Praise Worthy Prize

Rheology on the Way from Dilute to Concentrated Emulsions

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Abstract – *The short review presents the analysis of the consecutive evolution of the rheology of emulsions starting from dilute systems (behavior of an individual liquid droplet in a continuous liquid phase) till the highly concentrated emulsions, in which droplets loose their spherical shape and become polygons. Along with the increase of the internal phase concentration, this is the transition from a simple Newtonian fluid via non-Newtonian fluid and up to a plastic medium demonstrating solid-like behavior at low shear stresses, yield stress threshold and non-Newtonian time-dependent properties. The special features of the emulsions rheology are related to the droplet deformation, orientation in flow, break-up and interdroplet interaction in concentrated emulsions. The similarities and differences in the rheology of suspensions and emulsions are discussed.* **Copyright © 2010 Praise Worthy Prize S.r.l. - All rights reserved.**

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I. Introduction

Emulsions are a multi-component compounds formed by liquid droplets dispersed inside a liquid medium. In the row of technological materials, emulsions occupy a position between suspensions and foams. It means that viscosity of an internal phase may vary from zero (limiting case of foams) to infinity (solid particles of the dispersed phase in suspensions). An intermediate case is two-component systems with internal phase comprising slightly cured colloid-size micellar or polymeric compounds. They cannot flow but easily deform under the action of external stresses like liquid droplets.
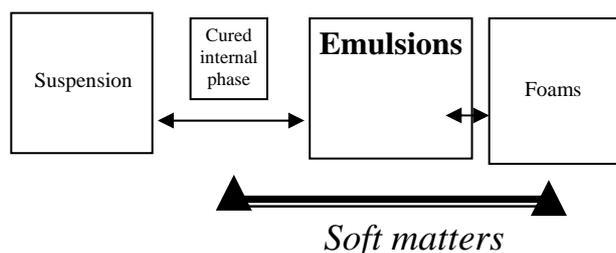
Fig. 1. The place of emulsions in the row of multi-component materials

These materials belong to the general class of "soft matters", or "soft condensed matter" (term introduced possibly by de Gennes and became very popular in scientific literature). These materials demonstrate many interesting and sometimes unusual features, which cannot be directly predicted on the atomic or molecular base because soft matters are inclined to self-arrangement into mesoscopic structures of the nano- or even micro-scale level. This is the reason of the living

interest of fundamental science to these objects. On the other hand, soft matters (and emulsions, in particular) occupy a tremendous technological niche in the food industry and machinery, in cosmetics and pharmaceuticals, in medicine and human organism and so on. There are two sides of the story about emulsions (like other soft matters). One of them is their structure and the other is their mechanical properties, and the rheological properties occupy the dominating place among them. Actually, this is two sides of one object as there is the closest correlation between structure and properties of these matters. The central parameter of emulsions is the concentration φ of the internal phase because it determines the whole complex of rheological properties (and thus technology and application of emulsions). The following consequence of emulsions can be formulated:

- dilute emulsions: the distortions of the flow lines in a continuous phase vicinity of a single droplet does not influence the situation around other droplets;
- semi-dilute emulsions: there is a hydrodynamic interaction between flow fields around different droplets;
- concentrated emulsions – different emulsions touch each other and the percolation takes place with the creation of a continuous network; the upper limit of this concentration range is the closest packing of spherical droplets; depending on the droplet size distribution, this limit, φ*, roughly corresponds to app. 0.70-0.75;
- highly concentrated emulsions – it is evident that solid (rigid) droplets cannot be introduced into a space beyond φ*, so φ* is a absolute concentration

boundary for suspensions, but deformable droplets can be compressed and then fill much larger volume than φ*.

The traveling along the concentrations axis leads to the great and in some cases crucial evolution in the rheology of emulsions. Surely, some other factors also are influential. That is the chemistry of both phases, the presence of a surfactant and its nature, the droplet size distribution and so on, but the concentrations of an internal phase is the principle determining factor. Then just the concentration will be used as the guide in structurizing this review. The historical perspective of the problem under discussion was reviewed in the previous publication [1]. That one also contains the long list of references on publications on the rheology of emulsions. So, this review is the short discussion on the critical points in the modern state of this field of investigations.

