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Physicochemical dynamics of disperse systems

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Abstract. Results of studies of physicochemical dynamics of disperse systems, which is a new and rapidly developing field of physical chemistry, are generalised. Most attention is given to frequently occurring disperse systems composed of a solid phase and a liquid dispersion medium. The dynamics of contact interactions between particles of disperse solid phases is a key element of the dynamics of such systems. The physicochemical factors responsible for contact interactions are considered in relation to the bulk structural – rheological properties of disperse systems. The bibliography includes 114 references.

I. Introduction

Among disperse systems, highly dispersed systems characterised by a highly developed interface are of most interest. These are first and foremost structured systems [1, 2] in which dispersed structures form spontaneously through intermolecular interactions due to contacts between particles. Traditionally, the properties of these systems were studied primarily under static conditions.[3] The present review is devoted to problems associated with the behaviour of such systems in dynamic conditions typical of both various chemical engineering processes and many natural phenomena.

Such fields of science as molecular and Brownian dynamics have been extensively developed.[4, 5] The case in point is physicochemical dynamics of microheterogeneous systems [6] containing particles, whose sizes can be substantially (by 2 – 3 orders of magnitude) larger than the sizes of colloidal particles. This area of physical chemistry of disperse systems borders on physicochemical hydrodynamics,[7] which deals with processes occurring in the vicinity of the surface of an individual particle of a solid phase (or a solid – liquid interface), as well as on physicochemical hydrodynamics of capillary systems.[8]

Physicochemical dynamics of disperse systems treats predominantly dynamic processes taking place in ensembles of particles of dispersed phases linked in a spatial structural network through dispersion forces, the mechanism of decomposition of such systems under dynamic exposure conditions to form aggregates, their evolution, interactions with each other and a dispersion medium (up to decomposition into individual particles to release a dispersion medium immobilised in these aggregates). Within the framework of physicochemical dynamics, not only destruction of aggregates but also reverse processes of structure formation under conditions of dynamic action on a dispersion medium are considered.

Physicochemical dynamics includes dynamics of contact interactions between particles as the major component,[9 – 13] which determines the characteristic features of destruction and the mechanism of structure formation in disperse systems in dynamic conditions.

The present review is devoted to the following problems: conditions and the mechanism of structure formation in disperse systems, criteria for their destruction under dynamic conditions, verification of the type and intensity of dynamic actions on structured disperse systems, the dynamics of contact interactions between particles of dispersed phases, including those in the presence of a surfactant adsorption layer on their surface, the flow mechanism for structured disperse systems (fundamentals of the flow theory) in dynamic conditions with substantiation of ways and procedures for achieving the maximum fluidity upon complete deaggregation.

The maximum fluidity is required for creating the optimum dynamic state of disperse systems corresponding to the main condition for optimisation and intensification of various heterogeneous chemical engineering processes in such systems as well as processes for the production of a broad spectrum of dispersed composition materials.

The main concepts in physicochemical dynamics of disperse systems were finally developed in the last 10 – 15 years. However, since some fundamental aspects in this field of physical chemistry of disperse systems have been published before that time, the earlier studies are also briefly considered and analysed in the present review.

II. Main conditions for structure formation in disperse systems

1. Types of contacts between particles in disperse systems

In spite of an enormous variability in the chemical composition and physical properties of disperse systems, most of them are characterised by a combination of two major features: the presence of a highly developed interface and a high concentration of a dispersed phase in a liquid (or gaseous) dispersion medium. As a consequence, these systems have a high interface free energy (F^*). The free energy of systems always tends to decrease. Hence, processes accompanied by a decrease in this energy (ΔF^*) can occur spontaneously in disperse systems.[14]

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The free energy can decrease due to formation of contacts between particles on coagulation, which proceeds particularly extensively in lyophobic aggregation-unstable disperse systems. When a certain critical concentration of particles of dispersed phases in liquid or gaseous dispersion media (φ_c) is achieved, this process leads to the spontaneous formation of a spatial structural network. The major components of the latter are the contacts between the particles and the particles as such, which form spatial cells in the bulk of the disperse system. In this case, the disperse system becomes structured, *i.e.*, is transformed from a free dispersed state to a bound dispersed (aggregated) state.

The formation of three-dimensional structures leads to radical changes in the main structural and mechanical properties of such systems. These systems completely lose aggregation stability but become stable with respect to sedimentation, because a structural network prevents particles of immobilised dispersed phases from precipitating. At the same time, such systems lose fluidity and high mobility. Their viscosity continuously increases as the dispersity increases (and, correspondingly, as the size and concentration of particles in dispersion media decrease). Structured disperse systems are characterised by the modulus of elasticity and the ultimate strength τ_p (or P_m). These are only the most typical features of such systems.

Of numerous factors responsible for the properties of structured disperse systems, two main groups are associated with the following fundamental parameters:[9–13,15–17] first, the cohesive force f_c and the cohesive (interaction) energy E_c in contacts between particles of dispersed phases; second, the number of contacts n between particles per unit volume.

The strength and energy of interactions in contacts between particles depend on the type (nature) of contacts (Fig. 1, Table 1). The characteristic feature of relatively unstable structures with contacts of the first and second types is their complete reversibility with respect to strength. A consideration of direct (atomic) and coagulation contacts as two different types is somewhat tentative. For example, in the case of strong lyophobic interactions between particles, a liquid in coagulation structures can be completely displaced from the interspace between the particles, and the difference between these types of contacts disappears. After cessation of external mechanical actions, contacts in the destroyed structure can be spontaneously restored to the initial level. This property (so-called thixotropy) is typical of various powder- and paste-like dispersions. Structures with strong phase contacts do not possess this property at all. Such structures (so-called condensation structures) are formed in disperse systems, in which contacts are reversible with respect to strength as a result of phase and/or chemical transformations, for example, upon crystallisation from supersaturated solutions or melts (on their cooling), polymerisation, sintering, plastic deformation on pressing, removal of a liquid dispersion medium, *etc*. The minimum phase

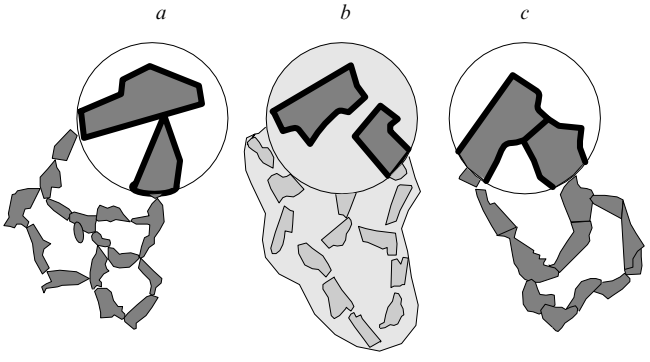


Figure 1. Main types of contacts between particles of dispersed phases according to Rehbinder.[1]
Contacts: (*a*) direct (atomic), (*b*) coagulation, (*c*) phase.

Table 1. Types and characteristics of contacts between particles.

Contacts	f_c/N	E_c/J	Note
Direct (atomic)	10^{-8}–10^{-9}	10^{-17}–10^{-16}	contacts occur in finely dispersed powders
Coagulation	10^{-10}–10^{-8}	10^{-19}–10^{-18}	contacts occur in pastes (suspensions) or emulsions through a thin liquid interlayer
Phase	$\geqslant 10^{-7}$–10^{-6}	$\geqslant 10^{-17}$–10^{-16}	strong contacts typical of condensation structures of dispersed materials

contact corresponds to $\sim 10^2$ interatomic bonds. This contact is essentially no different from an atomic contact typical of finely dispersed powders. Since the contact surface area is only $\sim 10^{-16}$ m^2, the probability of occurrence of a defect is very low, and the strength of the contact approaches that of an ideal solid body. As the area of the phase contact increases, the force f_c generally reaches $\sim 10^{-3}$ N.

The mechanical properties of disperse structures appeared in different steps of structure formation depend on the force f_c for an individual contact determined by its nature as well as on the number of such contacts per unit volume. Coagulation structures play an important role in the properties of disperse systems and (particularly) dispersed materials. It is their formation that is the first step in the synthesis of structured disperse systems and materials.

2. Criteria for the formation of dispersed structures

a. Characteristic critical particle size

Dispersed structures can be generated if two conditions, which determine the critical particle size of a dispersed phase d_c and their critical concentration in liquid or gaseous dispersion media, are fulfilled.

