including micellar colloidal solutions) are considered. The formation of highly concentrated emulsions is treated as the concentration glass transition leading to suppression of the molecular and supermolecular mobility and, subsequently, to the existence of a solid-like state of the systems in question. The emphasis is placed on analysis of visco-plasticity which manifests itself in the possibility for emulsions (unlike suspensions) to undergo irreversible deformation (to flow) at stresses exceeding some threshold (critical value) called the yield stress. The thixotropic nature of the transition through the yield stress, governed by the kinetics of the breakup/recovery of the inherent structure is considered in detail. It has been shown that structure formation in highly concentrated emulsions can extend to a macroscopic level and result in the onset of heterogeneity of a flow in the form of shear bands.
The bibliography includes 202 references.

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I. Introduction

The term ‘emulsion’ originates from Latin ‘mulge’ (milk) because milk is a true emulsion and was the first system identified as emulsion.

Formally, an emulsion is a dispersion of liquid droplets in a continuous liquid medium, both liquids being mutually insoluble. Emulsions are divided into two main classes:

— oil-in-water (o/w), or direct emulsions, and
— water-in-oil (w/o), or inverse emulsions.

This is a conditional classification because the non-aqueous phase should not necessarily be an oil (usually, various organic nonpolar media are used). Other possible combinations include, *e.g.*, emulsions formed by a continuous hydrocarbon phase and dispersed fluorocarbon droplets or emulsions formed by incompatible aqueous solutions of two different polymers. It should be noted that emulsions, being thermodynamically unstable systems, should be stabilized owing to formation of surfactant thin-film droplets on the surface (this significantly reduces the surface tension at the interface due to formation of an interfacial layer). Therefore, all emulsions are multicomponent systems.

Various types of emulsions of different composition have been well documented in textbooks and scientific literature,[1,2] so there is no need to dwell on the issue.

The droplet size in emulsions treated as colloidal dispersions can be estimated conditionally. Usually, the lower and upper bounds are assumed to be 10 – 20 nm and 10 μm, respectively. The optical spectral region (380 – 780 nm) is at the centre of this range; therefore, emulsions are prone for light scattering by the dispersed droplets whose refractive index differs from that of the dispersed medium; thus, emulsions seem opaque or turbid liquids. Recently, there has been considerable interest in emulsions containing droplets a few tens of nanometres in size. Unlike conven-

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tional colloidal systems, nano-emulsions are transparent liquids.[3,4]

Let us specify the validity scope of the definition of the notion 'emulsion' (see above) because classification is always to one or another extent conditional. There are no strict boundaries between different types of materials and one can always find a variety of transient situations. For instance, the lower bound of the particle size for disperse media can be exemplified by solutions of molecularly dispersed substances. Considering polymers, individual molecules can be large enough to be treated as dispersed 'liquid' particles stabilized by the interaction with the solvent, *i.e.*, formally one deals with quasi-emulsions. Also, molecules can form associates, *e.g.*, polyelectrolyte complexes.[5] Same-type blocks in block copolymer solutions can form polymolecular aggregates.[6–9] Surfactant solutions can form micelles, *i.e.*, colloid particles representing associates of surfactant molecules.[2,9,10] The formation of discrete supramolecular ensembles comprising an indefinite number of molecules is possible in solutions; this may result in macroscopic structures including membranes, vesicles, liquid crystals, *etc.*[11]

Deformation can lead to formation of nanoscale clusters. This was observed by direct methods in the studies of solutions of block copolymers[12–14] and crystallizable polymers where nanoscale clusters act as nuclei of the future crystalline phase.[15,16] Clustering is possible even in dilute micellar solutions.[17] The rheology of micellar solutions is close to that of polymer solutions and resembles the rheology of emulsions; this will be emphasized when necessary in the text below. On the other hand, the rheology of micellar solutions occupies a specific position, which was clearly demonstrated in a review.[18]

Supermolecular aggregates can be rather large and comparable in size with emulsion droplets. However, most of them can hardly be considered as emulsions because (i) their composition (in contrast to emulsion droplets) is unknown and varies with time and (ii) they do not form an individual phase which can be isolated as a liquid.

By definition, emulsion droplets are those of a liquid. But they can also be formed by labile gels which readily break up under stress or by networks with persistent intermolecular bonds. It follows that an intra-droplet transition from a liquid to an elastic medium and, by and large, transition from an emulsion to a suspension is possible, the transition boundary being undefined (an example is provided by blood). An apt term to describe this kind of systems is 'soft matter' because it covers both the limiting cases and transient situations. When analyzing the rheological properties of emulsions, they should be compared with those of suspensions because, as will be shown below, these types of disperse systems have much in common and drawing a well-defined boundary between them is problematic in some cases. Modern approaches to the rheology of suspensions, as well as problems and general trends of research into such systems have been documented in a review.[19]

Now we will dwell on the role of droplet concentration in emulsions. The definition (see above) deals with individual droplets, *i.e.*, assumes no inter-droplet contacts and interactions. In this respect, a trivial example of emulsion is provided by a slightly turbid liquid (milk). From the standpoint of rheology, milk exhibits the properties of a Newtonian fluid similarly to dilute suspensions.[20] As the droplet concentration in an emulsion (concentration of hard-particle dispersion in a suspension) increases, droplets begin to interact with one another. Subsequent increase in the droplet concentration leads to a structure that is responsible for non-Newtonian behaviour of the emulsion.

Eventually, the inter-droplet interaction mentioned above causes emulsions to transform to elastic liquids and then to visco-plastic media as a threshold concentration is reached. It follows that inter-droplet interaction leads to formation of a solid-like structure of a 'soft' gel type. Such a gel is to some extent stiff system characterized by the yield stress (σ_Y) and thus emulsions represent solid-like gels at stresses below σ_Y and behave as liquids at stresses above σ_Y.

The threshold concentration corresponding to these changes in the rheological properties is governed by the volume concentration of emulsion droplets. There is considerable literature on analysis of possible structural forms built of spherical (including polydisperse) particles (see, *e.g.*, Ref. 21). The key issue is to estimate the closest packing of space. Obviously, there exists a limit of the closest packing. It clearly manifests itself for monodisperse suspensions, because the volume concentration of solid spherical particles cannot exceed the critical concentration of the closest crystal-like packing, $\varphi^* \sim 0.74$.

By analogy, there exists a critical concentration of monodisperse emulsion droplets. However, solid particles in a suspension are fundamentally different from deformable droplets in an emulsion. First, as mentioned above, the interaction between interfacial layers in emulsions leads to manifestation of elastic properties at droplet concentrations below the limit of the closest packing (see above). Next, as the φ^* value is reached, spherical liquid droplets can be compressed, so they will adopt a polyhedral shape and the volume concentration of the droplets can be much higher than the threshold value, φ^*. In this case, the continuous phase will exist as very thin layers separating droplets of the dispersed phase (similarly to foam-forming films) and near the vertices of polyhedra (Fig. 1). This is the case of highly concentrated emulsions where the concentration of the dispersed phase may be significantly higher than 90%.

Thus, highly concentrated emulsions are multicomponent systems where the dispersed phase is composed of deformable (soft) substances and the continuous phase represents a liquid of low viscosity which forms thin layers between dispersed particles. Also, the concentration of

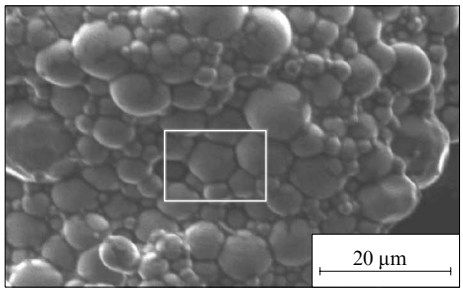


Figure 1. Photomicrograph of a highly concentrated emulsion containing deformed droplets that adopted polyhedral shape. Well-defined polyhedra are clearly seen.
Courtesy of A Ya Malkin and I Masalova (CPUT, Cape Town, South Africa).

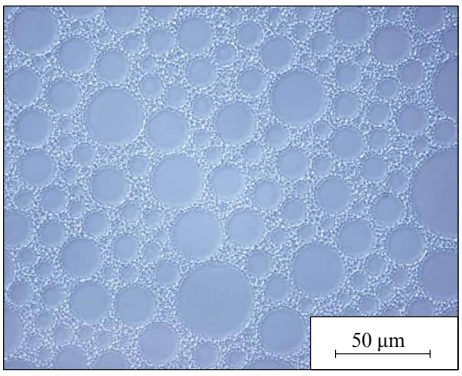


Figure 2. Photomicrograph of a highly concentrated polydisperse emulsion.
Courtesy of R Foudazi (New Mexico State University, USA).

dispersed particles exceeds the limit of the closest packing of monodisperse spherical droplets, so the particles undergo deformation and adopt the shape of compressed polyhedra.

It should also be noted that the concentration of dispersed particles (droplets) in emulsions can exceed the threshold value because of polydispersity of the droplets.[21–23] In this case, droplets can retain the spherical shape even at very high concentrations (Fig. 2).

Highly concentrated emulsions, as representatives of the family of multicomponent materials, have been considered in detail in a review [20] and a monograph;[24] therefore, there is no need to give a general view of emulsions, as well as possible compositions and properties of these systems.

This review includes two Sections. First, the structure and the concentration glass transition of concentrated emulsions will be discussed. Next, we will dwell on structure-dependent features of the rheological properties of highly concentrated emulsions including the formation of heterogeneous structures and flow instability.

II. The structure of highly concentrated dispersions

II.1. The glass transition of concentrated colloidal systems

A successive description and detailed analysis of the evolution of rheological properties on going from dilute to concentrated and then to highly concentrated emulsions can be found in a monograph.[24]

The key point is that at low concentrations, there is a complete analogy between the rheological properties of hard-sphere suspensions, deformable (soft)-media suspensions and emulsions.[24–28] However, the situation changes fundamentally as the volume concentration of dispersed particles increases and approaches the limiting value. Nevertheless, in this case the fundamental laws governing the behaviour of suspensions still hold for emulsions; therefore, it is appropriate to consider the formation of dense suspensions in more detail.

First of all, one should determine the type of the structure formed upon increase in the concentration of dispersed particles. The limit of the closest packing of spheres can be reached for a regular arrangement of structural elements. In this case, a face-centred cubic packing corresponding to a volume concentration $\varphi \approx 0.74$ is formed (Fig. 3).

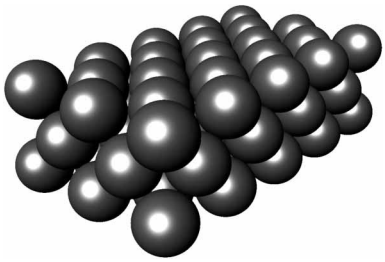


Figure 3. Structure with close face-centred cubic packing of spherical particles.

At optimum packing, one deals with a long-range order similar to that of atomic arrangement in a geometrically equivalent crystal. The formation of the close packing is an analogue to crystallization treated as phase transition. In most real systems, spheres are packed in space irregularly; nevertheless, this results in a close packing which precludes further free motion of dispersed spherical particles (Fig. 4). This structure is in essence a quasi-solid and it is reasonable to consider the concentration glass transition of the colloidal system as a reason for stiffening. This glass transition is physically analogous to the glass transition due to mobility suppression on cooling to a certain threshold temperature, namely, free motion of structural elements becomes impossible in both cases.

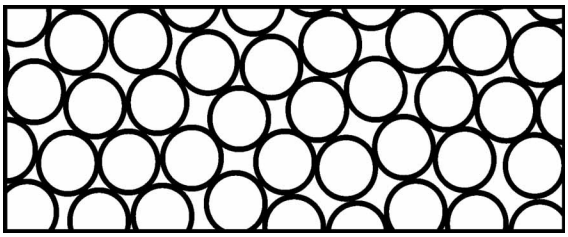


Figure 4. Irregular (defective) packing of spherical particles.

This conceptual approach to formation of close packings in colloidal systems is applicable to not only suspensions, but also emulsions. It follows that by the glass transition of dispersions is meant a situation where particles become confined in space at a certain limiting concentration, so their mobility becomes restricted due to the close packing of neighbouring spherical particles.[29–34]

When analyzing the structure and behaviour of soft colloidal systems, one should distinguish between the following limiting cases:

— dispersion of very small particles where the situation is governed by Brownian motion; and

— dispersion of rather large particles where the decisive role is played by hydrodynamic factors and inter-particle interactions due to various physical mechanisms, while Brownian motion is ignored.

These cases are distinguished according to the Péclet number (Pe)

$$\mathrm{Pe} = \frac{6\pi d^3 \eta \dot{\gamma}}{k_\mathrm{B} T} \qquad (1)$$

where d is the characteristic size of dispersed particles, η is the viscosity of the medium, $\dot{\gamma}$ is the shear rate, k_B is the Boltzmann constant and T is absolute temperature. At $Pe \ll 1$, the behaviour of a system is determined by Brownian (thermal) motion; at $Pe \gg 1$, the hydrodynamic factor dominates. From expression (1) it follows that the Péclet number is crucially dependent on the characteristic size of dispersed particles.