It is also necessary to draw attention of a reader to the reviews [2], [3] specially devoted to the role of liquid interface layers in the rheology of emulsions. It is worth noting that the following discussion will touch multi-component materials with the characteristic size of the ingredients allowing us not to take into account the Brownian effects of molecular movements and interactions. So, we will limit the discussion inside the arguments of continuum hydrodynamics.

II. Dilute Emulsions

II.1. Viscosity

The starting point for all discussions concerning both theoretical and experimental studies in the rheology of multi-component fluid materials is the famous linear Einstein equation for the concentration dependence of the dilute suspensions viscosity of small solid balls in a Newtonian liquid. The development of this approach to emulsions (in the studies of Hadamard, Rybczynski, Boussinesq, Taylor) finally has lead to the most general rigorous solution of the viscosity problem for dilute emulsions formed by two Newtonian liquids (Oldroyd [4]). This expression looks as:

$$\eta_r = 1 + \frac{\eta_0 + 2.5\eta_{dr} + \dfrac{2\eta_s + 3\eta_d}{3}}{\eta_0 + \eta_{dr} + \dfrac{2(2\eta_s + 3\eta_d)}{5R}} \varphi \qquad (1)$$

where: η_r is relative viscosity of an emulsion,
η_0 is the viscosity of a continuous medium,
η_{dr} is the viscosity of a fluid inside dispersed droplets,
η_s is the surface or interfacial shear viscosity,
η_d is the surface or interfacial dilatational viscosity,
φ is the volume concentration of the disperse phase, and
R is the radius of the (monodisperse) dispersed liquid droplets.

As one can see, this is the linear approximation of the dependence of viscosity on concentration and the parameters entering this equation include all possible physical effects including special effects of surface properties of a liquid. It is rather difficult to carry on the experimental analysis of this equation due to the problems related to independent measurements of the different components entering the equation and bearing in mind that it should be done in the limit of dilute emulsions. Meanwhile, this equation is the determining guide for estimation of different factors input on the emulsion viscosity.

The most convenient way for this is the transformation of this equation into the dimensionless form. This transformation was made by Danov [5] who also took into consideration the influence of the surfactant absorption. His final equation is:

$$\varepsilon = \frac{\lambda + \dfrac{2}{5}(Gi + Bo)}{1 + \lambda + \dfrac{2}{5}(Gi + Bo)} \qquad (2)$$

where:
λ is the ratio of viscosities of a continuous and dispersed phase liquids,
ε is the intensity of energy dissipation produced by the flow of emulsions,
Bo is the Boussinesq Number, as a measure of the ratio of surface to volume viscosities, and
Gi is the Gibbs Number which takes into account the elasticity of the interfacial layer and diffusion of a surfactant onto the interface.

Eq. (2) might be useful for the analysis of the role of a surfactant because one of the main results in studying the rheology is the understanding of the determining influence of the surface interface layer. It would be especially expressive in examining the concentration dependence of viscosity for concentrated emulsions.

II.2. Elasticity

Here, we understand "elasticity" as the tendency to come back to the initial state after cessation of deformation created by external forces. There are several reasons for elasticity of emulsions. The first one is related to the change of the shape of a liquid droplet in flow and elasticity is obliged to surface tension. Indeed, shearing leads to the transformation of the initial (at rest) spherical drop to the ellipsoidal particle characterized by the degree of asymmetry D, which can be expressed as:

$$D = \frac{R_{max} - R_{min}}{R_{max} + R_{min}} \qquad (3)$$

where R_{max} an R_{min} are semi-axis of an ellipsoid,

formed in shear flow. The value of D depends on shear rate, $\dot{\gamma}$. In the linear approximation, this dependence is expressed by the following theoretical equation (Taylor, 1934):

$$D = \frac{16 + 19\lambda}{16(\lambda + 1)} Ca \qquad (4)$$

where:

$$Ca = \frac{\eta_0 \dot{\gamma}}{\sigma / R} \qquad (5)$$

is the Capillary Number and σ is the surface tension.
The principle scheme of the non-interactive droplet deformations is presented in Fig. 2, where an arrow shows the direction of flow.
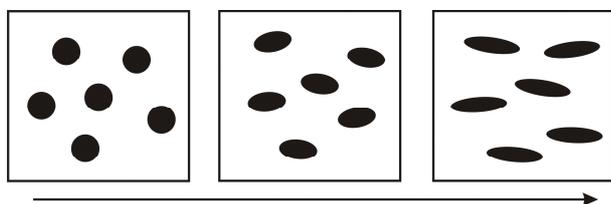

Fig. 2. Principle scheme illustrating the orientation and deformation of droplets in flow

Initially spherical droplets (left picture) turns along with the direction of flow and deform, though the distribution of orientation still remains (middle picture). Then – at higher deformations of an emulsion and/or higher deformation rates – the deformation of droplets increases and the scatter in orientations decreases (right picture). So, deformation leads to the formation of an anisotropic structure of an emulsion. Finally liquid droplets transfer to prolonged fibers and can break as will be discussed in the next Section.