To a first approximation, these conditions can be described as follows.

1. Depending on the type of contacts, systems have a particular characteristic critical particle size; if $d < d_c$ (d is the characteristic particle size), the structure can form and exist; if $d > d_c$, the structure becomes unstable in a gravitational field, *i.e.*, can be self-destructed under gravity forces of the particles involved in this structure.

2. At the critical concentration of particles of dispersed phases in a dispersion medium, a spatial structure with the strength $\tau_p > 0$ can form spontaneously.

Let us consider successively the quantitative values of these criteria.

According to the first conditions, the criterion for aggregability characterising the possibility of formation of dispersed structures is based on a simple principle: a coagulation structure in disperse systems can appear if the cohesive forces between particles are comparable to the particle weight (or larger than this weight in a particular dispersion medium [2])

$$f_c \geqslant G^*, \tag{1}$$

where

$$G^* = \rho_{ef}\, d^3 g, \tag{2}$$

G^* is the particle weight, ρ_{ef} is the effective density of the particle in a dispersion medium ($\rho_{ef} = \rho_0 - \rho_1$, where ρ_0 is the density of the solid phase and ρ_1 is the density of the dispersion medium), g is the gravitational acceleration.

For structures with direct atomic contacts (the coordination number of the particle $z = 1$),[1,2,15]

$$d_c \sim \left(\frac{f_c}{\rho_{ef} g}\right)^{1/3}. \quad (3)$$

For dispersions with a liquid medium (pastes, suspensions), which have lyophobic coagulation contacts [15–18] and contain particles in a short-range potential well ('short-range' coagulation: $h \approx h_2$, h is the distance between the particles),[17]

$$\overline{d}_c \sim \frac{k}{h_2}\left(\frac{A^*}{\rho_{ef} g}\right)^{1/2}, \quad (4)$$

where k is the dimensionless coefficient equal to ≈ 0.2 and A^* is the Hamaker constant.

For coagulation structures containing particles in a long-range potential well ('long-range' coagulation, $h \approx h_1$),[15]

$$\overline{d}_c \sim \frac{1}{h_1}\left(\frac{\pi}{2}\frac{B}{h_1 \rho_{ef} g}\right)^{1/2}, \quad (5)$$

where B is the Lifshits constant.

An important result of calculations of d_c for the typical values $A^* \sim 10^{-19}-10^{-20}$ J, $B \approx 10^{-28}$ J m and $\rho_{ef} \sim 2$ is that $d_c \gg 1$ μm and can amount up to 100 μm. This value is several orders of magnitude larger than the size of colloidal particles. Relations (3)–(5) are given with respect to one contact between two particles. This is a hypothetical limiting case characteristic of the initial step of formation of aggregates from particles.

In actuality, the coordination number of particles in the structure is $z \geqslant 2$. Hence, d_c for each of the above-considered structural types can be larger than those calculated by Eqns (3)–(5).

In the general form, the criterion for aggregation in the case of solid phase — liquid medium dispersions can be determined from the condition that the potential energy of interaction between particles in a contact must be comparable to the energy of external actions on the disperse system.[19]

Let us assume that the potential energy of interaction between two spherical particles of radius $r = d/2$ is expressed by the equation

$$U(r, h) = r\,[C_1(h) + C_2(h)], \quad (6)$$

where C_1 describes the contribution of the molecular attractive forces [18]

$$C_1(h) = -\frac{B}{h^2} \quad \text{at } h \gg h_k, \quad (7)$$

$$C_1(h) = -\frac{A^*}{12h} \quad \text{at } h \ll h_k, \quad (8)$$

$h_k \cong 10^{-8}$ m corresponds to the characteristic wavelength of the line in the absorption spectra of atoms and molecules of the contacting particles; $A^* \cong 10^{-19}$ J, $B \cong 10^{-27}-10^{-28}$ J m; $C_2(h)$ reflects the contribution of the Coulombic repulsion forces.[18, 20, 21]

Let us write $C_2(h)$ as follows

$$C_2(h) = 64\pi \frac{NT}{k^2}\gamma^2 e^{-\kappa_1 h}, \quad (9)$$

where N is the concentration of the electrolyte, T is the temperature expressed in terms of energy,

$$\gamma = \text{th}\frac{U_1}{4},\ U_1 = q\frac{\Psi}{T},$$

Ψ is the electrical potential on the particle surface, q is the charge on ions of the electrolyte,

$$\kappa_1 = \left[8\pi q^2 N(\varepsilon T)\right]^{1/2},$$

ε is the dielectric constant.

A sequence of transformations of Eqn (9) gives the following expressions for low ($U_1 \ll 1$) and high ($U_1 \gg 1$) energy potentials at $\kappa_1 h \ll 1$: [21]

$$C_2(h) = A_0\,|\ln \kappa_1 h|, \quad (10)$$

where

$$A_0 = \frac{\delta \varepsilon T^2}{q^2},$$

$$\delta = \begin{cases} \dfrac{\pi^2}{4} & \text{at } U_1 \gg 1, A_0 \sim 10^{-11} \text{ J m}^{-1} \\ 2U_\infty^2 & \text{at } U_1 \ll 1, A_0 < 10^{-11} \text{ J m}^{-1}. \end{cases}$$

Here, U_∞ is the value of U_1 with $h \to 0$.

From Eqns (6)–(8) and (10), it follows that h_{max} corresponding to the maximum of the barrier separating the short- and long-range potential wells can be calculated as follows:

$$h_{max} = \frac{A^*}{12A_0}. \quad (11)$$

In the case of short- and long-range coagulation, the equations for the binding energy of the particles in the structure are as follows:

for short-range coagulation

$$U_2 = z[U(h_{max}) - U(h_2)] = -zA_0 \ln\frac{h_{max}}{h_2} + \frac{zA^* r}{12}\left(\frac{1}{h_2} - \frac{1}{h_{max}}\right), \quad (12)$$

for long-range coagulation

$$U_1 = -zU(h_1) = z\frac{Br}{h_1^2}\left(1 - \frac{2}{\kappa_1 h_1}\right). \quad (13)$$

If the potential energy of interactions between particles (6) is represented as a model function composed of two potential wells taking the shape of parabolic curves of depth U_2 and U_1, the stability (or aggregation) criterion for static conditions is expressed in the general form as follows:

$$U_i > \frac{4}{3}\pi \rho_{ef} r^3 g h_i, \quad (14)$$

The index $i = 1$ corresponds to long-range coagulation, and $i = 2$ corresponds to short-range coagulation. Equation (14) serves as the energy criterion for stability of the structure with respect to sedimentation, *i.e.*, to destruction followed by sedimentation of the particles under their own weight.

A combination of Eqn (14) and the condition for stability of the structure with respect to Brownian motion [3, 15] gives an equation, which determines the range of the critical sizes of particles capable of forming structures stable in static conditions,[19]

$$\frac{d_i}{2} = r_i = \left[\frac{U_i}{r}\left(\frac{4}{3}\pi \rho_{ef} g h_i\right)^{-1}\right]^{1/2}. \quad (15)$$

Assuming that $A^* = 10^{-19}$ J, $A_0 = 10^{-11}$ J m^{-1}, $B = 10^{-27}$ J m, $h_1 \sim 5 \times 10^{-8}$, $h_2 = 10^{-9}$ m, $\rho_0 \sim (1-2) \times 10^3$ kg m^{-3} and $z = 6$, one obtains $d_c/2 \sim 10^{-7}-10^{-5}$ m for systems with long-range coagulation of particles and $d_c/2 \sim 5 \times 10^{-5}-10^{-4}$ m for systems with short-range coagulation.

The maximum values of $d_c/2$ correspond to the criteria for aggregability (4) and (5).

Therefore, calculations of the criterion for aggregability according to Eqns (4), (5) and (15) give analogous results. The values of d_c demonstrate that coagulation structures can form spontaneously in dispersions with particle sizes of tens or even hundreds of micrometers. This indicates that the surface phenomena, contact interactions and structure formation are to a large extent responsible for the properties and characteristic features of most natural disperse systems, which were traditionally assigned to coarsely dispersed materials (for this reason, these materials were treated within the framework of mechanics of continua and hydrodynamics). The following systems belong to such materials: various powdered materials,[2, 22] for example, mineral binders (cements, lime, gypsum); fillers for varnishes and dyes, resins and

polymers; powdered fuels; mineral fertilisers, powders for fire extinction; nutritive disperse systems (flour, sugar powder), paste systems and suspensions, including slurries of chemical industries, suspensions of cellulose fibres used in the production of paper and cartons, suspensions and pastes for the production of porcelain, faience and ceramics; heterogeneous fuels; powdered and paste-like by-products and wastes from manufacturing, in particularly, from concentration plants; numerous natural disperse systems (grounds and soils); bottom sediments of rivers, lakes, seas and oceans.