II.2. Microscopic structure of concentrated dispersions

The structure of soft dense dispersions (suspensions, foams, emulsions) should be considered as intrinsically metastable, spatially disordered system. This physical picture is basic to understanding the properties of highly concentrated dispersions.

The microscopic approach used in the studies of the behaviour of dense colloidal systems is based on analysis of interacting particles participating in Brownian motion.[35] It also allows one to consider the influence of shear deformations on the structure of the system and thus to study its rheological properties.[36,37] The microscopic approach was extended by taking account of the particle distribution function.[38–40] A complete analysis of this approach and conclusions concerning the rheology of colloidal dispersions of Brownian particles can be found in a review.[41] This model is based on the assumption that density fluctuation is the main type of fluctuation whose relaxation causes structural rearrangement and thus predetermines the viscoelastic properties of the medium. The model uses the simplest type of the equilibrium structure which depends on a single parameter, *viz*., the average effective packing (volume concentration) of spherical particles, which determines the characteristic size, time factor, characteristic frequency and shear rate.

Key results obtained using this model include predictions of peculiar features of the rheological properties of a dispersion approaching the glass transition limit. As should be expected, it was found that the viscoelastic properties of the dispersion depend strongly on the relative volume concentration

$$\varepsilon = \frac{\varphi - \varphi_c}{\varphi_c}$$

where φ_c is the critical volume concentration corresponding to the structural glass transition. Calculations were carried out assuming that $\varphi_c = 0.516$, which is much lower than the limiting value for a regular packing because the dispersion structure is treated as a disordered (amorphous) system. The dispersion is considered to be a glassy solid at $\varepsilon > 0$ and as liquid at $\varepsilon < 0$. Correspondingly, at small stresses ($\varepsilon > 0$), the system relaxes to a certain limiting (equilibrium) value of the elastic modulus, whereas at $\varepsilon < 0$, it relaxes to zero. Theory also predicts (i) a Newtonian flow at $\varepsilon < 0$ and (ii) a flow with an effective viscosity decreasing with increasing shear rate at $\varepsilon > 0$. In this sense, stress is a factor leading to 'melting' of the glass and corresponding acceleration of structural rearrangements.[42] Naturally, at $\varepsilon > 0$ there should exist a yield stress dependent on the structural parameter ε.[43,44]

At the same time, shear deformation can lead to ordering up to the formation of a crystal structure from spherical particles (probably, this can also be explained by enhancement of diffusional mobility), both the induction period and crystal growth rate being dependent on the shear rate.[45] This is analogous to a well-known influence of deformation on the crystallization rate of polymers (see, *e.g*., a recent publication [46]).

Usually, it is diffusion that was considered as the relaxation mechanism determining the rheological properties of concentrated dispersions. Based on these ideas, a generalized approach to the description of nonlinear viscosity of concentrated dispersions was proposed.[47] The characteristic times of transfer are determined by diffuse-wave spectroscopy. The flow curves of various soft systems including emulsions are governed by the minimum relaxation time τ_β, which separates two different diffusion modes of particles confined within the cage by the surrounding particles, namely, intra-cage transfer and escape from the cage. In turn, the τ_β value is normalized to the solvent-viscosity-to-elastic-modulus ratio. In this case, the overall flow curves of different soft media can be represented in a unified form using stress normalization to the yield stress and shear rate normalization to the τ_β value.

Experimental data underlying conclusions drawn in Ref. 47 were obtained for polyelectrolyte microgels swollen in water or in water + glycerol mixture. Pastes prepared from these systems contain soft, readily deformable particles and occupy an intermediate position between emulsions and suspensions. From this study,[47] it follows that nonlinear viscous properties of the systems in question are determined by the ratio between structure relaxation and influence of external factors (shear rate). Generally, this seems to be true, although particular values of parameters may appear to be different for different systems.

By and large, the theoretical considerations mentioned above give a reasonable correspondence between experimental data and results of calculations for the rheology of Brownian colloidal systems provided appropriately chosen fitting parameters.

An analysis of the role of the stiffness of spherical particles in structure formation and manifestation of the rheological properties of dispersions near the glass transition point is of fundamental importance when comparing the properties of suspensions and emulsions. Studies performed using a microscopic model based on analysis of Brownian motion [48] showed that the stiffness of structural elements plays a significant role only when considering the local environment of particles and short-term processes and that at long distances (estimated in the inter-particle distance units), the structure of the colloidal system becomes identical to the structure of dispersions with particles of different stiffness. The key parameter is the 'distance' to the glass transition point rather than the density of dispersion. The closer the system to the glass transition point the less pronounced the differences in the structure and behaviour between soft- and hard-particle dispersions.

It is essential that the relaxation times of dispersions obtained from calculations [48] based on analysis of the Brownian dynamics of particles or on the ideas of Newtonian mechanical inter-particle interactions appeared to be close. Hence the conclusions formulated above are valid for not only very small Brownian particles, but also larger non-Brownian particles. This result again demonstrates the lack of fundamental differences between the behaviour of emulsions and suspensions approaching the glass transition point but not above this point because emulsions can while

suspensions cannot exist above the limiting volume concentration.

Viscoelastic properties of dispersions of hard and soft spherical particles were studied experimentally by the large-amplitude oscillatory shear (LAOS) method in the concentration range near the glass transition point.[49] It was found that in the linear regime the elastic modulus of soft particles determined at maximum admissible concentrations exceeds that of hard particles. This is due to compression of soft particles similarly to the case for emulsions (see Fig. 1). The mechanical properties of soft spherical particles are determined by their permanent contact and deformation. The internal elastic modulus of soft particles is of the order of a few kPa,[50] being of the same order of magnitude as the experimentally observed elastic modulus of the entire dispersion. That is why the specific structural features of emulsions rather than suspensions begin to manifest themselves.

Studies by direct methods[51, 52] showed that the relaxation mechanisms of dispersions of hard and soft media differ in that structural rearrangement of the hard-sphere system occurs at much shorter distances than that of the soft-sphere system. Measurements of the centre-to-centre distances between soft particles in the dispersion also showed that the radius of the first coordination sphere decreases with increasing the concentration of particles, thus indicating compression of the particles. This difference manifests itself in different character of transition through the yield stress near the glass transition point.

However, thermal motion is insufficient for full structure relaxation[29] and one should consider motions occurring on a longer time scale (*e.g.*, rearrangement of droplets of the dispersed phase in emulsions). It is accepted that each mesotropic element is characterized by its own rheological properties, in particular, elastic energy accumulated until the yield stress. An analysis of the dynamics of mesotropic structural elements made it possible to predict the key rheological properties of colloidal systems near the glass transition point.[31] In particular, it was shown that these systems represent visco-plastic viscoelastic media. Correspondingly, there should exist a well-defined yield stress σ_Y and the region of non-Newtonian flow at stresses above σ_Y. The frequency dependences of components of the dynamic modulus [elastic modulus (G') and loss modulus (G'')] are given by exponential functions

$$G' \propto \omega^x \text{ and } G'' \propto \omega^x$$

with the exponent x lying between 1 and 2.

Thus, the model predicts that soft dense disperse media should exhibit viscoelastic properties. This approach remains to a great extent phenomenological because it is based on conditional structural ideas.

A simple model for viscoelastic properties of close-packed particles in disordered colloidal dispersions was reported.[53] This is a model of a mesotropic structure, which treats processes from the standpoint of interaction between mesomorphous structures rather than microscopic level of inter-particle interaction. Eventually, the model leads to a hierarchical organization of the system under study. The structure is considered as being composed of relatively small clusters. The fact that the elastic modulus of a disordered dispersion is much lower (by orders of magnitude) than that of a homogeneous structure can be explained by the influence of structural heterogeneity, such as clusters present (more exactly, inter-cluster interaction). The properties of a dispersion are thus governed by aggregates that are larger than the dispersed particles. It is these aggregates rather than dispersed particles that lose their mobility owing to the influence of the environment, *i.e.*, a structural glass transition occurs.[54] Thus, the model clearly discriminates the behaviour of a homogeneous structure (inter-particle interactions within clusters dominate) from that of a dispersion at a lower concentration (inter-cluster interactions dominate).

The trend to clustering depends strongly on short-range forces. Structural heterogeneity becomes more pronounced as the interaction strengthens. This is confirmed by the changes in the fluctuation distribution density in the bulk of the medium.[55]

Structural heterogeneity of concentrated colloidal systems is also clearly seen in the systems comprising particles of different size. For instance, there are two relaxation time scales for binary mixtures. Probably, they characterize the fact that actual fractions become size-separated rather than mixed.[56]

Since all types of colloidal systems are nonequilibrium, kinetic structural effects (changes in properties with time) are of importance for them. These effects characterize thixotropic phenomena of recovery of the broken deformed structure (see below) and are often called 'ageing'. The process occurring near the glass transition point is particularly pronounced for soft-particle dispersions whose properties resemble those of emulsions. Possible models for such systems include, *e.g.*, highly branched star-shaped polymers[28, 57] for which one has $G'' < G'$ at low frequencies in the linear viscoelasticity region. Ageing causes G' to increase and G'' to decrease, *i.e.*, the colloidal system stiffens. In the high-frequency region of the relaxation spectrum, ageing has no effect on the properties of the medium. Also, ageing exhibits a pronounced two-step character. As deformation increases (LAOS case), softening of the colloidal system occurs.

Nonequilibrium character of the structure formed upon a glass transition of a colloidal system leads to hysteresis in the temperature dependence of the elastic modulus measured on cooling and on heating and to an increase in the elastic modulus with time in the course of gel ageing.[58, 59] Of particular importance and interest is a direct correlation between changes in the characteristic scale length r_{loc} on which thermal motions are localized (it was determined experimentally by X-ray photon correlation spectroscopy) and the elastic modulus observed in the course of ageing of a colloidal system (gel). The correlation has the form[60]

$$\frac{G'R^3}{k_B T} = \frac{9\varphi R^2}{10\pi r_{loc}^2} \quad (2)$$

The left side of this equality is similar to the expression for the Péclet number, while the right side is the ratio of the average particle size R and the localization length of particles.

II.3. The structure and glass transition of non-Brownian dispersions

There is a huge array of publications on the structure and rheological properties of non-Brownian dispersions. They include the results of experimental studies, theoretical

research and computer simulation. In contrast to the problems considered in the preceding Section, in the case of rather large dispersed particles (at Pe $\gg$ 1) an analysis is based on the Stokes dynamics ignoring the contribution of Brownian motion. On going to concentrated systems one should first of all take into account inter-particle physicochemical interactions. This equally holds for hard-particle suspensions and emulsions because their rheological properties below some critical concentration corresponding to start of deformation (compression) of soft particles in emulsions are very similar, as was confirmed by many authors (see above).

The results of calculations of the behaviour of non-Brownian dispersions (see, *e.g.*, Ref. 61) are in reasonable agreement with experimental data.[62] Analogous calculations were also carried out for polydisperse systems and transition to high concentrations made it possible to prove the existence of glass transition (infinite increase in viscosity).[63, 64]

We are interested in considering the glass transition region. There exists a deformation glass transition of highly concentrated suspensions, which manifests itself in an increase in the effective viscosity with increasing shear rate followed by the formation of a slug (due to infinite increase in viscosity) characterized by the term 'jamming'.

An example of this type of behaviour of non-Brownian dispersions is shown in Fig. 5. Here, transition from flow to the deformation glass transition occurs in a narrow concentration range between 57.3% and 59.1%. Similar results were obtained for $CaCO_3$ dispersions in poly(ethylene glycol) where the deformation glass transition occurred in the concentration range between 30% and 31%.[66] At higher concentrations, flow is impossible, namely, the material either slips on the boundary surface[65, 67, 68] or breaks down as a result of macroscopic cracking. Shear banding[67, 69] (see below) in the region of structural glass transition is probable. It should also be noted that jamming (impossibility of flow due to the lack of mutual displacements of close-packed solid particles) depends on the rheological properties of the continuous medium.[70] Jamming also manifests itself in abrupt increase in the effective elastic modulus measured by the LAOS method as a threshold strain amplitude is reached.[71]

The flow of dense multicomponent materials near the glass transition point is always accompanied by strong dynamic fluctuations which in turn can be accompanied by the formation of transient spatial structures.[72]

Judging from the relaxation characteristic of a system measured by dynamic light scattering, emulsions as well as suspensions undergo a glass transition once the critical concentration is reached. However, there are some differences due to the fact that this method of investigation also 'senses' the possibility of deformation of liquid droplets.[73] Indeed, unlike hard-particle suspensions, emulsions are characterized by the yield stress at any (arbitrarily high) concentration; above the yield stress, flow is still possible at rather high stresses. This is the fundamental difference between hard- and soft-particle suspensions including emulsions.

Compression of emulsion droplets beyond the limit of the closest packing of spherical particles, φ^*, belongs to crucially important factors determining their rheological properties. Compression of droplets in highly concentrated emulsions is basic to the Princen model,[74, 75] which explains the elastic properties of the systems in question as follows. To compress droplets, an external pressure should be applied. The pressure work resulting in compression by the value shown by small arrows in Fig. 6 is compensated by the energy stored due to the increase in the droplet surface area upon the change in their shape from spherical to polyhedral.