Such a picture looks very impressive in elongational flows (as was directly demonstrated in [6]) and is accompanied by the droplet rotation in shearing.
When the flow ceased, an ellipsoid aspires to return to the initial spherical shape. The theory (initially developed by Oldroyd (1953) and then reformulated in [7]) says that the restoration process for viscous (not manifesting elasticity) droplets follows the simplest Maxwellian mode of retardation with the characteristic time θ expressed as:

$$\theta = \frac{\eta_0 R}{\sigma} \frac{(3 + 2\lambda)(16 + 19\lambda)}{40(\lambda + 1)} \qquad (6)$$

It is clearly seen that the force preventing deformation of a droplet is surface tension (eq. (4)) and the driving force of the retardation is also surface tension (eq. (5)) because deformation leads to the increase of the surface area of a droplet, while other physical characteristics also influence the degree of deformation and the rate of retardation.

The second source of elasticity is the viscoelasticity of a medium inside a droplet. This is especially important if an internal phase consists in a polymeric substance having its own relaxation properties. The theory of this case was based on the Palierne model [8]. Later a large volume of investigations were made in this line (Bousmina et al, Maffettone and Minale, and others; see corresponding References in [1]). The theory gives the expression for complex dynamic modulus of an emulsion as the mixture of two components with stabilizing layer on the droplet surface, $G_{bl}^*(\omega)$. The theory presents the linear approximation of the viscoelastic behaviour of an emulsion in a rather complicated form for the arbitrary droplet size distribution. The final expression will not be write down here, but one can easily find it in the original publications cited in [1] and they can be used in practice via computer calculations.

The detailed simulation of the viscoelastic droplet behavior inside a Newtonian liquid was numerically developed in [9]. The viscoelastic source of elasticity gave its own input to the elasticity of an emulsion in addition to usually considered effect of surface tension. Two differences of normal stresses were calculated as a function not of the Capillary Number, Ca, but also of the Deborah Number, De, as the measure of viscoelasticity of droplets. Computer simulation of the Newtonian droplet movement in a viscoelastic continuous medium was performed in [10]. The most complete numerical simulation of the droplet deformation (including the final act of droplet break-up) in fluid pairs with different combination of liquid properties (Newtonian pair, viscous drop in a viscoelastic medium, viscoelastic drop in a viscous continuous medium) was carried out in [11].

So, one can assume that the linear theory of elasticity of dilute emulsions now is constructed in its rigorous form. Moreover numerous computer simulations of the behaviour of a single drop in a fluid demonstrate various versions of the deformation and orientation of a drop with varying rheological properties of both components in different geometries of flow. This serial of studies proves the power of modern computer technique and can (and will) be spread for new unlimited number of versions of the components rheology and for the flow in different conditions.

It is worth mentioning that the droplet size (as well as the droplet size distribution) does not enter any analytical solutions. It is natural because only the net volume concentration was assumed as the determining factor.

II.3. Break-Up of Droplets

The principle difference in the behavior of

suspensions and emulsions is a possibility of the break-up of liquid drops at some specified conditions. The determination of these critical conditions is a hydrodynamic problem and it was discussed in several publications. The complete and rigorous theory for a pair of Newtonian liquids was developed in [12]. The calculated dependence of the critical values of the Capillary Number, Ca*, as a function of the ratio of dispersed-to-continuous phase viscosities is presented in Fig. 3.