At the same time, particles in these systems cannot participate in thermal Brownian motion, because their characteristic size is several orders of magnitude larger than the colloidal particle sizes. Hence, the conditions for the creation of a dynamic state of particles in such systems (*i.e.*, the movement of these particles necessary for various chemical engineering processes, for example, mass transfer processes) cannot be achieved through thermal motion. To produce a dynamic state analogous to Brownian motion in dilute aggregation-stable (lyophilic) colloids, it is necessary to deliver energy from external sources with an acceleration of no smaller than g.

b. Concentration factor and strength of coagulation structures

Let us consider quantitative estimates of the concentration factor, which determines the possibility of formation of dispersed structures. In essence, the minimum strength of a structural network, which can hold its constituent particles in a gravitational field, can serve as this criterion. Eventually, it is the strength of the structure that is responsible for its stability in dynamic conditions.

The theories of strength developed in the studies [23–26] are based on an additive approximation, which can be represented in the general form as follows:[3]

$$P_m \sim \chi f_c,$$

where χ is the number of contacts between particles per unit surface.

The corresponding plot of the structure strength *vs.* the concentration of a dispersed phase in a dispersion medium is shown in Fig. 2 *a*. A series of additional parameters characterising the degree of an increase in the strength depending on the concentration can be proposed: $\tan\alpha = dP_m/d\varphi$ for $\varphi_0 < \varphi < \varphi_c$ and $\tan\beta'$ for $\varphi > \varphi_c$, where φ_0 and φ_c are the minimum concentrations at the beginning of structure formation and at the beginning of a sharp strengthening, respectively.[2,26]

Assuming the irregular random particle distribution in the bulk (unlike the distribution assumed in the studies [23–26] and the regular particle distribution in the bulk [27–29]),[30] a more general dependence of the strength on the porosity of dispersed structures was obtained. This approach is based on the concepts of the percolation theory.[31,32]

An earlier attempt to solve this problem [33] was based on the use of a simplified model of the Bethe lattice,[34] which is far from real coagulation structures formed in disperse systems.

A model of a lattice of randomly packed spheres [27] used in the study [30] made it possible to take into account the possibility of the formation of dispersed structures characterised by various particle distributions in a broad range of the coordination numbers from 3 to 9.

When developing a theory for the description of the dependence of the structure strength on its relative porosity $v = \varphi/\varphi_0$ by analogy with the dependence of the conductivity on the porosity of the structure consisting of current-conducting spheres,[30–35] the authors proposed the parameter C, which reflects a particular topological property of a disperse system and is determined by the equation

$$C = \frac{P_m(v)}{P_m(I')}, \tag{16}$$

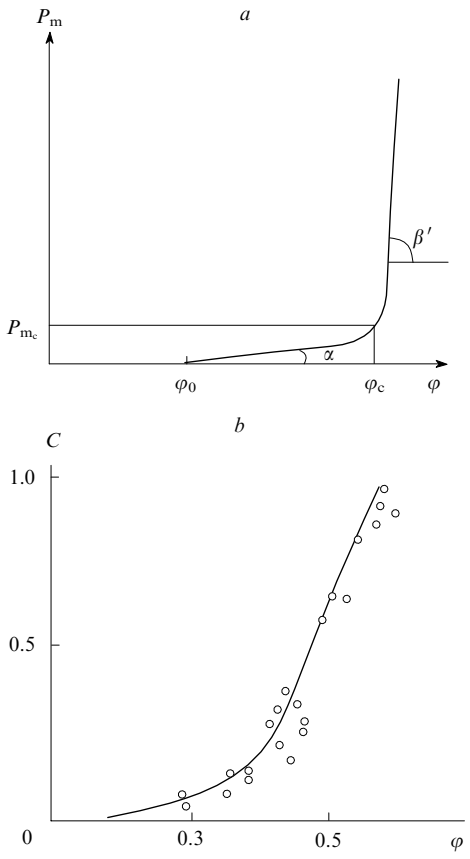


Figure 2. Plots of the strength of dispersed structures *vs.* the concentration (porosity) of a dispersed phase in a dispersion medium.
(*a*) The general character of the dependence,[24] (*b*) the dependence found using the percolation theory; the experimental data are shown by circles.[26]

where $P_m(v)$ is the strength of the porous structure with any effective porosity, $P_m(I')$ is the strength of the system at the maximum volume concentration of the particles (φ_{max}) in the dispersion medium.

The critical relative porosity $v_c = \varphi_0/\varphi_{max}$ corresponds to the maximum porosity at which a structural network is formed in the bulk of a dispersion.

At $v < v_c$,

$C(v) = 0$;

at $v > v_c$ (or $v \to v_c$),

$C(v) = (v - v_c)^{\mu}$,

where μ is determined by the dimensionality of the space (for a three-dimensional space, $\mu \approx 1.8$);[35,36]

at $v \to 1$,

$$C(v) = 1 - K(1 - v), \tag{17}$$

the coefficient K, in turn, depends on the coordination number z

$$K = \frac{2z - 2}{z - 2}. \tag{18}$$

The latter equation allows one to find the dependence of $C(v)$ on the coordination number in the range from 3 to 9, *i.e.*, virtually for all types of quasi-lattices. From Eqns (17) and (18) taking into account the values of K for various z, one has

$$C(\Pi) = 1 - K\left(1 - \frac{1 - \Pi}{1 - \Pi_0}\right) \approx 2.7 - 4.2\,\Pi \tag{19}$$

where $\Pi = 1 - \varphi$, $\Pi_0 = 1 - \varphi_0$.

The experimental data obtained for a model porous structure formed from monodispersed spherical particles of polystyrene and the theoretical dependence (19) are presented in Fig. 2 *b*. It can be seen that there is a good agreement between the theoretical and experimental results.

Based on this theory, the dependences of the strength on the porosity of spatial structures formed in finely dispersed structured systems consisting of clusters and particles and, in a more general case, of aggregates of primary particles (at $d \ll d_c$), were found.

The strength of structures consisting of aggregates can be described by the following equation:[30, 37]

$$C(\varphi) \sim \left(\frac{\varphi}{\varphi_{max}}\right)^{\gamma} \tag{20}$$

where

$$\gamma = 3 + \frac{f/f_a}{3-f},$$

f is the fractal dimensionality of the structure and f_a is the fractal dimensionality of the cluster (aggregate).[38]

This equation is true at $f < 3$. In particular, for percolation clusters, $f_a = 1.8$ at $f = 2.5$, and then $\gamma = 8.8$. For branched clusters, $f_a = 1.5$ at $f = 2$, and then $\gamma = 4.3$.[38–40]

Therefore, Eqns (17), (19) and (20) derived with the use of the percolation theory made it possible to describe the dependence of the strength on the porosity for a random distribution of particles and aggregates in the bulk of the structure. This is the most general case corresponding to real conditions.[41]

III. Destruction of disperse systems in dynamic conditions

1. Dynamic state of disperse systems

Due to the spontaneous formation of a spatial structural network at $d \leqslant d_c$ and $\varphi > \varphi_0$, both a disperse system as a whole and its constituent phases completely lose mobility, *i.e.*, the possibility of relative movement, under static conditions, which is accompanied by the corresponding increase in the viscosity, strength and modulus of elasticity. These structural and rheological characteristics particularly sharply increase at $\varphi > \varphi_c$, whereas φ_c (as well as φ_0) substantially decrease as the dispersity (S) increases at $d \leqslant d_c$. This is also favoured by an increase in the degree of particle anisometry and the occurrence of lyophobic-lyophilic mosaicity on the particle surface, particularly, if the particle surface is predominantly lyophobic. If there are no conditions for easy mobility (fluidity) and, hence, for the possibility of movement of the particles of dispersed phases with respect to each other and relative to a dispersion medium, there is no possibility to carry out various chemical engineering processes and control structural and rheological properties.