The energy balance is given by

$$-\Pi \mathrm{d}V = \Gamma \mathrm{d}S \tag{3}$$

This equation shows that the work of osmotic pressure Π leading to the change in the volume $\mathrm{d}V$ is equivalent to the change in the surface energy, *i.e.*, the product of the surface tension Γ by the change in the surface area $\mathrm{d}S$. This is the basic equation for the model of droplet compression as the reason for the appearance of elastic properties of the system.

Eventually, the static shear modulus (G) is:

$$G = 1.769 \frac{\Gamma}{R_{32}} \varphi^{1/3} (\varphi - 0.712) \tag{4}$$

where R_{32} is the average radius of droplets (the ratio of the total volume to the total surface area of droplets in the polydisperse system). Clearly, in this model the elastic

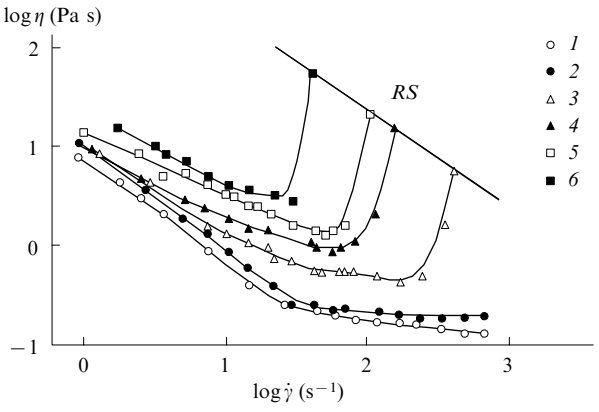


Figure 5. Flow curves of silica dispersion (particles 1 μm in diameter).[65]
c (%): 56.0 (*1*), 57.3 (*2*), 59.1 (*3*), 59.9 (*4*), 60.5 (*5*) and 61.1 (*6*); *RS* stands for slip region.

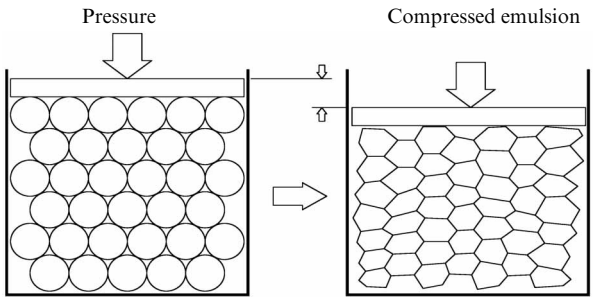


Figure 6. Scheme illustrating structure formation in highly concentrated emulsion.

properties appear only at concentrations above the limit of close packing, $\varphi^* = 0.712$. The model was further developed and theoretically substantiated.[76–79]

According to Mason *et al.*,[77] the concentration dependence of the static shear modulus is somewhat different, namely,

$$G \propto \varphi^2(\varphi - \varphi^*) \quad (5)$$

but G is still normalized to Γ/R_{32}.

Two predictions made by this model can be directly checked in the experiment. There are (i) the form of the concentration dependence of the shear modulus and (ii) its proportionality to the reciprocal average droplet size (R_{32}^{-1}).

The theoretical models considered above unambiguously relate the nature of elastic properties of highly concentrated emulsions to the deformation of droplets upon compression above the limit of the closest packing. Meanwhile, an important role can be played by the interaction between droplets (or interfacial layers). An analysis revealed a significant role of this interaction in evaluating the elastic properties of emulsions and first of all in the character of the droplet size dependence of the shear modulus.

Inter-droplet interactions can be of different nature from pure mechanical interaction leading to development of contact stress[80,81] to physicochemical interactions of different origin.[82–84] It should be noted that these interactions produce forces that are directed normal to the surface of a droplet, whereas the surface tension acts in the direction tangent to the droplet surface.

The role of physicochemical interactions in the manifestation of elastic properties of highly concentrated emulsions is clearly demonstrated in the studies of the properties of highly concentrated binary mixtures with no droplet compression.[22,23] The flow curves and frequency dependences of the elastic modulus are presented in Fig. 7. One can see the formation of a solid-like structure with a number of characteristic features, *viz.*, the existence of the yield stress, the frequency independent behaviour of the elastic modulus (see items *1–5* in Fig. 7 *b*) provided no droplet compression (see Fig. 2).

A theoretical analysis carried out taking into account the contributions of the increase in surface energy due to droplet compression and the energy of inter-droplet interaction to the elastic properties of highly concentrated dispersions was reported.[85–87] It was found that the results obtained with inclusion of the effect of inter-droplet interaction significantly deviate from those predicted by the model based only on the decisive role of changes in the droplet surface area upon compression. As an example, Fig. 8 presents the results of calculations. As can be seen, the elastic modulus values at the same concentration of dispersed droplets differ from those predicted by the theory of surface tension, being strongly dependent on the droplet size.[85] In other words, one can expect significant deviations from linearity of the dependence of the elastic modulus on the reciprocal droplet radius depending on the character of inter-droplet interaction in the interfacial layer.

According to calculations, the concentration dependences of the elastic modulus above the limit of the closest packing may have different shapes determined by the peculiar features of the mutual arrangement of deformable spherical particles in space.[85] In the general case, this dependence obeys a scaling equation

$$G \propto \varphi^{\alpha}(\varphi - \varphi^*)^{\beta} \quad (6)$$

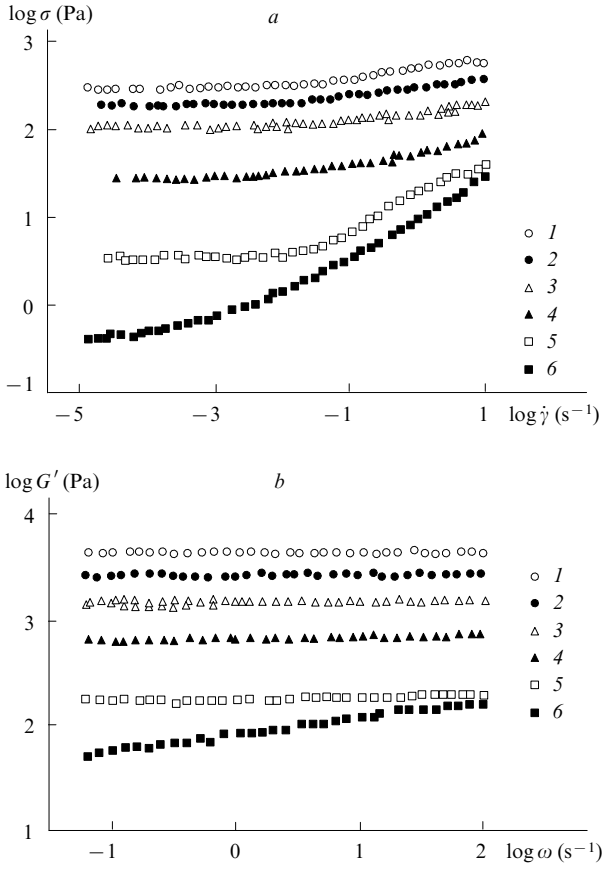


Figure 7. Flow curves (*a*) and frequency dependences of elastic modulus (*b*) for binary mixtures of monodisperse emulsions containing uncompressed droplets.[22]
Large-droplet/small-droplet fraction ratio: 0 : 100 (*1*), 20 : 80 (*2*), 40 : 60 (*3*), 60 : 40 (*4*), 80 : 20 (*5*) and 100 : 0 (*6*).

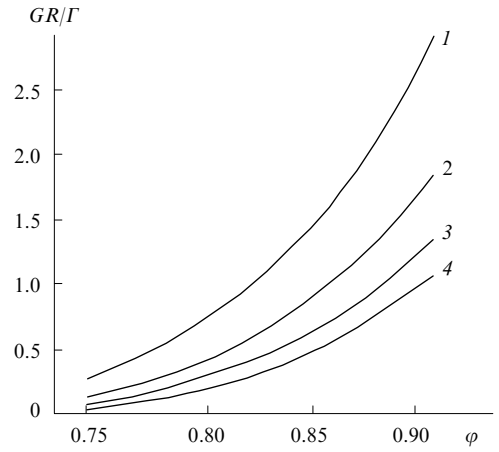


Figure 8. Scaled elastic modulus plotted *vs.* droplet size.[85]
Droplet diameter/μm: 0.5 (*1*), 1 (*2*), 2 (*3*) and 4 (*4*).
G is the elastic modulus and R is the characteristic size of droplets.

where the exponents α and β depend on the geometry used in the model for spatial arrangement of compressed droplets.

Particular experimental data and their correspondence to or deviations from theoretical predictions will be considered below.

II.4. Particle orientation in flow and the onset of dynamic structure

Fast deformation of multicomponent dispersions is accompanied by various nonlinear effects. Some of them follow from the isotropic structural models for concentrated dispersions of close-packed particles and were analyzed above. However, there is one more group of experimentally observed phenomena that have been poorly studied theoretically. These are anisotropy of the structure and properties of the systems in question. Anisotropy, namely, anisotropy of the free space distribution, appears in the formation of disordered structure at rather high volume concentrations of spherical particles.[88] It is most pronounced form in the case of shear deformation owing to inhomogeneous distribution of particles in the medium and their orientation in flow. Structural anisotropy, first of all and to a greater extent, manifests itself in the formation of chain structures rather than in the appearance of inhomogeneous concentration profile.[89–92] However, the question as to the bulk or wall-induced nature of the effect remains debatable. It was assumed that it is limitations that cause migration of dispersed particles perpendicular to the flow direction,[93,94] which is particularly characteristic of strained flow.[95] Such a migration can be due to *e.g.*, the action of elastic forces in the medium on dispersed particles under shear flow.[96] A more general reason for the appearance of anisotropy under shear flow consists in that shear deformation influences the interaction between Brownian particles in the flow provided that the shear rate is above some critical value.[97]

Shear flow of emulsions is accompanied by transformation of spherical polydisperse droplets to ellipsoidal ones (Fig. 9), the deformation being first of all characteristic of large droplets. Clearly, the structure being formed will also be anisotropic.

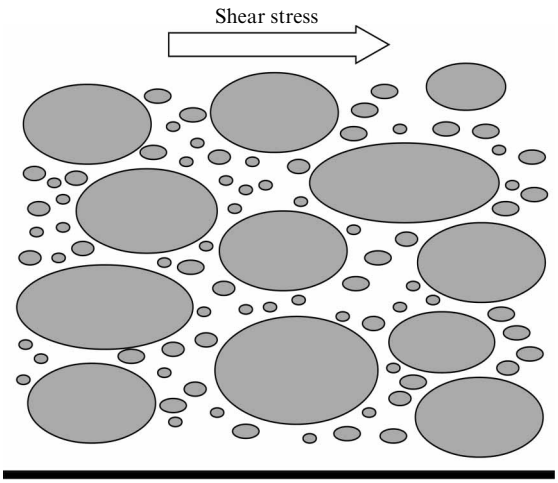


Figure 9. Deformation of large droplets under shear flow of polydisperse emulsion resulting in the formation of anisotropic structures.

An analysis of the breakup (emulsification) of anisodiametric liquid droplets under shear deformations as a step following an increase in the aspect ratio of flowing particles goes beyond the scope of this review. Mention may only be made that further increase in the aspect ratio of droplets leads to formation of bottlenecks and eventually large droplets break up into smaller ones (see Section 2.3 in Ref. 24).

The results of computer simulation of the dynamics of dispersions containing particles of different size show that flow should be accompanied by not only the appearance of anisotropy, but also segregation of particles.[98]

Naturally, anisotropy appears in shear flow of aspherical particles that undergo flow-induced orientation;[99] this seems to be quite obvious. The appearance of anisotropy in concentrated dispersions is an experimentally observed fact (it was also analyzed using computer simulation); however, induced anisotropy of the properties of such a medium has almost not been discussed in the literature.

III. Rheology of highly concentrated emulsions

III.1. Highly concentrated emulsions as gels

Highly concentrated emulsions belong to complex fluids. These systems are characterized by manifestation of various rheological effects including closely related elastic properties of the fluids and nonlinear mechanical behaviour. Meanwhile, elastic properties of emulsions may appear at concentrations much lower than the limit of close packing. This is due to the formation of worm-like surfactant micelles that form nanoscale structural aggregates. They behave like flexible-chain macromolecules. Similarly to viscoelastic polymer solutions, surfactant solutions (if a surfactant dispersion can be treated as solution) form a network of entanglements.[18,100–103] These systems are characterized by a single relaxation time, *i.e.*, they mainly behave as Maxwellian fluids; deviations from the simplest model for viscoelastic fluid are observed only in the high-frequency limit.[103] However, even micellar viscoelastic (colloidal) solutions (precursors of emulsions) may exhibit some features characteristic of complex fluids, namely and first of all, viscoelastic phenomena and flow heterogeneity in the form of shear bands [103–105] (see below).