The existing experimental data confirm the validity of this theoretical result. It should be treated as an outstanding achievement in the theory of deformation and break-up of unit drops because it covers more than 7 decimal orders of the argument values. The calculations show that in the wide range of rather small the critical values Ca* depends on λ as λ-2/3. Besides, there is such limiting λ value close to 4 (i.e. viscosity of a fluid in droplets is much higher than viscosity of a continuous medium) beyond which liquid droplets stay stable at any intensive shearing. However it is worth reminding that all these results are valid for laminar flows.
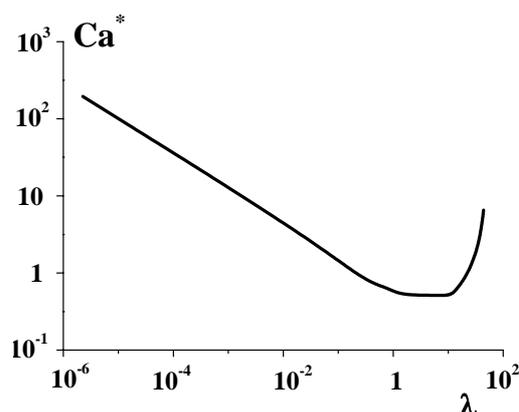

Fig. 3. The results of calculations of the critical Capillary Number as the function of viscosities ratio dependence (according to [12])

Thus, one can suppose that the above collected results present the full and closed picture of the behavior of a single viscous droplet (in dilute emulsions) in unrestricted shearing. It seems that no unclear effects or dependencies remind in this field. This is important because the behavior of dilute emulsions in the benchmark in discussing more complicated cases of emulsions with higher concentration of a dispersed phase (beyond the linear domain of concentration dependence of viscosity).

Meanwhile the break-up conditions of a droplet in flow inside restricted volumes depend of the geometry of the stream. It was demonstrated for deformation and break-up of droplets placed between coaxial cylinders with different gap between rotating surfaces [13]. Deformation of droplets in restricted streams is especially interesting when flow takes place in contractions because this is a model of several important

situations, e.g. the blood flow in a vascular of the changing cross-section. This problem was also simulated by means of the computer modeling in several latest publications [14], [15].

III.   Semi-Dilute Emulsions

Semi-dilute emulsions are a sub-class of concentrated emulsions. It covers the concentration range form dilute emulsions consisting of individual non-interacting dispersed particles till really concentrated emulsions characterized by the formation of the percolation three-dimensional structure.

The initial characteristic feature of semi-dilute emulsions is the deviation of the viscosity-vs.-concentration dependence from the linear law. This is explained by mutual interactions of hydrodynamic fields created due to the movement of neighboring liquid droplets. The central question in this Section is the concentration dependence of viscosity. Generally speaking, non-Newtonian effects can arise in this concentration range due to deformation, orientation and disorientation of liquid droplets. However, in semi-dilute emulsions, these effects are not severe and can be neglected at the first approximation. So, let us focus on the concentration dependence of viscosity, $\eta(\varphi)$.

Any $\eta(\varphi)$ dependence can be presented by the power series as

$$\eta\varphi = \eta_0 \left(1 + A_1\varphi + \sum_2^N A_n\varphi^n \right) \qquad (7)$$

where: η_0 (as before) is the viscosity of a continuous medium,
A_1, A_n are numerical coefficients.

It is evident that $A_1 = 2.5$ (Einstein's coefficient). If to assume that A_2 is the value of the order of 10, then the second (squared) term is immaterial at $\varphi << 0.25$, really the linearity is expected in the concentration range $\varphi < 0.02$, and above this limit we come to the domain of semi-dilute emulsions. Actually, $\varphi = 0.02$ is a very low concentration! However there were quite successful experimental attempts to confirm the Einstein coefficient in the range of low concentrations [16].

Earlier theoretical investigations showed that A_2 (sometimes called the second virial coefficient) equals 6.2 (Batchelor, 1977). Then power computer resources were included in order to solve the standard Navier-Stokes equations for the movement of many particles in a viscous fluid. Meanwhile, it is important to stress that the theoretical efforts were focused on suspensions (not emulsions). So, concentration dependence of suspensions was calculated by Ladd [17] and his result is presented in Fig. 4 for the concentration range from 0 till 0.25 as the dependence of the reduced viscosity η_r on volume concentration, φ. The η_r, as usual, is understood as the

ratio $\eta_r = \eta / \eta_0$. Then, according to Eq. (7) $\eta r = 1$ at $\varphi = 0$. Two other lines are drawn in this Figure. The first one presents the Einstein linear law and the second one corresponds to the Batchelor squared dependence.
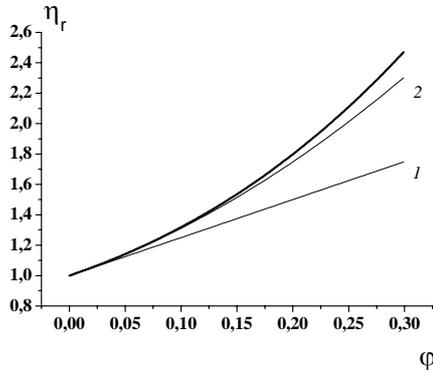