For highly concentrated and, particularly, finely disperse systems, this problem is much more difficult to solve because of a spontaneous increase in the number of contacts between particles per unit volume. The line of attack on this problem consists in going from static conditions, in which highly viscous and stable dispersed structures are formed (particularly, at $\varphi \geqslant \varphi_c$ and $d \ll d_c$), to dynamic conditions, in which these structures can be efficiently destroyed due to breaking of coagulation contacts between particles of dispersed phases. These conditions can be achieved by creating an isotropic dynamic state in a disperse system such that an equally probable degree of destruction occurs throughout the bulk of the disperse system. In the limit, coagulation structures are completely destroyed and all coagulation contacts are broken (Fig. 3). It is these conditions that could provide the maximum fluidity and the corresponding lowest viscosity level of the ultimately and isotropically destroyed structure. The dynamic aggregation stability of a disperse system corresponds only to this 'limiting' isotropic dynamic state produced by delivering an energy higher than the cohesive energy to each particle.

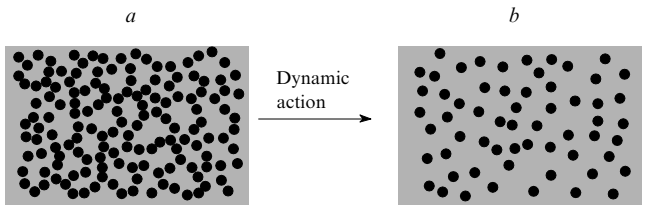


Figure 3. Scheme illustrating conditions for the creation of the optimum dynamic state of disperse systems.
(*a*) A structured dispersion, (*b*) complete ultimate deaggregation.

The type of this energy, its values and conditions of energy delivery to a system depend on the particle size of a dispersed phase, the number of the particles per unit volume, the binding energy between particles (lyophilic or lyophobic interactions) and the viscosity of a dispersion medium.

To determine the main parameters of actions (or their combination) on a disperse system with the aim of creating a controlled dynamic state, it is necessary to determine responses of both individual particles of dispersed phases and the disperse system as a whole to various actions. The responses of particles of dispersed phases to various actions can be described using the characteristic times (τ) of the following microprocesses, which were determined using the dimension theory:[6, 9]

interparticle interactions ($f_{c,\mu}$) through surface forces (molecular attractive forces f_c and Coulombic repulsive forces f_μ)

$$\tau_{f_{c,\mu}} \sim \frac{\eta d^2}{f_{c,\mu}};$$

thermal motion due to the internal energy of molecules of a dispersion medium

$$\tau_B \sim \frac{\eta d^3}{kT};$$

inertial motion of particles under external forces

$$\tau_i \sim \frac{\rho_{ef} d^2}{\eta};$$

sedimentation under gravitational forces

$$\tau_s \sim \frac{\eta}{\rho_{ef} d^2 g},$$

where η is the viscosity of the dispersion medium.

The dependences of the inverse relaxation times of various microprocesses on the particle size are shown in Fig. 4. It can be seen that the contribution of each of the actions on particles to τ (and, correspondingly, to $\dot{\varepsilon} = 1/\tau$) changes substantially (by orders of magnitude) with changes in the particle size; correspondingly, the conditions for producing a dynamic state of disperse systems change.

A combination of the factors responsible for a dynamic state of finely disperse colloidal systems, which are classical objects of physical chemistry of disperse systems and surface phenomena, have been studied in most detail.

For such systems, the main characteristic times of microprocesses of a dynamic state are determined by the ratio between $\tau_{fc,\mu}$ and τ_B. For such systems, the contributions of the inertial effects and sedimentation processes are insignificant due to small masses and sizes of particles.

The possibility of formation of dispersed structures or their self-destruction (deaggregation) in the case of colloidal dispersions is determined by the known criterion [3]

$$U_c \sim \frac{\beta^* kT}{(1/2)z}, \tag{21}$$

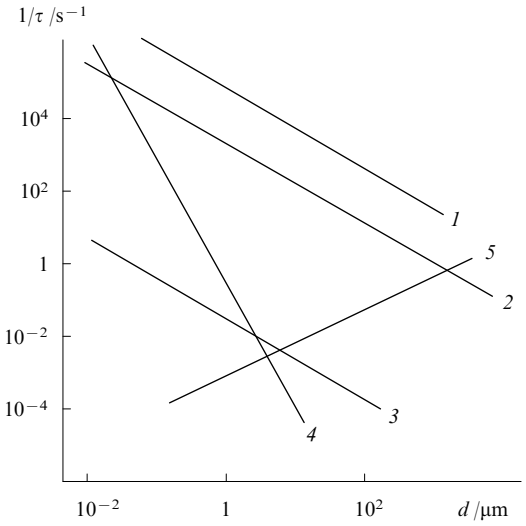


Figure 4. Dependence of the characteristic times of microprocesses on the particle size of a dispersed phase.[9, 30]
(*1*) Inertial effects, (*2*) molecular attraction, (*3*) Coulombic repulsion, (*4*) Brownian motion, (*5*) sedimentation. The results were obtained at $A^* \sim 5 \times 10^{-20}$ J, $\eta \sim 1$ mPa s, $\rho = 2 \times 10^3$ kg m^{-3}.

where U_c is the energy of molecular interactions between the particles in a structural network, β^* is the coefficient

$$\beta^* = \ln \frac{n_a}{n_p},$$

(n_a is the number of particles in the aggregated state, n_p is the number of particles in the deaggregated (peptised) state) and z is the coordination number of particles in a loose aggregate (~ 2).

The coagulation structure in a colloidal disperse system is stable if the energy of molecular interactions between particles is higher than that calculated by Eqn (21). If this energy is lower than the energies of thermal motion and random Brownian oscillations of the particles of dispersed phases, this structure undergoes self-destruction.

In essence, Eqn (21) determines the conditions for the creation of an isotropic dynamic state in colloidal systems. However, if $U_c > (10-15)\,kT$, such systems lose aggregation stability and become also unstable with respect to sedimentation. The dynamic state of such systems loses an isotropic character. When the size of aggregates formed from colloidal particles is larger than 1 μm, the possibility of the creation of a dynamic state under the action of thermal energy of molecular oscillations in a dispersion medium is very low, if at all.

For disperse systems with a particle size larger than 1 μm, the occurrence of an isotropic dynamic state is determined primarily by the relation between $\tau_{fc,\mu}$, τ_i and τ_s.

Based on the above-considered facts, the conditions (criteria) for the attainment of an isotropic dynamic state in disperse systems can be represented in the general form:

for a region of colloidal systems ($d_c < 1$ μm)

$$U_c \geqslant (10-15)\,kT,$$

$$\frac{1}{\tau_B} > \frac{1}{\tau_{f_{c,\mu}}};$$

for a region of microheterogeneous structured disperse systems (1 μm, $< d_c < 100$ μm)

$$E_c = \frac{mV^2}{2} > U_c,$$

$$U_c \sim \frac{k^* d}{h^n},$$

where E_c is the kinetic energy imparted to a particle from an external source of mechanical power, m is the mass of the particle, V is its relative velocity, U_c is the total energy of molecular interactions in contacts between a particle and the adjacent particles, k^* is the constant of molecular interactions between condensed phases, n is the coefficient;

for the region of coarsely disperse systems

$$A > g,$$

where A is an acceleration imparted to a particle from an external source.

Taking into account these criteria, the conditions for the creation of an isotropic dynamic state in structured disperse systems ($\varphi > \varphi_0$ and $d \ll d_c$) are determined by a combination of macroscopic ($\eta_{ef} = \eta_{min}$, where η_{ef} is the effective viscosity) and microscopic parameters.

The conditions for the delivery of energy to a disperse system from an external source depend on the nature of a disperse system. In two-phase systems, such as solid dispersed phase – liquid dispersion medium (pastes, suspensions), liquid – liquid and liquid – gas (foam), the energy is supplied predominantly in the course of their deformation

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt},$$

where $\dot{\varepsilon}$ is the deformation rate, ε is the relative deformation, t is the time. In two-phase systems, such as solid phase – gaseous medium (powders), and three-phase systems, such as solid phase – liquid medium – gaseous medium, the energy is supplied in a combined way by changing both the volume and shape.

However, the choice of the type of action on disperse systems is not limited to only changes in their volume and shape. The determining factor is the possibility of the creation of a controlled isotropic dynamic state in a system under conditions of the chosen type of action.