Structure formation in colloidal systems approaching the concentration glass transition point and in 'compressed' emulsions above that point unavoidably leads to a solid-like behaviour of these materials. This manifests itself in two main effects:

— in the linear region of mechanical behaviour, at low stress, where the structure of the material remains unchanged, the elastic modulus is independent of frequency and the loss modulus is much lower than the elastic modulus; these properties are characteristic of solids (or solid-like state of materials);

— at higher stress (or deformation rate), the structure of the material breaks up; this allows irreversible deformations (flow) to occur, *i.e.*, one deals with transition from the solid-like state to a liquid state; this transition is observed at some stress value called the yield stress (σ_Y).

A colloidal system which exhibits no flow behaviour when unloaded or under low stress can be called a gel. This definition is valid for systems that underwent a concentra-

tion glass transition (see above), *i.e.*, they lost the flow ability due to mobility loss by structural elements upon the formation of a 'trap' by the neighbouring elements. Note that structure formation in emulsions exhibiting the properties of gels can occur not only on glass transition of the close packing of droplets, but also at very low concentrations of the dispersed phase owing to formation of physicochemical bonds between droplets. The possibility of existence of such a solid-like, gel-like structure in dilute emulsions at droplet concentrations $\varphi \approx 10^{-3}$ was established by direct physical methods [106] and explained by the formation of bonds between clusters that restrict the mobility of structural elements. Similar data obtained experimentally for close concentrations were also explained by the formation of a supramolecular structure.[107–109]

One can assume the existence of two types of gel with different connectivity of structural elements. If chemical bonds between structural elements are rather strong, raising the strain will cause the gel to break up mechanically (no flow!). If bonds originate from relatively weak physical interactions, structure breakup will allow structural elements to execute some motions provided no loss of the continuity of the medium, *i.e.*, it will lead to flow. Structural elements may include aggregates of different size from individual molecules to dispersed particles in emulsions and rather large associates involved in co-operative motion.

The evolution of the transition from solution to gels is illustrated in Fig. 10. A solution of low viscosity gradually transforms to a gel characterized by the yield stress σ_Y, the structure stiffens with gelation time but still does not lose the flow ability at stresses above σ_Y. Eventually, the gel loses the flow ability and breaks up as the limiting stress σ_{lim} is reached.

A physically similar sol–gel transition occurs in the case of cross-linking polymerization leading to formation of a gel. This is confirmed by a monotonic increase in the elastic modulus which goes to a plateau.[110] Similar experimental data were obtained for various gel-forming systems (*e.g.*, gelatin hydrogels [111]).

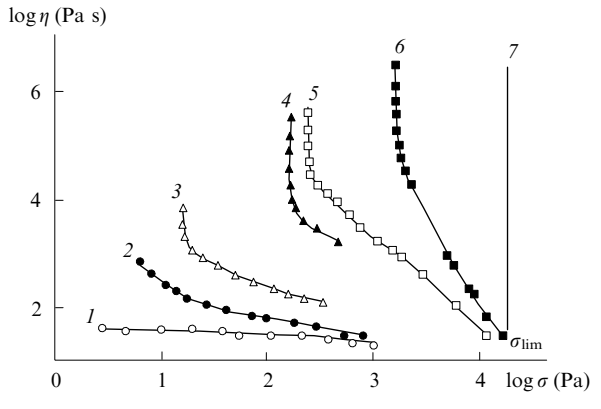


Figure 10. Changes in rheological properties of material on going from polysulfone solution in DMSO + water mixture to a flowing yield-stress gel and then to non-flowing gel which breaks up at $\sigma = \sigma_{lim}$.
Gelation time /h: < 22 (*1*), 29 (*2*), 32 (*3*), 48 (*4*), 53 (*5*), 72 (*6*) and > 72 (*7*).

III.2. Solid-like state of highly concentrated emulsions

Below the yield stress, highly concentrated emulsions, like many other multicomponent materials (suspensions, foams, filled polymers), behave as solid-like materials. This is due to the existence of a more or less rigid stable structure which does not change with time. From the standpoint of rheology, in this case flow should be impossible and the elastic modulus should be frequency independent.

A key experimental proof of the existence of a highly concentrated emulsion in the solid-like state (*i.e.*, below the yield stress) is frequency independence of the elastic modulus, which was experimentally observed in various studies of different emulsions (see Refs 77 and 112–116). An example for w/o inverse emulsions is shown in Fig. 11.

As can be seen, the elastic modulus remains unchanged over a very wide frequency range spanning at least four decimal orders of magnitude, while the loss modulus (its frequency dependences are not shown) is much lower than the elastic modulus, which indeed indicates a solid-like state of the emulsion. At higher frequencies, the elastic modulus increases due to gradual 'freezing' of low-frequency relaxation.[24, 78]

Elastic properties of an emulsion depend on the concentration and size of dispersed droplets. In our analysis of theoretical approaches to the determination of these dependences we pointed out that if elastic properties are governed by the compression of droplets upon transition

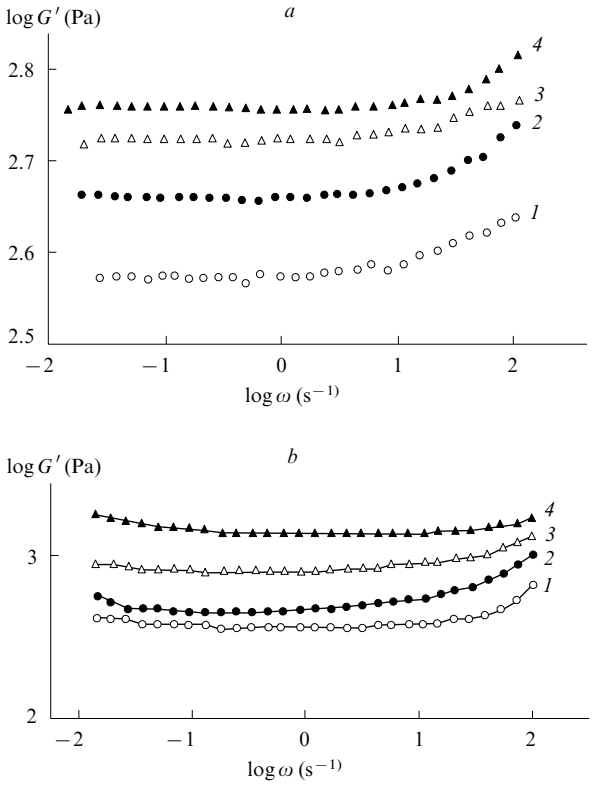


Figure 11. Frequency dependences of elastic modulus of w/o emulsions;[114]
(*a*) emulsions with different concentrations of aqueous phase (%): 92 (*1*), 93 (*2*), 94 (*3*) and 95 (*4*); (*b*) emulsions with the same concentration of aqueous phase (91%) and different droplet size /μm: 20.5 (*1*), 14 (*2*), 11 (*3*) and 8.2 (*4*).

through the close-packing limit, the elastic modulus should be proportional to the reciprocal droplet radius (see above). However, numerous experimental data demonstrate that the elastic modulus can depend on the particle size in different manner.[114, 116–123] Various explanations for these deviations are possible; however, a most probable common reason for different values of the exponent n in the $G(R^{-n})$ dependence is the interaction between droplets (or interfacial layers), as has been shown recently.[85–87] In particular, if the normal force acting between droplets obeys a formally van-der-Waals type equation, one can expect a quadratic dependence of the elastic modulus on the reciprocal droplet size (see Refs 114, 117–119, 122 and Fig. 12).

As to the concentration dependence of the elastic modulus of emulsions above the limit of close packing, the concentration range under study is rather narrow, so the exact form of the $G(\varphi)$ dependence is difficult to determine taking into account the limits of possible measurement errors. In any case, linear approximation using the Princen equation may appear to be sufficient to generalize experimental data. A relevant example is presented in Fig. 13. Here, the elastic modulus normalized to $\varphi^{1/3}$ is indeed proportional to the difference $(\varphi - \varphi^*)$ and elastic properties appear at the critical concentration $\varphi = 0.71$.

Figure 13 illustrates the situation where an emulsion is formed by droplets characterized by monomodal (or rather narrow) size distribution. The case for bimodal particle size distribution is more interesting and informative, because the elastic modulus depends not only on the mean particle size, but also on the large-droplet/small-droplet fraction ratio. An example is shown in Fig. 14 where the outermost points correspond to monomodal particle size distributions and, since the right outermost point corresponds to large droplets, while the left outermost point corresponds to small droplets, the elastic modulus decreases with increasing droplet size (see Fig. 13). However, at a certain point the elastic modulus abruptly decreases, thus deviating from the overall dependence on the mean droplet size. Seemingly, this effect is related to the ratio of the contributions of (i) droplet deformation upon compression and (ii) inter-droplet interaction (as function of the large-droplet/small-droplet fraction ratio) to elastic properties.

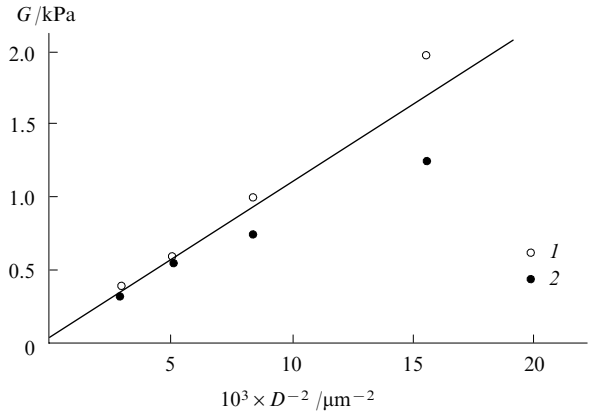


Figure 12. Elastic modulus [determined from the height of the plateau in the frequency dependence of elastic modulus G'_{plateau} (*1*) and from elastic deformation G_{recoil} (*2*)] plotted *vs.* squared reciprocal droplet diameter for w/o emulsions with a volume concentration of 91%.[119]

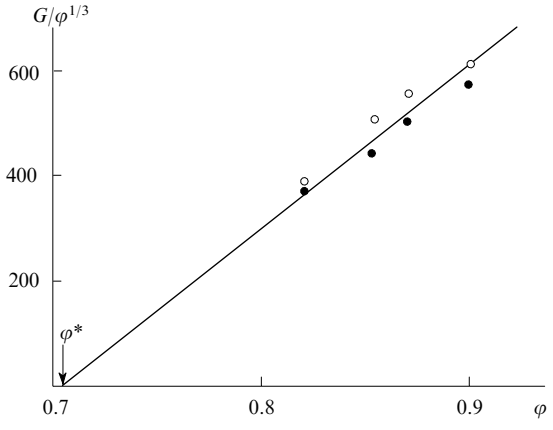


Figure 13. Concentration dependence of elastic modulus of a w/o emulsion.[119]
Mean droplet size is 16 μm. Two types of circles correspond to different surfactants.

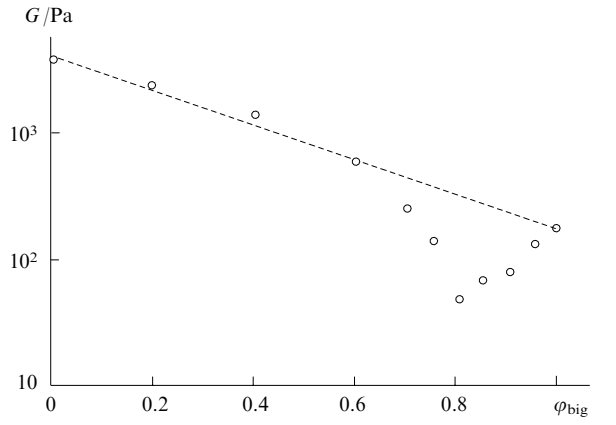


Figure 14. Elastic modulus plotted *vs.* proportion of large particles (φ_{big}) at the same overall content of aqueous phase in w/o emulsions.[23]

Thus, in the region of the solid-like state the elastic modulus is independent of frequency. However, many authors assumed that flow below the yield stress is possible, although at very high viscosity, and proceeds by some different mechanism than the flow of a system with broken internal structure. The 'viscosity of the system with unbroken structure' (here we follow P A Rebinder) can be very high, namely, of the order of 10^9–10^{12} Pa s, which corresponds to the viscosity of real glasses. This seemed to be quite logical because below the yield stress a dispersion (suspension or emulsion) exists in the structural glass state (see Section II). Then, the overall flow curve, *i.e.*, the dependence of viscosity on the shear stress measured in a wide stress range should look as shown in Fig. 15.

Interestingly, in the studies of the overall flow curve the viscosity η_0 below the yield stress was almost independent of the concentration of dispersed phase and temperature.

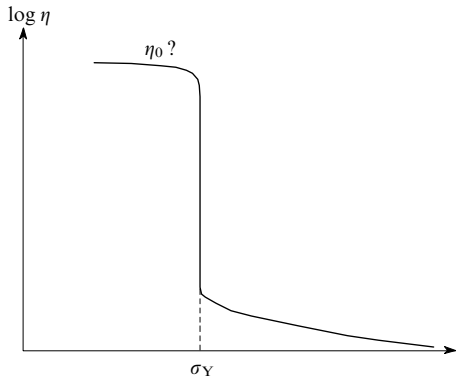


Figure 15. Entire flow curve. The question mark denotes ambiguity of the determination of the maximum Newtonian viscosity for visco-plastic multicomponent materials.