Fig. 4. Concentration dependence of the viscosity of suspensions. Solid line is the result of calculations by [17]. Line *1* – linear approximation, curve *2* – squared approximation with $A_1 = 2.5$ and $A_2 = 6.2$

The comparison of these lines with the Ladd curve reflects the limits of applicability of these approximations in the semi-dilute domain. These limits are close to $\varphi \approx 0.05$ for linear and to $\varphi \approx 0.15$ for squared with A1 = 2.4 and A2 = 6.2) laws, respectively.

Then we calculated the coefficients of the series (7) for this curve assuming beforehand the Einstein (A1 = 2.5) and Batchelor (A2 = 6.2) coefficients are valid. The third virial coefficient appeared equal to A3 = 6.29 ± 0.45 and in this case the three-member sum excellently presents the Ladd curve with.

Meanwhile, it is interesting to mention that if to treat the Ladd curve as a formal presentation of the $\eta r(\varphi)$ dependence then it is quite well approximated with squared formula with the coefficients A1 =2.22154 ± 0.11734 and A2 = 8.86629   0.55667 with least-squared error equal to 0.00015. Both empirical coefficients are not far from the rigorous values.

One can ask the author, why we pay so much attention to concentration dependence of suspension if the review is devoted to emulsions. The physically based answer to this concern was given in [18]. The data on concentration viscosity of emulsions of two kinds were presented in this publication. The difference was in the ratio between the viscosities of a fluid of droplets, ηdr, and a continuous phase, η0. In the firsts and the second cases, these ratios were: ηdr/η0= 12/0.997 = 12.4 and ηdr/η0=12/104 = 0.115, i.e. the difference was by 100-fold. However all experimental points fell on the Ladd curve calculated for suspensions of hard spheres. It means that liquid droplets in emulsions regardless the viscosity of a continuous medium behave in a solid-like manner. And all theoretical results obtained for suspensions are valid for emulsions. This result seems to be of fundamental value for the rheology of emulsions.

One can suspect that it is true for the domain of low shear rates only where deformation and orientation of droplets are negligible. But there is no systematic experimental data of this kind for the domain of high shear rates. One of the promising approach might be to try to examine non-linear effects. It might be expected that non-Newtonian behavior as well as normal stresses would be some function of the dimensionless product $(\dot{\gamma}\theta)$, where the characteristic relaxation time θ is estimated by eq. (6). For $\lambda \gg 1$ this product, being an analogue to the Weissenberg Number, transforms to:

$$Wi \cong \frac{\dot{\gamma}\eta_0 R\lambda}{\sigma} = \frac{\dot{\gamma}\eta_{dr}R}{\sigma} \qquad (8)$$

So, non-Newtonian effects special for emulsions might be observed for droplets formed by a high viscous fluid, e.g. polymers.

IV.   Concentrated Emulsions

The transition point from semi-dilute to concentrated emulsions is rather conventional and depends on the nature of a dispersed phase too. Meanwhile, when the percolation threshold is reached the formation of a "structure" of some kind becomes possible. This structure appears due to the interdroplet interaction of different kind and includes primarily interface layers and surfactant interactions. Then it becomes necessary to take into account the effect of destroying this structure under deformation and the reverse process of its formation at rest. It immediately leads to strong non-linear rheological effects. Among them, the central and the most evident effect is the non-Newtonian flow. The development of this phenomenon along with the increase of the dispersed phase concentration can be illustrated by the scheme shown in Fig. 5.
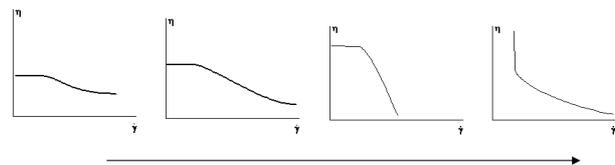

Fig. 5. The transformation of flow curves with increasing concentration of s dispersed phase. (The increase of the concentration is shown by an arrow)

The following characteristic transformations take place along with the increase in the concentration of a disperse phase inside the domain of concentrated emulsions:
- the upper (initial or maximal) Newtonian viscosity increases;
- the gap between the maximal and minimal Newtonian limits widens;
- the lower Newtonian limit disappears and the non-Newtonian flow becomes strongly expressed;

- the upper Newtonian limit changes for the yield stress and the flow at lower shear stresses becomes excluded.