The main problem in the description of the dynamic state of disperse systems is to reveal the relationship between the contact interactions of the particles of dispersed phases and the bulk properties of the dispersion. For static conditions, this problem was, in essence, solved. The functional relationship between the strength of individual contacts of the particles and the strength of the structure as a whole was found in the context of the theories of strength of dispersed structures. For dynamic conditions, this problem is substantially complicated already because the formation and breaking of individual contacts between the particles occur in non-equilibrium conditions with a simultaneous change in the distance (interspace) between the particles and a manifestation of the hydrodynamic factor associated with leakage of a dispersion medium inside and outside the interspace. Therefore, let us consider the characteristic features of contact interactions between particles of dispersed phases under such conditions prior to analysis of the conditions for the creation of a dynamic state of disperse systems.

2. Dynamics of contact interactions in disperse systems

a. Non-equilibrium as an important feature of the dynamics of contact interactions

To describe the behaviour of most disperse systems in the course of various heterogeneous chemical engineering processes,[41] which proceed under conditions of forced convective diffusion of dispersed phases, as well as of many natural phenomena involving natural disperse systems, it is necessary to go from a consideration of contact interactions in static conditions to non-equilibrium dynamic conditions.

For such processes, a non-equilibrium dynamic state of disperse systems prevails. Interactions between particles to form contacts or, on the contrary, the breaking of contacts can occur at high particle velocities. Therefore, it is incorrect to consider the conditions for their coagulation (breaking of contacts) without regard for the dynamics of their movement toward or away from

each other.† For example, in real heterogeneous processes, $\dot{\varepsilon}$ is as high as 10^2-10^3 s^{-1} under deformation of disperse systems. An analogous situation is observed also when a deformable disperse system is subjected to orthogonally directed oscillation. In the study,[9] it was demonstrated that the relative particle velocities reach 1–1.5 m s^{-1} at the oscillation frequency $f_v = 50$ Hz and the amplitude of $10^{-2}-10^{-3}$ m. The non-equilibrium is even more pronounced in the case of oscillations of polydisperse systems and also in the presence of anisometric particles. As the oscillation frequency increases (particularly, when such dispersions are subjected to low-frequency mechanical oscillation in combination with high-frequency ultrasonic oscillation region), the velocity can substantially exceed 10^3 s^{-1}.

Below are considered the basics of the dynamics of contact interactions predominantly in systems composed of a solid phase and a liquid dispersion medium. The preparation of such dispersions is generally preceded by dynamic processes in solid phase–gas (S–G) systems. In the case of the addition of a liquid medium, the preparation is also preceded by dynamic processes in intermediate solid phase–liquid–gas (S–L–G) systems. Hence, this section of the review deals with certain aspects of the dynamic theory of contact interactions in powders and three-phase systems.

b. Dynamics of contact interactions in two-phase dispersions composed of a solid phase and a liquid dispersion medium

Consideration of the Coulombic component of the disjoining pressure and the slip of a dispersion medium. The solution of problems of dynamic coagulation of particles and, correspondingly, the determination of the conditions for the formation of coagulation contacts are based on calculations of dependences of the force F, which prevents two particles from approaching each other, on the initial velocities, the distance between the particles h and the viscosity of a dispersion medium η.[9–11]

For $h \gg r$ (where r is the particle radius) and the initial velocity V, this force is determined by the equation:

$$F(V,h) = -6\pi\eta r\frac{\mathrm{d}h}{\mathrm{d}t} \equiv \sigma\pi\eta r V. \tag{22}$$

In the case of interaction between two particles in concentrated dispersions, $h \ll r$. Then, taking into account the slip effect of a liquid determined by the coefficient β, the force $F(V,h)$ is given by the expression [9]

$$F(V,h) = \frac{\pi V r^2}{12\beta^2\eta}\left[(h+6\beta\eta)\ln\left(1+6\frac{\beta\eta}{h}\right)-\right.$$
$$\left.-(r+6\beta\eta)\ln\left(1+6\frac{\beta\eta}{r}\right)\right]. \tag{23}$$

In the case of strong slip over the surface of lyophobic particles ($6\beta\eta \gg r$),[47,48] Eqn (23) is simplified

$$F(V,h) = \frac{\pi V r^2}{2\beta}\ln\frac{r}{h}, \tag{24}$$

In the case of weak slip (lyophilic systems, $6\beta\eta \ll r$), $F(V,h)$ is given by the following equation:[9]

$$F(V,h) = \frac{3\pi}{2}\eta\frac{Vr^2}{\beta}. \tag{25}$$

The solution of the problem of inertial coagulation (dynamic conditions) for lyophilic systems in the presence of a high ($U_1 \gg 1$) and low ($U_1 \ll 1$) potential barriers between particles (U_1 is the potential barrier in units of kT) consists in determining the initial critical velocity at which particles approach each other (V_{c_0}), *i.e.*, the maximum velocity above which the particles undergo coagulation,[9]

$$V_{c_0} = V_1\left[\frac{|\ln(A^*kr/12A_0)|}{krA^*/A_0}\right] + V_2\ln\left(12\frac{h_0A_0}{rA^*}\right), \tag{26}$$

where

$$V_1 = \left(\frac{A^*rk'}{6m}\right)^{1/2},$$
$$V_2 = \frac{3}{2}\frac{\pi\eta r^2}{m}, \tag{27}$$

h_0 is the distance between the particle surfaces at the start time ($h_0 \sim r$), m is the effective mass of the particle and k' is the inverse Debye radius.

If the velocity V, at which particles approach each other under an external action, is higher than that calculated by Eqn (26), the particles undergo coagulation.

Analysis of stability in dynamic conditions showed that the Coulombic factor is of importance only in the case of relatively low-intensity external actions. The contribution of this factor decreases, for example, as the deformation rate increases and in the case of deformation of polydisperse systems (particularly, in the presence of strongly anisometric particles). The slip effect of a dispersion medium over the particle surface of a dispersed phase increases substantially as the relative particle velocity increases and the distance between the particles decreases.[9,11–13]

The slip effect is most pronounced when particles with a hydrophobic surface approach each other in a polar liquid.[11] For water, this effect can be attributed, in particular, to the fact that the dipoles of water molecules are parallel to the hydrophobic surface, which substantially facilitates their mobility in the tangential direction and, apparently, decreases the viscosity in a wall boundary layer.[47,48] For example, the slip coefficient β of water relative to hydrophobised quartz can be as high as $\sim 10^{-4}$ m^3 N^{-1} s^{-1} (see Ref. 48). In this case, the contribution of the slip effect is much larger than that for hydrophilic particles. Hence, the corresponding critical velocities will also be substantially different. In the case of weak and strong slip of particles, the critical velocities at which particles approach each other are calculated by the equations [10]

$$V_{c_0} > \frac{9\eta}{4\rho r}\ln\frac{h_2}{h_0}, \tag{28}$$

$$V_{c_0} > \frac{3}{4\beta\rho}\frac{h_0}{r}\gamma, \tag{29}$$

where h_2 is the distance between the particle surfaces at which they are fixed due to dynamic coagulation and γ is the coefficient

$$\gamma = 1 + \ln\frac{r}{h_0}.$$

According to the results of the study,[10] the distance h_2 corresponds to the distance at which the potential energy of interactions between particles has a positive maximum. It should be noted that, due to lyophobic–lyophilic mosaicity of the particle surfaces in real dispersions, the critical coagulation rates are determined by the probability of pair collisions between particles at lyophobic, lyophilic or both lyophobic and lyophilic regions.[49] Taking into account the above three types of collisions, the probability of particle coagulation under dynamic conditions is given by the expression [50]

$$E^* = \alpha(1-\Theta)^2 + \beta^*\Theta + \gamma^*\Theta(1-\Theta), \tag{30}$$

where E^* is the probability of the formation of a bond between two particles, α and β^* are the probabilities of coagulation and

† Strictly speaking, the breaking of a contact even as a result of very slow detachment of particles, *i.e.*, in 'static' conditions, cannot, in essence, be considered as an equilibrium process because the transformation from the 'contact-is-present' state to the 'contact-is-broken' state is accompanied by a series of non-equilibrium phenomena (for example, in a double electrical layer).[42–46]

flocculation, respectively, Θ is the fraction of a modified particle surface, γ^* corresponds to the probability of binding as a result of a contact between a stabiliser immobilised on the surface of one particle and the surface of another particle.