Seemingly, these results confirm the idea of a specific physical mechanism of flow below the yield stress.

An example of such a contradiction for highly concentrated emulsions, *viz*., independence of the elastic modulus of frequency and the results of measurements of the maximum Newtonian viscosity in the region of solid-like state (below the yield stress) is shown in Fig. 16.

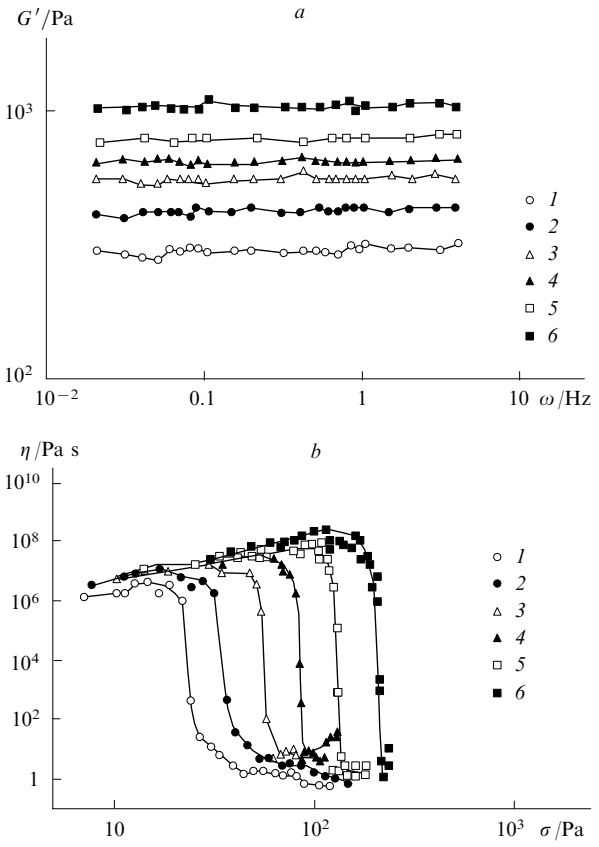


Figure 16. Frequency dependences of dynamic modulus (*a*) and the flow curves (*b*) of a model highly concentrated o/w emulsion.
The plots are constructed using reconstructed data taken from Ref. 124;
φ (%): 78.55 (*1*), 81.8 (*2*), 86.05 (*3*), 88.8 (*4*), 91.78 (*5*) and 94.02 (*6*).

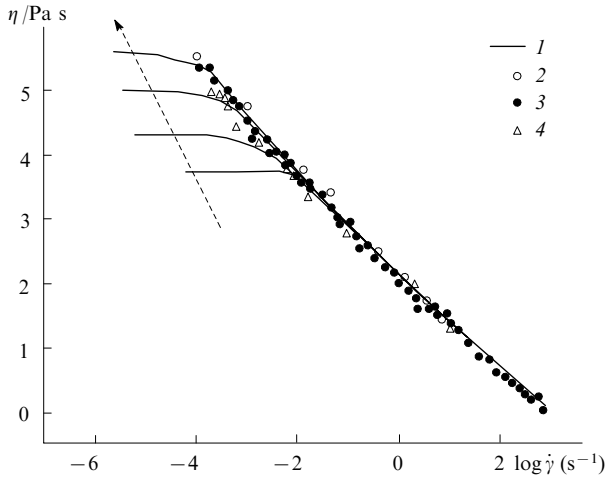


Figure 17. Flow curves of highly concentrated emulsion obtained at different shear rate sweep ramp.[117]
Measurement conditions: upward sweep (*1*); steady flow (*2*); downward sweep (*3*) and creep (*4*). Arrow denotes the downward sweep direction.

As can be seen, frequency independence of the elastic modulus unambiguously indicates a solid-like character of the structure of the highly concentrated emulsion (see Fig. 16 *a*), but the elastic modulus depends on the concentration of the dispersed phase. However, the apparent maximum Newtonian viscosity is almost independent of concentration. Here, we use the term 'apparent' not accidentally because the situation is not too simple and obvious, which is symbolically denoted by a question mark in Fig. 15.

Flow curve measurements carried out for highly concentrated emulsions at different shear rate sweep † revealed an increase in the maximum viscosity (of apparently unbroken structure) with decreasing shear rate ramp (Fig. 17), *i.e*., the longer the stress duration the higher the maximum viscosity.[117] The flow curve is independent of the deformation mode (points in the downward branch of the flow curve), whereas the initial (horizontal) portion of the flow curve corresponding to the maximum viscosity depends strongly on the stress duration. In essence, this is just manifestation of the thixotropy of the medium. One can suggest that in the limiting case (infinitely long stress) the region of the maximum viscosity should vanish and the running stress should tend to the yield stress.

The concept which does not use the notion 'limiting viscosity' of unbroken structure and where stresses tend to the yield stress was clearly and consistently reported recently.[125, 126] It was shown that the approach is valid for a wide range of visco-plastic disperse media. The conclusions were formulated peremptorily, *viz*., there is no steady state flows below the yield stress and the values of the maximum Newtonian viscosity below the yield stress reported by many authors are artifacts.

† Shear rate sweep measurements are a conventional experimental method for obtaining a flow curve. The procedure involves a stepwise increase in shear rate at variable shear rate ramp (step duration).

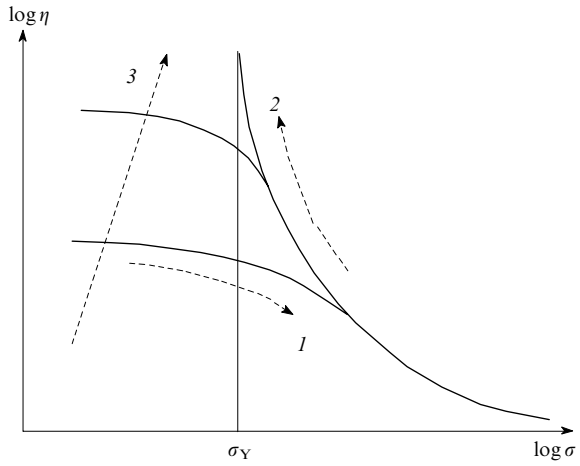


Figure 18. Illustration of transition from the apparent maximum Newtonian viscosity to the yield stress.
Upward (*1*) or downward (*2*) shear rate sweep; arrow *3* denotes the direction of downward shear rate sweep.

In this respect, the data for a highly concentrated emulsion shown in Fig. 17 can be explained using the scheme presented in Fig. 18. Thus, we deal with thixotropy of the structure and properties of emulsions which manifest themselves below the yield stress. The lack of steady flow below the yield stress and gradual transition to the yield stress are illustrated more clealy by the results of long-term measurements of the apparent viscosity at constant shear rate rather than in the shear rate sweep mode. Corresponding experimental data are shown in Fig. 19 *a*. Clearly, an infinite increase in viscosity is observed and no steady flow in the region of the solid-like state of gel is possible. A similar situation is also characteristic of the region of the solid-like state of colloidal suspensions.[127, 128]

The absence of the region of Newtonian flow for the solid-like state of colloidal systems cannot be extended to true polymer solutions where this region does exist and is reached after a rather short transient period (Fig. 19 *b*). It seems that the boundary between a true solution and gel lies near Pe ~ 1, *i.e.*, corresponds to the case where thermal motion can break up structural fluctuations in solution or the energy of structure-forming bonds exceeds $k_B T$.

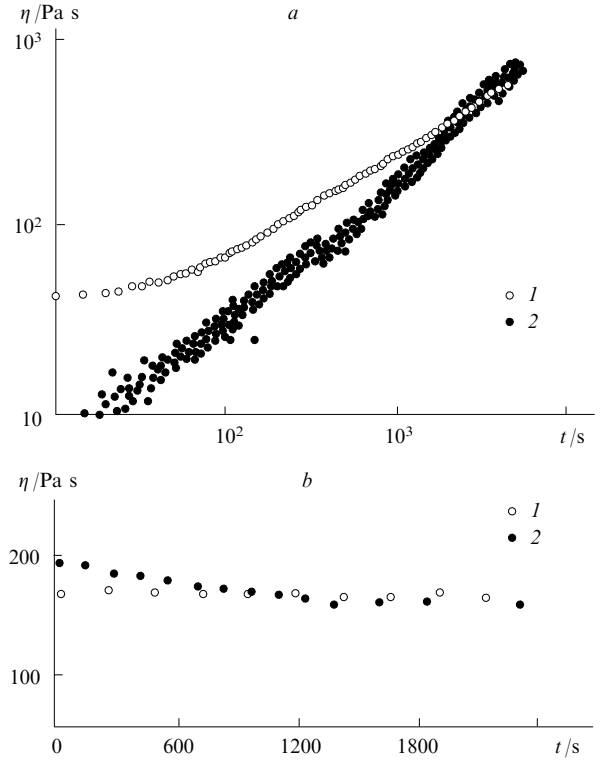


Figure 19. Increase in viscosity at a constant shear stress of 0.01 Pa (*1*) or at a shear rate of 10^{-4} s^{-1} (*2*) in the region of solid-like state of a polyacrylonitrile (PAN) soft gel in dimethyl slfoxide (DMSO) (*a*) and PAN solution in DMSO (*b*).[108]

III.3. Transition through the yield stress

A discussion concerning the existence and the possibility of physically correct definition of the yield stress began long ago. To ask the question whether the yield stress exists,[129] it should be defined unambiguously.

The notion 'yield stress' was introduced by Bingham,[130] who studied the rheological properties of paints and proposed to distinguish between the region of low stresses at which paints do not flow and the region of high stress at which paints behave as fluids. The boundary between these two states was called the yield stress. Media exhibiting this property are called visco-plastic ones.

III.3.a. The yield stress: determination from flow curves

Interpretation of the yield stress as transition from the solid-like state to the liquid at a particular shear stress can be formalized mathematically with ease. Graphically, the yield stress corresponds to the vertical line in the plot of effective viscosity *vs.* shear stress (Fig. 15).

However, real situations are not so simple. This is clearly seen in the flow curves of an emulsion measured at different concentrations of the dispersed liquid particles (Fig. 20). These experimental data characterize a transition from non-Newtonian behaviour of the emulsion to the appearance of the yield stress. Nevertheless, it is reasonable to ask what is the type of the media, namely, non-Newtonian or visco-plastic, described by the flow curves of

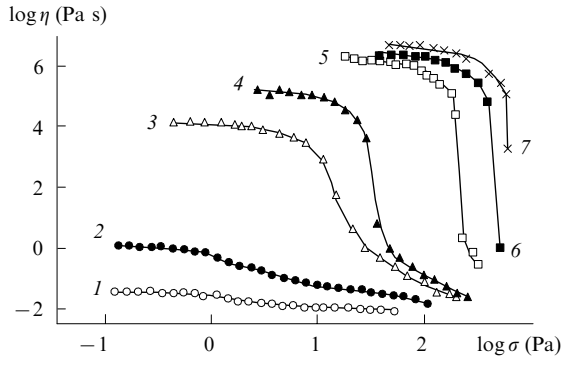


Figure 20. Changes in the shape of flow curves with increasing volume concentration of aqueous phase of a w/o emulsion (transition from viscous to visco-plastic flow).
Concentration (%): 60 (*1*), 65 (*2*), 67.5 (*3*), 70 (*4*), 75 (*5*), 80 (*6*) and 85 (*7*).

emulsions with 67.5%–70% concentrations of dispersed particles?

In determining the yield stress, problems arise in the case of gradual decrease in the effective viscosity with increasing shear stress rather than abrupt viscosity drop (the plots corresponding to concentrations of 67.5%–70% in Fig. 20 *vs*. the plot in Fig. 15, respectively); in the former situation, it is impossible to choose a single 'critical' point.

Yet another problem is to elucidate whether the yield stress is a characteristic point, *i.e*., whether the transition in question is 'equilibrium' and, correspondingly, whether the same σ_Y value can be obtained on going to the yield stress from the left and from the right. If the structure formed by dispersed particles is, *e.g*., brittle, the σ_Y value can be treated as a constant of the material. However, many systems (in particular, emulsions) exhibit thixotropy, *i.e*., a slow recovery of the structure broken under the action of high stress. Of course, thixotropy of the properties of materials manifests itself in different deformation modes.[131] In the preceding Section we considered thixotropic phenomena occurring below the yield stress (*i.e*., at low stresses) and related to transformations in the solid-like state of the material. Now we will dwell on the transition through the yield stress, which can also be related to changes in the structure (responsible for the strength of the material and for the existence of the yield stress).

Since recovery of the broken structure upon transition through the yield stress from the left may be time-dependent, two parameters were introduced to characterize the overall process. These are the static yield stress characterizing the transition from the solid-like behaviour to the liquid and the dynamic yield stress characterizing the reverse transition.[132] It was proposed to distinguish between two types of visco-plastic media, *viz*., media with thixotropic and non-thixotropic (or simple) transition through the yield stress.[133] Thus, the yield stress in simple visco-plastic media is indeed a constant of the material, whereas non-thixotropic visco-plastic media are characterized by ambiguity (bifurcation) of flow curves and the yield stress becomes dependent on the deformation prehistory.