The effects of such kind were described in numerous publications. Maybe the most interesting phenomenon is the appearance of the yielding due to structure formation with quite measurable strength (i.e. the yield stress) in approaching to the upper concentration boundary of the high concentration domain corresponding to the threshold of the closest packing of spherical droplets.

As was said the upper concentration boundary of this domain is the concentration of the closest packing of spherical droplets. Under this term, the infinite regular arrangement of monodisperse balls in 3D space is understood. This limiting concentration (firstly calculated by Gauss) is equal to $\pi/3\sqrt{2} \approx 0.74$. This type of packing is illustrated in Fig. 6. Actually, due to different reasons deviations from the ideal packing take place and the threshold concentration of the closest packing $\varphi*$ may be some lower, in the range from 0.71 till 0.74. Moreover, if the dispersion is polydisperse the $\varphi*$ value can be rather high because small balls are easily placed in the free space between larger balls. Just in this concentration domain, the transition from non-Newtonian flow behavior to plasticity with the yield stress appearance occurs.
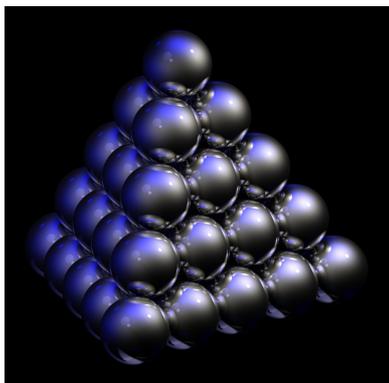

Fig. 6. The regular closest packing of spherical particles

The increase in viscosity of an emulsion results in the evident changes in shear stress acting on droplets. It requires the re-formulation of the Capillary Number with changing viscosity of a continuous phase $\eta 0$ for mean-field viscosity ηm of an emulsion in whole. Then the modified Capillary Number should be calculated as:

$$Ca_m = \frac{\eta_m \dot{\gamma}}{\sigma / R}$$

Such a re-formulation of the Capillary Number, as well as the ratio $\lambda m = \eta dr/\eta m$, allowed the authors [19] to explain the break-up of droplets in concentrated emulsions, generalizing the Ca(λ) dependence shown in Fig. 3 for the whole concentration range by introducing the coordinated Cam vs. λm instead of Ca and λ.

V. Highly Concentrated Emulsions

This is a rather special kind of soft matters, in which the concentration of a disperse phase exceeds the limit of the closest packing of spheres, $\varphi> \varphi*$ while a continuous phase exists in the form of thin streaks (layers) between liquid droplets. The concentration of the dispersed phase can reach 0.96. Such systems can exist only if liquid droplets loose their spherical shape and become "compressed", droplets having a polyhedral shape, as shown in Fig. 7.
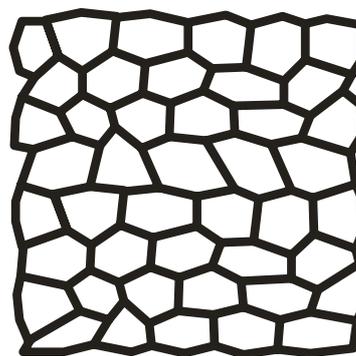

Fig. 7. The cross-section of a highly concentrated emulsion. Thick lines are an interdroplet continuous medium

The stability of such highly concentrated emulsions is obliged to the presence of a surfactant.