Consideration of the particle shape factor. The consideration of the particle shape is an important problem in the dynamic theory of contact interactions, which was solved in the general case in the studies.[9,10] Below are considered two typical cases. In one of them, the possibility of coagulation of strongly anisometric particles with a very small radius of curvature of the frontal surface (for example, as extended needle-like rods) was taken into account. In another case, the conditions for collision between two disk-like particles in the case of both parallel and 'edge – plane' orientations were considered. The critical rates of dynamic coagulation are expressed by the following equations, respectively:

$$V_{01} = \frac{9\eta}{\rho r_{\max}} \left(\frac{r_1}{r_{\max}}\right)^2, \tag{31}$$

$$V_{02} = 12\frac{\eta}{\rho r_0}\left(\frac{r_2}{r_0}\right)^{1/2} = 12\frac{\eta}{\rho r_{\max}}\left(\frac{3}{2}\right)^{3/4}\left(\frac{r_2}{r_{\max}}\right)^{5/4}, \tag{32}$$

where r_1 is the local radius of curvature of particles of linear size

$$r_{\max} = \left(\frac{3m}{4\pi\rho}\right)^{1/3},$$

m is the mass of particles, ρ is their density, r_0 is the radius of the disk-like particle with thickness $2r_2$, r_2 is the radius of curvature of its frontal surface, $r_2 \ll r_0$. In Eqns (31) and (32), r_1 and $r_2 > 0$.

The plots of the critical coagulation rate *vs*. the particle radius are shown in Fig. 5. It can be seen that the shape factor has a strong effect on the critical coagulation rate. For anisometric particles with a size ratio of 1 : 100, the rate decreases by an order of magnitude. Hydrophobisation of the surface, particularly, of anisometric particles, also leads to a decrease in the critical rate of dynamic coagulation by several orders of magnitude.

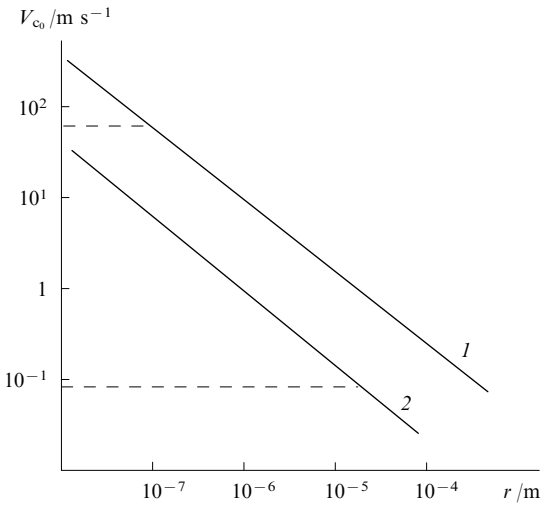


Figure 5. Plots of the coagulation rate *vs*. the particle radius r.[3,10,30] (*1*) For spherical particles ($r = r_0$), (*2*) for anisometric particles ($r_1/r_0 = 0.01$). Dashed lines correspond to particles with a hydrophobic surface.

Role of elastic properties of particles and the structure-mechanical barrier produced by a surfactant adsorption layer. Dynamic particle coagulation is preceded by the approach of the particles to each other accompanied by the displacement of a liquid medium from the interspace between their surfaces. This process is attended by an excess pressure in the interspace and corresponding particle deformation, whose value depends on the outflow rate of the liquid, its viscosity and modulus of elasticity of the particles.[51,52] The contribution of the structural component of the disjoining pressure should be taken into account if the particles are separated by a very small distance ($h_c \sim 2-3$ nm). The range of action of the structural component of the disjoining pressure is $h_c \geqslant 2$ nm.[3,18] For inertial coagulation of particles with a rough surface, the consideration of the roughness leads to an increase in h_c to 100 nm.

As mentioned above, the attainment of the critical coagulation rate V_{c_0} is a prerequisite for the formation of a 'dynamic' contact between particles. If V_{c_0} is higher than a particular value, elastic rebound of particles becomes possible because elastic 'recoil' exceeds the viscous resistance of a liquid to motion. Taking into account this factor, the range of the critical coagulation rates should satisfy the condition determined by the relation

$$\frac{10^2\zeta^2\eta}{\rho r_{\max}} \ll V_{c_0} \ll \frac{10^2\zeta^2\eta}{\rho r_{\max}E}\left(\frac{\eta}{\rho r_{\max}}\right)^2\zeta^4\left[\frac{1}{\zeta}\left(\frac{r_{\max}}{h_c}\right)^5\right]^{4/7}. \tag{33}$$

Here, $\zeta = r_1/r_{\max}$ and E is the modulus of elasticity of the particles. Inertial coagulation of particles under dynamic conditions can take place only in a particular range of the rates V_{c_0}, which depends on the elastic properties, the shape (the degree of anisometry), the density of the particles and the liquid viscosity.

The conditions of aggregation dynamic stability are substantially influenced by the presence of a surfactant adsorption layer on the particle surface and the properties of this layer, *viz*., the binding energy with the particle surface, the elasticity and the degree of lyophilicity of radicals exposed to a dispersion medium. The criterion for loss of aggregation stability under dynamic conditions in the presence of a surfactant adsorption layer on the particle surface can be expressed by the following equation:

$$V_{c_0}^2 - 9\frac{\eta}{\rho r_{\max}}\left(\frac{r}{r_{\max}}\right)^2\lambda^*\ln\left(\frac{h_0}{L}\right)V_{c_0} - \frac{E_L}{2\rho}\left(\frac{L}{r_{\max}}\right)^2\frac{r}{r_{\max}}(\lambda^*)^2\left(\frac{P_L}{E_L}\right)^3 > 0, \tag{34}$$

where r is the local radius of curvature of the particle surface with a surfactant adsorption layer, λ^* is the particle shape coefficient, L is the thickness of the surfactant adsorption layer, P_L and E_L are the strength and the modulus of elasticity of this layer, respectively.

The structure-mechanical barrier is an essential factor of aggregation dynamic stability of a system, if

$$E_L > E_{L_c} \equiv \left(\frac{E_L}{P_L}\right)^3 2\rho\left(\frac{r}{r_{\max}}\right)^3\left(\frac{r_{\max}^2}{L}\right)\left(9\rho\frac{\eta}{r_{\max}}\ln\frac{h_0}{L}\right)^2, \tag{35}$$

where E_{L_c} corresponds to the critical modulus of elasticity, below which a 'breakdown' of the adsorption layer is possible.

c. Aspects of dynamics of contact interactions in finely dispersed powders

A knowledge of the parameters of formation and breaking of direct (according to Rehbinder [1]) contacts between particles under dynamic conditions is necessary for the description of the macrorheological characteristics and properties of powders in processes of flow, compaction or creation of an air-boiling or vibroboiling layer.[53–55]

Contact interactions between particles of solid phases in air and various media under static conditions have been studied extensively (see, for example, Refs 3, 15–17 and 56). The extension of the views of contact interactions, which are based on results of static measurements, to dynamic conditions appeared to be incorrect for dynamic actions on dispersed powders.[9] In particular, this follows from the dependence of the work of detachment on the detachment rate of contacting solid phases.[57–59] The differences in the works of detachment in static and dynamic conditions can be as high as two or even more orders of magnitude. The available methods (even their advanced mod-

ifications) for high-precision measurements of the cohesive forces in contacts allow one to take into account the influence of the detachment rate only at very low values of the latter, which differ from the real values corresponding to conditions of flow, boiling or compaction of powders by several orders of magnitude.

In this connection, approaches were developed,[58–62] which enable one to determine the strength and energy of interactions between particles from the results of dynamic (vibration) measurements with the use of apparatus and methods described in the studies.[58, 59, 61, 62] These approaches involve measurements of the structural and rheological properties of powders (effective shear stresses and viscosities) in the course of compaction or transformation of a powder from the vibrofluidisation state to the vibroboiling state accompanied by breaking of contacts between particles. The developed theory of this process allows one to calculate the energy and strength of interparticle interactions from the results of rheological measurements under vibration.