Clearly, a bifurcation corresponding to two different states of a material causes the appearance of shear bands (for more detail, see Section III.4.d) co-existing at the same stress.[133, 134]

Examples of the yield stress thixotropy for two different systems, a soft gel formed in a cysteine colloidal solution and a dispersion of ice in aqueous solution of saccharose at -18 °C, are presented in Fig. 21. Before the shear deformation, there exists a region of the maximum Newtonian viscosity (for 'unbroken structure'). As the shear stress increases, the viscosity abruptly decreases by a factor of 10^6 in the former and more than 10^3 in the latter case. Eventually, the region of non-Newtonian flow is observed. As the shear stress decreases, the yield stress is not observed at all. However, structure recovery upon unloading occurs almost instantaneously in the former case and only after long-term (14-h) 'rest' in the latter case. This is a classical example of non-thixotropic visco-plastic medium.

In addition to rheological indications of structural transformations related to thixotropy of a colloidal system, direct experimental observations of structural changes in the material upon deformation and at 'rest' were reported.[136]

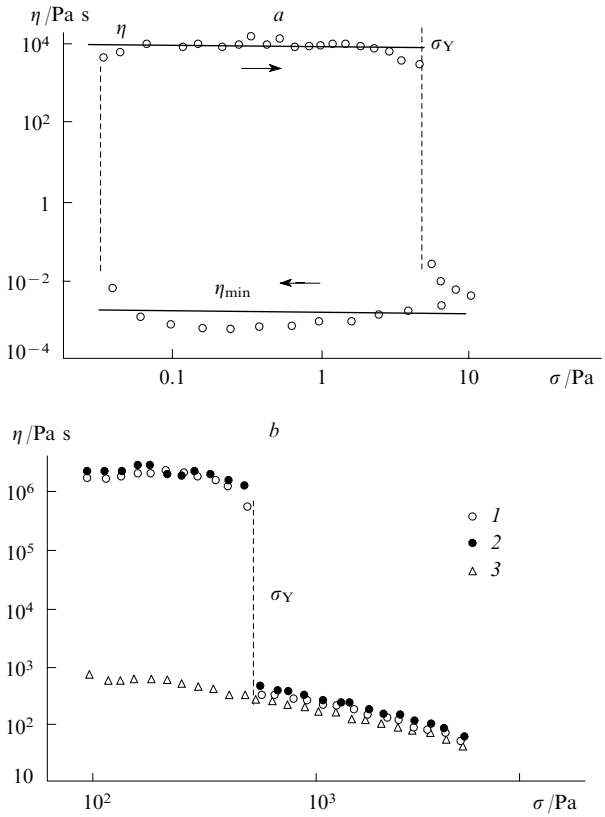


Figure 21. Thixotropy of the yield stress of a gel formed in cysteine colloidal solution (*a*) [108] and in ice dispersion in aqueous saccharose solution at -18 °C (*b*);[135]
(*b*) after recovery for 14 h (*1*), prior to deformation (*2*) and after deformation (*3*).

Finally, a non-thixotropic character of the transition through the yield stress is confirmed by the data, according to which the microstructures formed (and then being broken) in emulsions can be characterized by a kind of a lifetime. Figure 22 shows how the flow in road asphalt (multicomponent system containing liquid and solid structural elements) develops. The lower the stress applied the

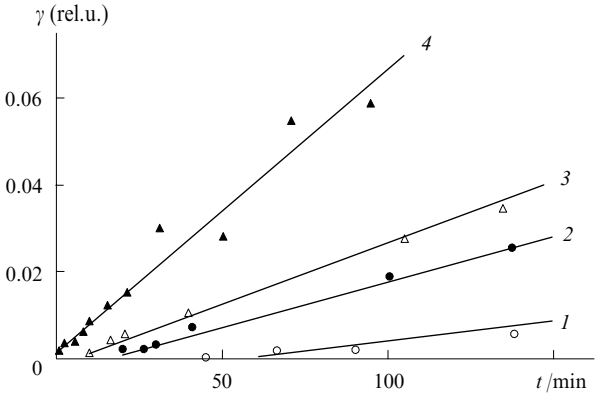


Figure 22. Evolution of flow deformation at different constant stress in road asphalt.
σ, Pa: 200 (*1*), 500 (*2*), 1000 (*3*) and 2000 (*4*).

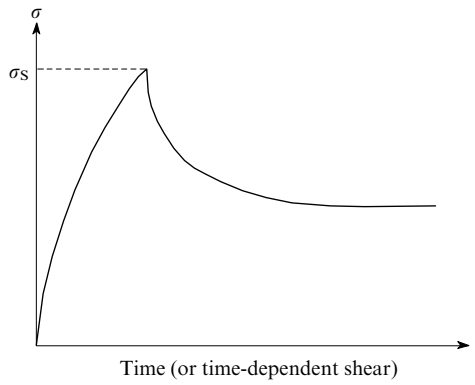


Figure 23. Stress σ in pre-steady region of shear deformation plotted *vs.* time or time-dependent shear.

longer the time before the start of flow (*i.e.*, the lifetime of the material). Similar experimental data were also reported in other studies.[137, 138] The dependence of the lifetime of the colloidal structure on the shear stress σ is rather mild. For the data shown in Fig. 23 it has the form

$$t^* \propto -\ln\sigma$$

or [138]

$$\log t^* \propto \sigma^{-1}$$

Various generalized models for a visco-plastic medium with variable yield stress have been analyzed in a review,[131] which also includes a large number of relevant references. Thixotropic character of transition through the yield stress under shear deformation is described by a kinetic equation for a non-specified 'structural parameter' λ.

A simple linear equation proposed for λ

$$\frac{d\lambda}{dt} = \frac{1}{\theta} - \alpha\dot{\gamma}\lambda \tag{7}$$

includes the temporal characteristic of thixotropy, namely, the characteristic time of the spontaneous evolution of the microstructure θ (see Refs 139 and 140) and the dependence of viscosity on the shear rate

$$\eta = \eta_0(1 + \beta\lambda\dot{\gamma})^n \tag{8}$$

where α, β and n are system-dependent constants. The character of the behaviour of the medium under study is determined by the value of the parameter n:

— $n = 1$ corresponds to a simple visco-plastic medium and

— $n > 1$ corresponds to bifurcation of the flow curves.

A generalized kinetic equation for the structural parameter λ has the form

$$\frac{d\lambda}{dt} = k_1\dot{\gamma}^a\lambda^b - k_2\dot{\gamma}^c(1-\gamma)^d \tag{9}$$

where k_1 and k_2 are the rate constants for structure breakup and recovery, respectively; the exponents a, b, c and d are empirical parameters; their values can be determined using a particular model.

In many well-known models the yield stress and viscosity are related to the structural parameter λ (see above) by simple (in the simplest case, linear) expressions. A detailed review of the available models and relevant references to numerous original studies can be found in a review.[131]

Thixotropic character of the yield stress was established for various materials, in particular, emulsions.[141]

III.3.b. The yield stress: determination from transient rheological curves

Based on the interpretation of the yield stress as a critical parameter responsible for transition of the medium from the solid to the liquid state, many authors proposed estimating this quantity from the characteristic points of transient rheological curves.

For instance, one can analyze the dependence of the shear stress on time (or on time-dependent shear deformation) at a constant shear rate (Fig. 23). In the early studies on colloidal systems and polymer solutions and melts, reported by researchers belonging to the scientific schools headed by G V Vinogradov, A A Trapeznikov, as well as by other researchers, the maximum in the pre-steady portion of the curve of stress development at constant shear rate was interpreted in such a manner that the σ_S value corresponds to breakup of the solid-like structure and subsequent transition to flow is possible. In this sense, the σ_S value was treated as an analogue of the yield stress which characterizes the strength of the structure. It should be noted that both σ_S and corresponding shear stress depend on the shear rate.

Recently, LAOS has been a popular method of investigation of rheological properties of any complex fluids including concentrated emulsions. There is considerable literature on the topic, but its analysis goes beyond the scope of this review. Relevant examples of recent publications are provided by Refs 142–147 (see also references cited therein). Determination of the yield stress from the amplitude dependences of the elastic modulus is illustrated by Fig. 24. The elastic modulus begins to decrease at a certain shear amplitude ε_{lim}. This is the boundary of the linear viscoelasticity region where the elastic modulus is independent of shear amplitude. It corresponds to the stress σ^* related to the apparent softening point of the material. However, it should be noted that in this case the yield stress is estimated with some uncertainty, namely, ε_{lim} can depend on the frequency at which the elastic modulus is measured.

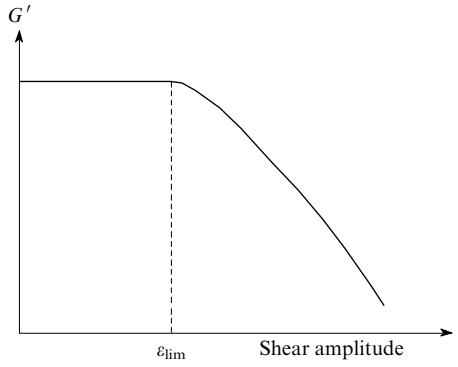


Figure 24. Amplitude dependence of elastic modulus (ε_{lim} is stress amplitude).

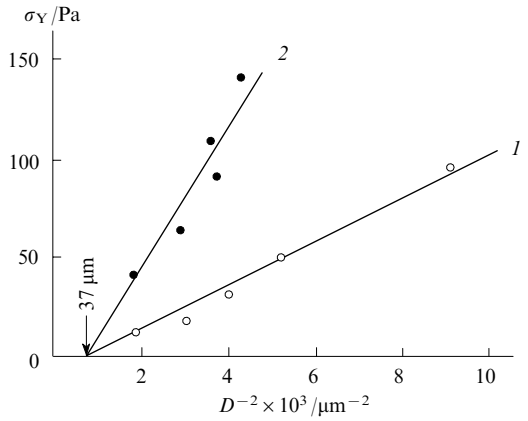


Figure 25. Yield stress plotted *vs.* size of dispersed particles for emulsions with concentrations of 92.6% (*1*) and 94.5% (*2*).[119]

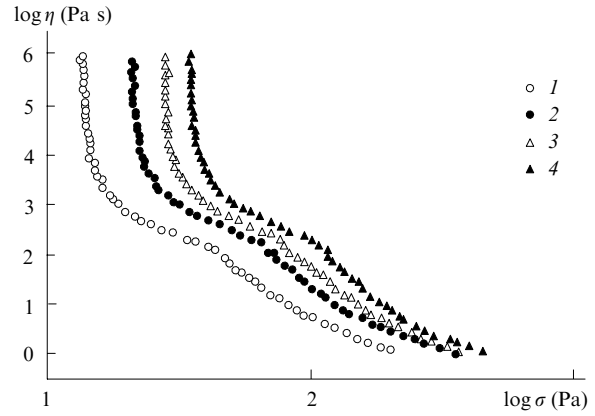


Figure 26. Flow curves of highly concentrated w/o emulsions.[119] Concentration (%): 92 (*1*), 93 (*2*), 94 (*3*) and 95 (*4*).

A direct comparison showed that, generally, σ_Y and σ^* are inequivalent and can differ by a large factor for some suspensions and emulsions.[148] Therefore, when determining the softening point in the dynamic mode (in particular, by the LAOS method), the results obtained should be interpreted with care and relation of the softening point to the yield stress measured under shear flow may cast some doubt.

The yield stress of real emulsions depends strongly on their compositions and on the concentration of dispersed droplets. An example of the concentration dependences of the yield stress of such emulsions is presented in Fig. 25. Here, two experimental facts deserve attention. These are the quadratic character of the dependence of the yield stress on the reciprocal droplet size and the existence of a limiting size (in this case, 37 μm) corresponding to zero yield stress.

Thus, the yield stress depends on the concentration of dispersed droplets similarly to the elastic modulus. One can suggest the existence of a correlation between the strength (yield stress) and stiffness (elastic modulus) of the structure of highly concentrated emulsions.

The maximum droplet size probably corresponds to the critical stability of emulsions (at least in this case) because a zero yield stress means a loose structure.

III.4. Steady and non-steady flow. Flow heterogeneity

III.4.a. Flow curves

Since concentrated emulsions are visco-plastic media, they behave as fluids (*i.e.*, flow) at stresses above the yield stress. An example of the flow curves (plots of effective viscosity *vs.* shear stress) of concentrated emulsions is shown in Fig. 26. One can see the yield stress which increases with concentration and the region of viscous flow at higher stresses. Taking into account an unusual kink of the curves, the region of viscous flow of highly concentrated emulsions can be to a reasonable accuracy described by the following equation:[149]

$$\sigma = \sigma + K\dot{\gamma}^{1/2} + (\sigma_{Y,1} - \sigma_Y)\left[1 - \exp\left(-\frac{\dot{\gamma}}{\dot{\gamma}^*}\right)\right] \qquad (10)$$

A rather large number of empirical (fitting) constants (K, $\tau_{Y,1}$, $\dot{\gamma}^*$) is due to the nonmonotonic form of the flow curve. If a rough approximation is sufficient, the flow curve is reasonably described by the Herschel–Bulkley equation

$$\sigma = \sigma_Y + K\dot{\gamma}^n \qquad (11)$$

i.e., the viscous properties in the flow region vary according to the power law with the exponents K and n. The viscous properties of highly concentrated emulsions can also be described [23] by the following theoretical model:[150]

$$\sigma = \sigma_Y + 18G\left(\frac{\dot{\gamma}\,\eta_c\,D_{32}}{\Gamma}\right)^{1/2} \qquad (12)$$

where G is the elastic modulus, η_c is the viscosity continuous phase and Γ is the surface tension.