This is the end of the evolution of the rheological properties of emulsions and these emulsions are quite different from the fluid emulsions with $\varphi < \varphi*$. The most striking peculiarity of the rheology of such emulsions is their solid-like behavior. It looks rather amusing because a mixture of two (more exact, three if to include a surfactant) low-viscous liquids behaves as a sold. Indeed, the frequency dependence of elastic modulus for highly concentrated emulsions is practically absent. One of the known numerous examples of the $G'(\omega)$ dependencies is presented in Fig. 8 (from [20]). The independence (or almost independency) of elasticity on frequency is the typical feature of solids. However highly concentrated emulsions can flow at stresses beyond the yield stress, τY. The existence of this limiting stress (the yield stress) is the reflection of the stress-induced solid-to-liquid transition. At $\tau > \tau Y$ such emulsions behave as typical non-Newtonian liquid and it is the consequence of the droplet deformation and destroying the structure of an internal phase. The structure formation is a kinetic process and it manifests itself in the time-dependent rheology [21]. And finally, emulsions of this type are elastic. It is quite natural for solids, but they demonstrate

elasticity both, in solid and liquid states. Rather unusual effect is the independence of the normal stress difference on shear rate in the domain of low shear rates [22]; possibly it takes place in the stress range below τY and consequently this phenomenon is also the manifestation of the solid-like behavior of highly concentrated emulsions.
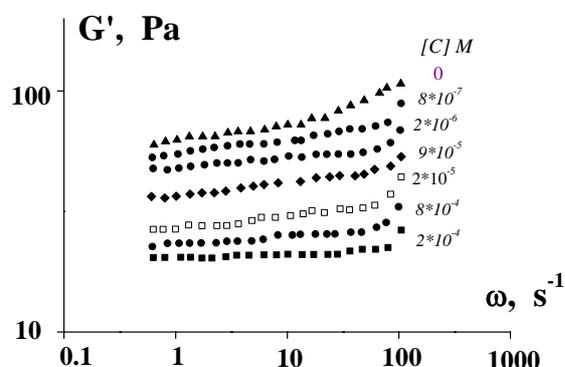

Fig. 8. Frequency dependencies of elastic modules of an emulsion on the substitution of the organic surfactant by protein – its concentration shown in the Figure (adopted from [14])

In conclusion, it is rather important to touch the physics of these systems that explains its behavior. The very popular and clear explanation of the highly concentrated emulsions behavior relates its properties to the "osmotic" model of compressed droplets [23]. According to this model, "compressed" (deformed) droplets in highly concentrated emulsions, like shown in Fig. 7, are created under the action of the osmotic pressure. The increase in the surface area and thus in the surface energy is the unique source of stored energy, which manifests itself in elasticity of emulsions. Here, as in several other cases discussed above, the behavior of emulsions is related to surface tension. This is the rather evident physical conception. However, during last years, new experimental facts were published, which do not lie in the frames of this model predictions. So, it appeared necessary to consider some additional sources of elasticity in highly concentrated emulsions. It was assumed that this source might be the interdroplet interactions, regardless of their nature this interaction provides some additional forces in deformation of droplets [24].

VI.   Conclusion

It is rather instructive to compare the rheology of dispersions of two kinds, suspensions (solid internal phase) and soft matters – emulsions (liquid internal phase). Above, several arguments were discussed showing the analogy in the behavior of suspensions and emulsions. Meanwhile, there are several principle differences between these systems and they become evident in comparing the properties of Table I

So, one can see that there are some analogies in the

evolution of the rheology of suspensions and emulsions and there are a principle difference between these objects. The similarity is rather evident in the comparison of the concentration dependencies of viscosity in dilute and semi-dilute concentration domains, while in approaching to the concentration of the closest packing of spheres the differences between suspensions and emulsions become principle. Indeed, in approaching to the threshold of the closest packing suspensions loose fluidity and the effect of jamming is observed, while emulsions transform to the plastic media, which are solid-like at low stresses but can flow at stresses beyond the limit of the yield stress.

The rheology of emulsions is determined by numerous factors. They include the rheological properties of both components of the systems (continuous and internal phases) which can be purely viscous or viscoelastic, the properties of the surface interface layers with interdroplet interaction, and, mainly, the concentration of a dispersed phase.

TABLE I

Characteristic features		
Internal phase	Suspensions – Solid particles	Emulsions – Liquid droplets
Concentration range 0 - φ_p	Linear growth of viscosity	Linear growth of viscosity
φ_p – percolation	Yield stress Non-Newtonian behavior	Non-Newtonian behavior
φ_p - φ^*	Visco-plastic behavior Sharp growth of viscosity, non-Newtonian effects	Sharp growth of viscosity with increasing concentration Non-Newtonian behavior
φ^* - closest packing		
φ^* - 1	Jamming	Yield stress
	Impossible	Visco-plastic behavior, strong non-Newtonian effects

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