Equations derived in the studies [58, 61] can be used for determining the characteristics of contact interactions under vibration in powders with the rigorously characterised parameters of the particles (monodispersed spherical particles). As an example, let us give one of these formulas

$$f_{cv}C_v = \frac{\pi a^2 \omega \eta_v^0}{\zeta^*(r^{*2} - r_1^2)\ln(r_2^*/r_1^*)}\,. \tag{36}$$

Here, f_{cv} is the average autohesive force in the contact under dynamic conditions, C_v is the number of autohesive contacts per unit volume in the vibroboiling state, a and ω are the amplitude and circular frequency of vibrations, respectively, r_1^* and r_2^* are the radii of coaxial cylinders of a viscosimeter, ζ^* is the distance of autohesion, whose minimum value is 0.4 nm, η_v^0 is the largest value of the effective vibroviscosity [59] determined by extrapolating the rate of shear deformation to $\dot{\varepsilon} \to 0$.

Calculations using Eqn (36) demonstrated that the cohesive forces under dynamic conditions depend on the rate and acceleration of vibrations. For a number of polymer powders [poly(vinyl chloride), Fluoroplast, polyethylene] in dynamic conditions, f_{cv} is 2–4 orders of magnitude larger than f_c determined in static measurements on an adhesiometer.[15, 16] For glassy particles, these forces differ by no more than a factor of 6–7 (Table 2). The disagreement between the results of static and dynamic measurements increases as the detachment rate of particles increases.

Table 2. Autohesive characteristics of powders in static (f_c) and dynamic (f_{cv}) conditions (at the harmonic vibrational frequency of 200 Hz).

Powder	$\bar{d}$ /μm	$10^8 f_c$ /N	η_k /Pa s	f_{cv} /N
Ion-exchange resin KB-4P2	250	40	–	–
Polystyrene	50	100	40	2×10^{-3}
Poly(vinyl chloride)	20	4	10	3×10^{-3}
Glass	10	30	20	2×10^{-6}
Fluoroplast F30P	5	5	10	9×10^{-5}
Polyethylene	5	2	3	1×10^{-4}

Upon elimination of physicochemical inhomogeneity (lyophilic–lyophobic mosaicity) due to formation of a saturated adsorption monolayer of a surfactant on the particle surface, the cohesive forces in contacts between particles not only sharply decrease (because the particles move away from each other to a distance equal to twice the thickness of the hydrocarbon fragment of the surfactant molecule) but also become virtually independent of the prehistory of the structure formation of a finely dispersed powder (Table 3). Correspondingly, the autohesion level in contacts between particles changes.

To describe the macrorheological and mechanical properties of finely dispersed powders,[62, 63] one should use the characteristics of autohesion determined not in static (as is often the case) but in adequate dynamic conditions.

Table 3. Autohesive forces in contacts between particles of SiO_2 and $CaCO_3$ powders.

φ	$f_{c1}/10^{-5}$ N (without surfactants)	$f_{c2}/10^{-5}$ N (surfactant monolayer)	f_{c1}/f_{c2}
Powder of SiO_2 ($s = 1\times10^3$ m^2 kg^{-1}), surfactant — octadecylamine			
0.45	6.8	2.61	2.6
0.5	22.5	2.25	10.0
0.536	114.0	2.86	40.0
Powder of $CaCO_3$ ($s = 3\times10^3$ m^2 kg^{-1}), surfactant — stearic acid			
0.3	0.645	0.55	1.26
0.35	1.22	0.425	2.88
0.38	1.93	0.48	4.0

Note. Specific surfaces (s) were determined by low-temperature adsorption of nitrogen [Brunauer–Emmett–Teller (BET) method].

d. Dynamics of contact interactions in three-phase systems

The formation of three-phase structures under dynamic conditions in the course of their transformation into two-phase S–L systems (in particular, under conditions of mixing under vibration) proceeds as follows.

Contacts between solid-phase particles in powders are the first to be broken,[62, 63] then a liquid dispersion medium penetrates between the particles [62] to form microgranules, which act as kinetic units. The final step of this process involves association ('coalescence') of granules upon their collisions accompanied by the transformation of the disperse S–L–G system into the S–L system. Let us consider the kinetics of this process.

The structure in a powder is destroyed under vibration if the following condition is fulfilled:

$$a\omega^2 \geqslant \frac{f_c}{\rho d^3}\,, \tag{37}$$

where ρ and d are the density and diameter of the particles, respectively.

If a liquid medium penetrates into a vibroboiling layer consisting of powder particles and wets their surface,[64, 65] a capillary meniscus appears [15] and a granular structure forms. Subsequent interactions between the granules can lead to either their coalescence or recoil.

It can be assumed that the average kinetic energy produced by collisions between granules is determined by the equation

$$\overline{E}_a = D^3\rho_a\left[\overline{(V_a + a\omega\cos\omega t)^2 - V_a^2}\right] \sim D^3\rho_a(a\omega)^2, \tag{38}$$

where D is the diameter of granules, ρ_a is their density, V_a is the granule velocity prior to collisions, the overline denotes the averaging over time.

'Coalescence' of granules occurs if the energy determined by Eqn (38) is smaller than the energy required for the rupture of the meniscus formed between the granules. The energy required for breaking of the contact between two granules linked through a capillary meniscus is equal to $D^2\sigma$, where σ is the surface tension of the liquid phase. From this, the first condition for coalescence of granules can be obtained

$$D \leqslant \frac{\sigma}{\rho_a(a\omega)^2}\,. \tag{39}$$

This inequality determines the condition for cohesion of not-too-large granules (or individual particles), whose collisions can be considered as purely elastic. As the granules grow, their rheological properties become increasingly important. The condition for 'coalescence' of large granules can be obtained by comparing the collision time t of elastic spheres with diameter D (see Ref. 66) and the time of stress relaxation in the granule τ

$$t \sim \frac{D}{C_1^*}\left(\frac{C^*}{V}\right)^{1/5}, \qquad (40)$$

$$\tau \sim \frac{\eta_a}{E_a},$$

where

$$C_1^* \equiv \left(\frac{E_a}{\rho_a}\right)^{1/2},$$

V is the vibrational rate, η_a is the viscosity of the granule, E_a is the modulus of elasticity of the granules.

From this, it follows that the second condition for 'coalescence' of granules is described by the relation

$$D > \eta_a\left(\frac{V}{\rho_a^2 E_a^3}\right)^{1/5}. \qquad (41)$$

By comparing Eqns (39) and (41) on the assumption that $V \sim a\omega$, the following condition, which provides association of the particles to form granules and their subsequent growth, can be written as

$$a\omega < (C_1^*)^{6/11}(C_2^*)^{5/11}, \qquad (42)$$

where

$$C_2^* = \frac{\sigma}{\eta_a}.$$

In simplified form, Eqn (42) can be written as follows:

$$a\omega \leqslant (C_1^* C_2^*)^{1/2} \equiv \left[\frac{\sigma}{\eta_a}\left(\frac{E_a}{\rho_a}\right)^{1/2}\right]^{1/2}. \qquad (43)$$

Conditions (37) and (42) define the range of vibrational rates at which the 'old' S–G structure is destroyed and the 'new' S–L structure is formed in the system:

$$\frac{f_c}{\omega\rho d^3} \leqslant a\omega \leqslant \left[\left(\frac{E_a}{\rho}\right)^{1/2}\left(\frac{\sigma}{\eta_a}\right)\right]^{1/2}. \qquad (44)$$

Hence, in particular, it follows that this range of rates $a\omega$ exists only under high-frequency vibrations.

It should be noted that Eqn (44) was derived on the assumption that the S–G structure is completely destroyed (up to primary particles). However, this process occurs rarely in real highly disperse systems ($d \sim 1$ μm). Therefore, the size of the microaggregates D and their cohesive force F_c should be substituted for d and f_c, respectively, into expressions (37) and (44). In this case, expression (44) takes the form

$$\frac{F_c}{\omega\rho_a D^3} \leqslant a\omega \leqslant \left[\frac{\sigma}{\eta_a}\left(\frac{E_a}{\rho_a}\right)^{1/2}\right]^{1/2}. \qquad (45)$$

In particular, from this it follows that this rate range exists at a relatively high frequency of vibrations, whose value can be calculated by the formula

$$\omega \geqslant \frac{F_c}{\rho_a D^3}\left[\frac{\eta_a}{\sigma}\left(\frac{\rho_a}{E_a}\right)^{1/2}\right]^{1/2}. \qquad (46)$$

As an example, let us consider a model system consisting of a quartz powder ($d \approx 1$ μm) and calcium bentonite serving as a binder. At $A^* \approx 10^{-20}$ J and $h_1 \sim 10^{-8}$ mm, the binding force f_c of particles is $\approx 10^{-11}$ N. Assuming that the modulus of elasticity of granules is of the same order of magnitude as their strength, E_a is taken to be approximately 10^6 N m^{-2}. The viscosity of granules is close to that of the structure formed upon their 'coalescence' $\eta_a \approx 10^2$ Pa s, $\sigma \approx 0.1$ N m^{-1}. Let us assume that the size of inhomogeneities in the structure after granule coalescence is no larger that 30 μm. According to Eqn (46), the minimum vibrational frequency providing the formation of this structure is higher than 100 Hz. From this it follows that the allowable vibrational rate at which an S–L–G system is transformed into an S–L system is ~ 1 m s^{-1}, which is consistent with the experimental data.[2]

All the above have the following important consequences.