Different methods of calculations of the viscosity of concentrated emulsions have been analyzed and compared with the available experimental data; it was also proposed to take into account the contribution of the viscosity of interfacial layers.[151] However, it should be noted that the method of approximation of the flow curves of concentrated emulsions in the viscous flow region is insignificant for quantitative predictions of their behaviour in real conditions, because here one deals with rather high flow velocities where the contribution of the near-yield-stress region is not too large.[152]

Of course, the rheological properties of concentrated emulsions depend on the composition, stabilizer nature and other physicochemical characteristics. Also, one should take into account the fact that emulsions are intrinsically unstable systems prone to ageing (variation of properties with time). Particular examples can be found in the literature. For instance, the influence of temperature, nature of surfactant and variation of the properties with time was studied,[153] as well as changes in the properties in the course of ageing due to crystallization of the aqueous phase.[154] In all cases, one deals with a steady flow of a homogeneous medium. As will be shown below, this type of flow by no means always occurs.

III.4.b. Self-oscillations

As mentioned above, emulsions in the region of solid-like state can co-exist in two different forms, which predetermines the onset of bifurcations. As applied to measurements

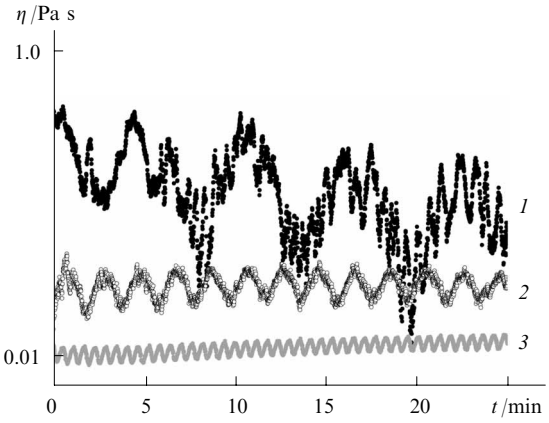


Figure 27. Self-oscillations under shear flow of 1% dispersion of PAN in DMSO at an average (specified) shear rate of 1 (*1*), 3 (*2*) and 10 s^{-1} (*3*).[108]

of the rheological properties of highly concentrated emulsions, this leads to periodic transitions between two structural forms, so the steady flow is transformed to self-oscillations characteristic of various types of multicomponent systems. An example of self-oscillations of a structure-forming dispersion of a polymer in DMSO is presented in Fig. 27. Analogous phenomena were reported for various materials (see, in particular, Refs 155–157); often, they are related to the formation of shear bands.[158]

An example of self-oscillations due to periodic structure breakup–recovery in the colloidal system is shown in Fig. 28. Of course, there is no question of an 'average' or 'effective' viscosity.

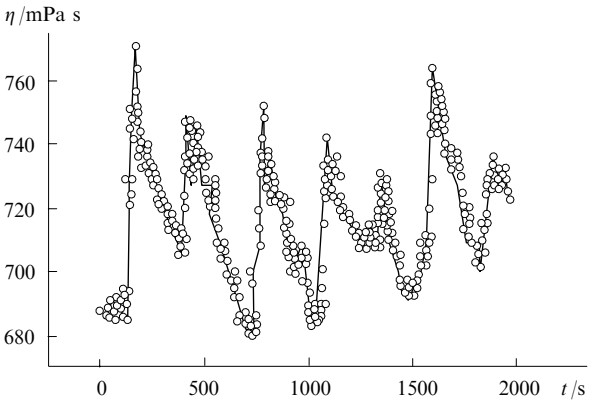


Figure 28. Self-oscillations under shear stress of 65% colloidal dispersion of Al_2O_3 in water at constant specified 'global' shear rate.[156]

III.4.c. Near-wall slip

When considering the flow of a fluid, the boundary conditions for the equations describing the dynamics of the medium should always be specified. Usually, the zero-slip hypothesis is used, according to which the velocity at the boundary (solid wall) is assumed to be zero. However, if the media (*e.g.*, highly concentrated emulsions) can exist in the solid-like state, this assumption is not always valid. This concerns, *e.g.*, polymer melts, which at a certain (rather high) velocity go to a forced rubbery state (*i.e.*, they no longer flow) and start to slip on the solid wall.[159] The existence of near-wall slip was confirmed by direct measurements of the radial velocity profiles.[160–165] Clearly, the onset of near-wall slip should be taken into account in evaluating the rheological properties of emulsions.[166]

If a dispersion flows in a channel, dispersed particles cannot uniformly fill the space near the wall for geometrical reasons, so a thin near-wall layer with changed properties (compared to the bulk properties) is formed. The near-wall slip can be either true (when the near-wall velocity is zero) or apparent. In the latter case, a very high velocity gradient appears near the wall; however, taking account of the fluid viscosity, this should not occur. But the high gradient appears because of separation of the flowing fluid. For instance, a continuous phase of low viscosity can separate from the dispersion for one reason or another and the medium will become inhomogeneous. Flow near the solid wall will occur on this thin layer of low viscosity (outside the layer, there is almost no shear; the material moves as a solid slug). This type of phenomena is characteristic of various soft media, in particular, suspensions, pastes and highly concentrated emulsions.[167–171] The situation looks like near-wall slip. In these cases, it is more appropriate to speak of apparent, or effective, slip.

Below the yield stress, the slip velocity V_s of microgel pastes and emulsions is proportional to the squared stress and near-wall slip occurs in the flow region (above σ_Y).[171] Direct velocity profile measurements also revealed near-wall slip under shear stress of hydrogel below the yield stress; above the yield stress, slip does occur, although its contribution to the flow rate decreases with increasing shear stress.[172]

The pressure (normal stresses) exerted on the walls by concentrated emulsions flowing below the yield stress is independent of apparent shear rate. These stresses can probably be related to the so-called Reynold's dilatancy, *i.e.*, the change in the volume of dispersions under shear stress. As the emulsion flow region is reached, normal

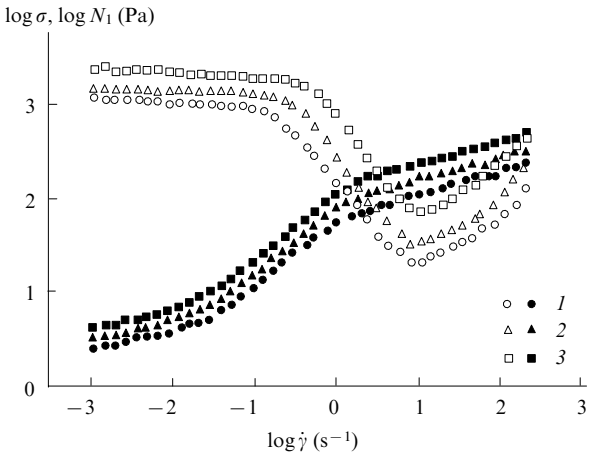


Figure 29. The first difference of normal stresses (N_1, open squares, rhombi and circles) and tangential stresses (σ, solid squares, rhombi and circles) under shear of concentrated emulsions.[173] Concentration (%): 92 (*1*), 93 (*2*) and 94 (*3*).

stresses dramatically reduce. Experimental data presented in Fig. 29 illustrate changes in the flow mechanism of concentrated emulsions as function of the shear rate specified at the boundary of the deformable emulsion specimen.

III.4.d. Formation of shear bands

An example of instability under shear stress of complex fluids is provided by the so-called shear bands [174–176] representing jumpwise changes in the shear rate at the boundary between two structural forms of matter (Fig. 30).

Flow of solid materials and suspensions of solid particles[177] with structural discontinuities is characterized by inhomogeneous motion of layers (Fig. 31).

Co-existence of different structures of a multicomponent material due to bifurcation of its properties was observed in various complex fluids including emulsions,[176–182] micellar solutions [183–189] and polymer solutions.[190–192] The effect is smoothed due to the wide molecular mass distribution of polymers, so one deals with a continuous nonlinear velocity profile under simple shear instead of the shear rate jump.[193]

For colloidal solutions of worm-like micelles the formation of shear bands is associated with the existence of negative differential viscosity, *i.e.*, with ambiguity of the flow curves of these systems.[178, 180] But this is not a necessary condition for the formation of shear bands. A possible explanation for their formation consists in assumption of the influence of shear rate (shear stress) on the concentration profile in the flow.[194] From the standpoint of physics of the phenomena one should distinguish between co-existence of two bands in the case of flow of visco-plastic media (fixed below the yield stress and flowing at higher stresses) and the shear bands appearing in flow of complex fluids. Probably, in many cases the formation of shear bands in flowing colloidal systems (including emulsions) is due to competition between two physical processes, *viz.*, destructuration under the action of external stress and restructuration in the course of ageing.[195]

The formation of shear bands is also possible under constant stress, the band width being completely determined by the 'global' (volume-averaged) shear rate.[196] The phenomenon is treated as 'generic feature of flows in the yield stress fluids and soft glassy materials'.[197]

The formation of shear bands depends on the shear rate, while the critical *Pe* value (shear-stress/thermal-motion characteristic time ratio) corresponding to the onset of shear bands depends on the colloidal solution concentration.[177]

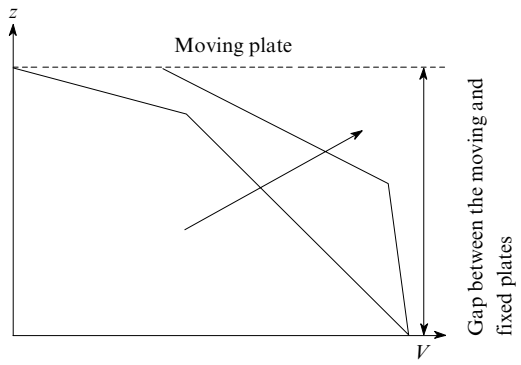


Figure 30. Velocity (V) profiles for the gap z in the formation of shear bands.
Different shear bands correspond to different shear rates characterized by the slopes of the plots. Arrow denotes the direction of increasing global shear rate.

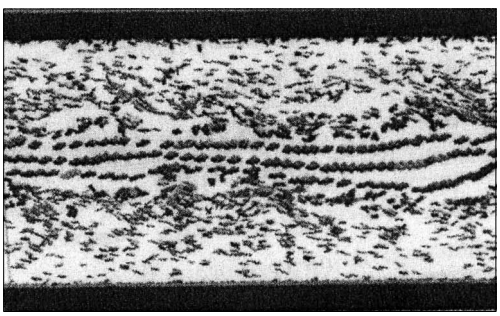


Figure 31. Flow discontinuities under shear of granulated materials or concentrated suspensions.[177]

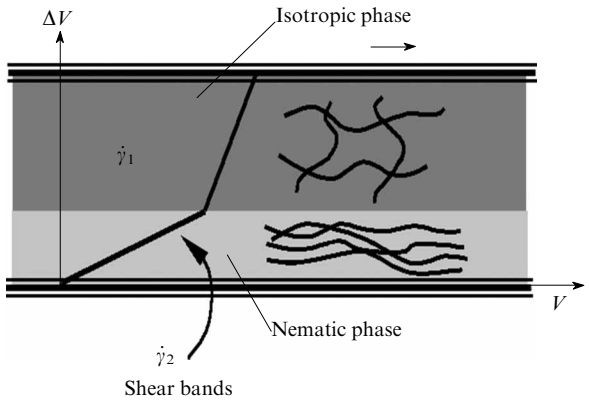


Figure 32. Phase separation of micellar solution accompanied by the formation of shear bands.[183]

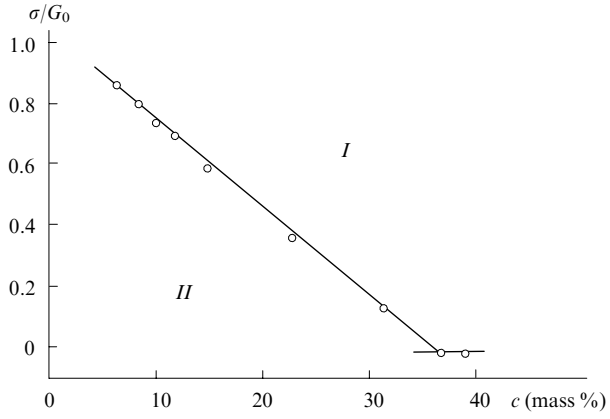


Figure 33. Dynamic phase diagram illustrating the dependence of phase separation conditions on the concentration of micellar solution.[183]
σ/G_0 is shear stress normalized to the elastic modulus of solution, c is the solution concentration; (I) region where shear bands are formed, (II) region of isotropic solution.

Differences in the structure of the material in the shear bands can be significant; it can manifest itself even in the phase separation of complex fluids into, *e.g.*, isotropic and liquid-crystalline phases [183, 186, 187] (Fig. 32). Phase separation accompanied by the formation of shear bands can be represented by a kind of a 'phase diagram' (Fig. 33) which, unlike conventional phase diagrams, characterizes the dynamic rather than equilibrium state of the system.

However, the formation of shear bands does not necessarily lead to co-existence of stable structures. Rather, a detailed study of spatial-temporal parameters of shear bands revealed large fluctuations of the flow structure and flow instability at high shear rates.[198]

III.4.e. Heterogeneity of macroscopic flow

Usually, the flow of fluids including emulsions is studied assuming that fluids are homogeneous media up to the molecular level. It is this interpretation that is basic to the flow curve measurements. The determination of the effective viscosity and the use of different types of rheological equations of states for constant-viscosity Newtonian fluids, non-Newtonian fluids with shear-rate dependent effective viscosity, visco-plastic media that can co-exist in the solid-like and liquid states, as well as viscoelastic media characterized by flow and elastic deformations. Nevertheless, all these rheological notions formally refer to a single point in space or to at least a very small volume (this allows molecular motions to be averaged so the volume is treated as homogeneous). In the text above we considered situations where application of a stress causes self-oscillations due to bifurcations or periodic breakup/recovery of the material structure and when stratification and phase separation of the flow into components of different composition occurs.

Colloidal systems approaching the limit of close packing exhibit flow heterogeneity. It manifests itself in abrupt (even jumpwise) variations of the shear rate in a narrow gap between the fixed and moving surfaces, as shown in, *e.g.*, Fig. 34 (although with no shear band formation). Often, a possible reason consists in the concentration inhomogeneity leading to formation of shear bands. This phenomenon is characteristic of various complex fluids representing multicomponent systems including highly concentrated emulsions. Interestingly, in the case demonstrated in Fig. 34 the flow inhomogeneity decreases with increasing shear rate up to a linear velocity profile corresponding to flow of a homogeneous medium.

The character of a flow depends on the dispersion concentration and particle size; at the same dispersion concentration, it influences the average interparticle distance.

Figure 35 presents a dynamic phase diagram illustrating a possible structure of a highly concentrated colloidal system. As can be seen, chaotic (*i.e.*, homogeneous on the average) flow is only possible in some variable range. At very short interparticle distances, jamming appears (see Section II.3). At relatively low concentrations and rather long interparticle distances, self-organization becomes possible.

Heterogeneity of macroscopic flow, where classical ideas of hydrodynamics of continuous media cannot be used at all, is pronounced under shear stress of emulsions, because

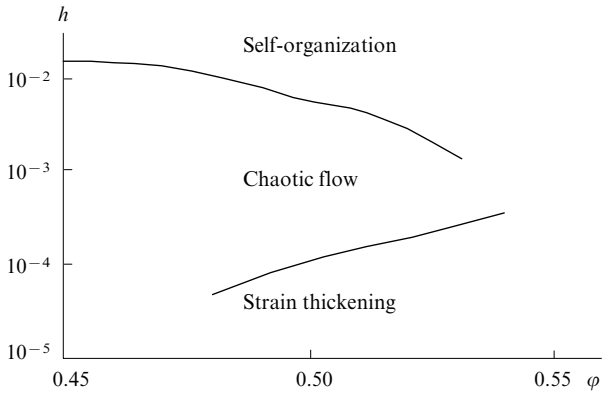


Figure 35. Dynamic phase diagram of possible states of a colloidal system under shear: interparticle distance (h) plotted *vs.* dispersion concentration φ.[198]

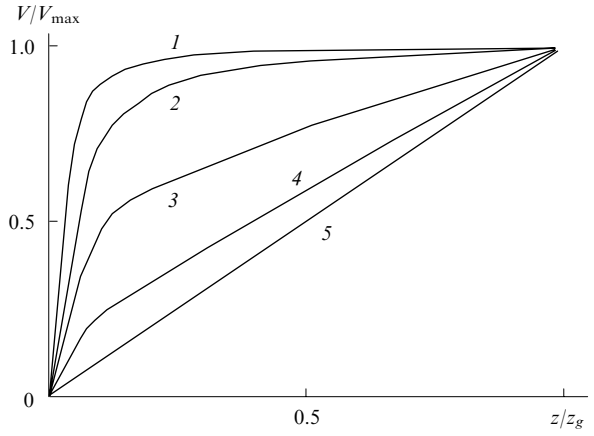


Figure 34. Velocity profiles for the flow of a highly concentrated colloidal system in a narrow gap (z_g = 170 μm) at constant shear stress and $\varphi/\varphi^* = 0.933$.
Global shear rates/s^{-1}: 0.02 (*1*), 0.05 (*2*), 0.2 (*3*), 1 (*4*) and 5 (*5*). The plots were constructed using the data taken from Ref. 176.

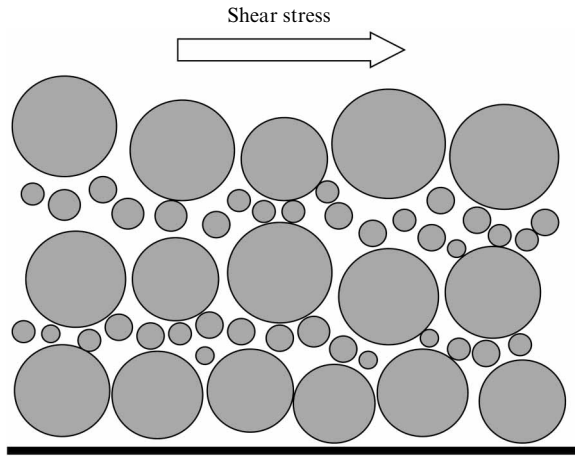


Figure 36. A schematic of the mechanism of flow of a highly concentrated emulsion at low shear rates: rolling of large droplets over smaller ones.[117]

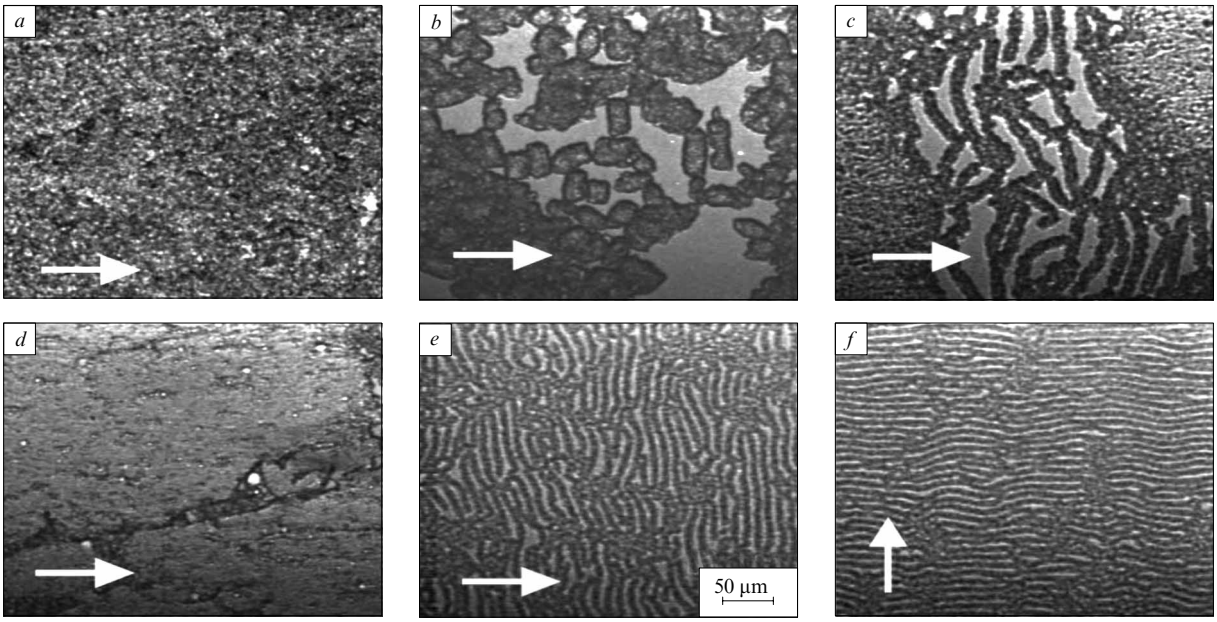


Figure 37. Heterogeneous flow of various emulsions of the same concentration ($\varphi = 0.58$) under shear; particle size of the dispersed phase is 20 μm ($a-d$) and 12 μm (e, f).
The scale length in Fig. *e* is the same for all images. Arrow denotes the shear direction.[199]

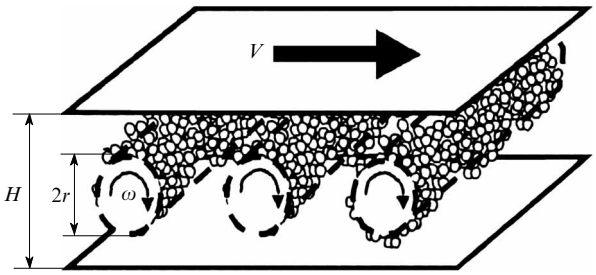


Figure 38. Schematic representation of the motion of rolling associates comprising particles of concentrated emulsions as macroscopic aggregates between two planes separated by the distance H.[199]
The size of the associate is $2r$.

in any case heterogeneity persists on at least a droplet-size scale rather than on the molecular level. At low 'global' (volume-averaged) shear rates, droplets in highly concentrated emulsions move by rolling larger droplets over smaller ones without noticeable deformation of the latter (Fig. 36). It is this flow mechanism that is responsible for independence of normal stresses on the shear rate (see above).[173]

Even more clear illustration of a similar mechanism of the motion of droplets in concentrated emulsions is shown in Fig. 37. A scheme of the flow mechanism of concentrated emulsions as the motion of macroscopic aggregates (Fig. 38) was also proposed.[199]

Conventional rheological measurements revealed a decrease in the effective viscosity of such systems on a macroscopic scale with increasing shear rate, although in some range of shear rates the viscosity did not vary while the first normal stress difference was negative.[199] The structure of such systems (see Fig. 38) was strongly dependent on the shear rate, which governed the formation and breakup of aggregates formed by droplets. The character of the motion of droplets and their associates was dependent on the width of the gap between two parallel plates acting as boundary surfaces for emulsion flows. Also, noteworthy is similarity between the discontinuity patterns of emulsions (see Fig. 37) and suspensions (see Fig. 31) under shear.

Dispersed particles are often prone to spontaneous aggregation.[200] This is a reason for inherent heterogeneity of colloidal systems at a length scale that much exceeds the particle size. Flow heterogeneity and the formation of a layered structure of dispersed particles were repeatedly reported in the literature.[128, 201, 202]

There are numerous observations of heterogeneous macroscopic character of the flow of highly concentrated emulsions and other colloidal systems. In this connection, the questions as to what is the viscosity of such systems and how can their rheological properties be estimated remain open and there is no idea of the answer to them. Clearly, the rheological properties can be estimated only on a length scale that is significantly larger that the size of the moving structural aggregates. The issue what to do on a smaller length scale remains unanswered.

IV. Conclusion

Highly concentrated emulsions where the concentration of dispersed droplets can exceed 95% belong to 'soft media' They represent systems that underwent the concentration induced glass transition. The mobility of dispersed droplets is suppressed by the dense environment that forms a dynamic 'cage' for each droplet. The rheological properties of highly concentrated emulsions are completely determined by their structure. At low stress, 'glassy' systems behave as solid-like materials, namely, the elastic modulus is almost frequency independent, the loss modulus is much lower than

the elastic modulus and flow (irreversible deformation) is impossible. In this state, the systems in question behave as gels. At higher stresses, the yield stress is reached, because high stress enhances the mobility of structural units and thus creates prerequisites for irreversible flow. Emulsions and suspensions exhibit similar rheological properties below the limit of close packing (*i.e.*, below the concentration glass transition point). However, transition through the limit of close packing leads to fundamentally different behaviour of these systems. Namely, at high stresses, suspensions are characterized by the impossibility of flow and by the appearance of discontinuities or structural jamming, whereas emulsions can flow. Thus, from the standpoint of rheology, highly concentrated emulsions belong to viscoplastic media.

Destructuration upon transition through the yield stress is thixotropic in character, so changes in the apparent viscosity upon direct and back shear rate sweep can be different and the yield stress can increase for a long time. The structure of emulsions can be ordered up to a macroscopic level and shear stress may favour structure formation and even induce phase transitions. These features lead, in particular, to clearly seen flow heterogeneity, namely, the formation of shear bands and the existence of large aggregates acting as moving structural elements.

Numerical values of the rheological properties of highly concentrated emulsions are governed by the nature of emulsion components. The elastic modulus as a parameter characterizing structural rigidity and the yield stress characterizing the strength of the structure of emulsions depend on the concentration, extent of droplet compression upon transition through the limit of the close packing of spherical particles and on physicochemical interactions between droplets and interfacial layers.

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