The energies and strength of contact interactions between particles in dynamic conditions differ substantially (in some cases, by several orders of magnitude) from the corresponding values measured or calculated in static conditions. This difference depends on the chemical nature and physical properties of dispersed phases and the intensity of external mechanical actions on disperse systems.

The inertial effects and hydrodynamic resistance of a medium[66] as well as the particle shape and lyophobic–lyophilic mosaicity of the particle surface are important factors determining the critical parameters corresponding to conditions of formation or breaking of contacts between particles in liquid media.

Under dynamic conditions, the structure-mechanical barrier (according to Rehbinder) formed by surfactant adsorption layers on the particle surface and the properties of these layers play an essential role in achieving dynamic aggregation stability of dispersions. Micelles in solutions of surfactants can serve an analogous function.[67]

In the case of finely dispersed powders, the energy and strength of interparticle interactions depend substantially on the intensity of external actions.

The dynamics of contact interactions in three-phase disperse systems is determined by a combination of complex processes of formation and breaking of coagulation and direct point contacts between particles, capillary meniscuses between the aggregates and their structural and mechanical properties.

At the same time, the kinetics of structure formation under dynamic conditions and the properties of the resulting structures also depend on the intensity of external actions, in particular, on the frequency and amplitude of oscillations.

3. Dynamic state of two-phase disperse systems of the solid phase – liquid medium type under continuous shear

The method most commonly used for describing the properties of S–L structured disperse systems under continuous shear deformation consists in constructing complete rheological flow curves.[68–73] These curves characterise the dependence of the effective shear viscosity η_{ef} on the shear rate $\dot{\varepsilon}$ or the shear stress P under the necessary condition of isotropic destruction‡ of a dispersion located in the interspace between the surfaces of coaxial cylinders or in a measuring cell of rotational viscosimeters. It is assumed that the shear at a given rate is extended throughout the interspace (or throughout the cell),[69,74] thus providing the isotropic character of destruction.

The complete flow curve of structured dispersions with viscosity drop $\eta_{ef} = f(\dot{\varepsilon},P)$ of up to 8–10 orders of magnitude on the assumption that the above conditions are fulfilled, *i.e.*, under purely homogeneous shear (according to Rehbinder), was first reported in the study.[75] The authors of the cited study introduced the notions of the highest viscosity of a virtually non-destroyed structure (η_0), which corresponds to the upper plateau in the flow curve, and the lowest Newtonian viscosity of an ultimately destroyed structure (η_{min} or η_∞).

‡ For the same degree of destruction in the bulk of the disperse system under consideration.

It was assumed that each level of the measured effective viscosity corresponds to a particular equilibrium level of isotropic destruction characterised by a certain ratio between the broken and acting coagulation contacts between particles of dispersed phases.

Consequently, the minimum level of the lowest Newtonian viscosity and, accordingly, the maximum fluidity should correspond to the limiting isotropic dynamic state. This interpretation of the flow mechanism of structured dispersions under continuous shear was embodied in studies of the rheological properties of various disperse systems.[68, 69, 71, 74] These notions were developed, primarily, by elaborating the idea of the aggregation (cluster) mechanism of destruction with complete deaggregation at $\eta_{ef} = \eta_{min}$ (Refs 76–81) as well as by introducing Krieger's correction (d^3/kT),[82] which takes into account the contribution of Brownian motion. This contribution is essential for dispersions containing particles of characteristic size $\ll 1$ μm (Fig. 6).

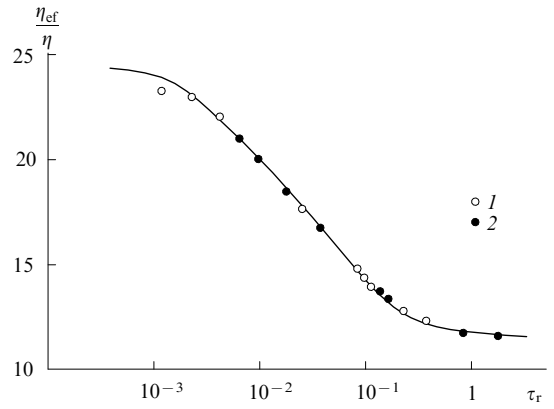


Figure 6. Plot of the relative viscosity *vs*. the effective shear stress τ_r for a suspension of polystyrene particles taking into account Krieger's correction.[82]
(*1*) In benzyl alcohol, (*2*) in cresol.

According to these views, the flow mechanism of structured dispersions as successive destruction under the action of the increasing shear rate $0 < \dot{\varepsilon} < \dot{\varepsilon}_\infty$ (or increasing shear stress P) is as follows: breaking of the bonds followed by their virtually complete recovery in a flow ($\eta_{ef} \approx \eta_0$ with $\dot{\varepsilon} \to 0$), destruction first into superaggregates and then into aggregates with the possible formation of new aggregates through inertial coagulation (at $\eta_\infty < \eta_{ef} < \eta_0$ and $0 < \dot{\varepsilon} < \dot{\varepsilon}_\infty$) and, finally, complete deaggregation at $\eta_{ef} \approx \eta_{min}$ and $\dot{\varepsilon} \geqslant \dot{\varepsilon}_\infty$.

The known flow theories involving this mechanism can be arbitrarily divided into two groups.[30, 76] The theories of one group are based on the concept of the 'average field',[77, 78] which assumes that particles linked in poorly deformable spherical aggregates exist in a homogeneous medium with viscosity η_i. These theories are applicable primarily to dilute and moderately concentrated structured dispersions.

The effective viscosity of thixotropic systems can be estimated according to the equation [9, 30]

$$\frac{\eta_{ef}}{\eta_1} = 1 + \frac{1}{\eta_{ef}/\eta_2 + (\dot{\varepsilon}\tau)^n}, \tag{47}$$

where $\eta_1 \equiv \eta_{ef}(\dot{\varepsilon} \to 0)$, τ is the relaxation time of the major process of interactions between particles through surface forces

$$\tau = \frac{\eta_1 d^2}{f_c},$$

the exponent n depends on the type of the structural model (for weakly aggregated systems, $n \sim 1/2$).

The results of calculations using Eqn (47) and by analogous expressions [71, 83–86] are in good agreement with the experimental data for monodisperse suspensions containing spherical particles, if their concentration (φ) is lower than 60% (this concentration corresponds to a random cubic packing φ_c). For dispersions with $\varphi \sim \varphi_c$ and $\varphi > \varphi_c$, the calculated data differ substantially from the experimental results, and these differences increase with $\dot{\varepsilon} \to 0$, *i.e*., as the highest viscosity of the virtually non-destroyed structure (according to Rehbinder) is approached.

For structured dispersions, this viscosity level $\eta_{ef} \sim \eta_0$ is adequately described in a broad concentration range ($\varphi < \varphi_c$) relying on the concepts of the quasi-crystalline character of the structure on the assumption of its continuity.[87–89] In the general form, this viscosity level is determined by the equation [87]

$$\frac{\eta_{ef}}{\eta_1} \sim C_1 \exp\left[\frac{h}{d}\left(\frac{\tau_B}{\tau_{f_c}} - \frac{\tau_B P}{\eta_1}\right)\right], \tag{48}$$

where

$$C_1 \equiv \lambda\left(\frac{d\tau_1}{h\tau_{f_c}}\right)^{1/2},$$

$$\lambda \equiv \left\{1 + \left[\frac{d}{h}\left(\frac{\eta_0}{\tau_i}\right)^2 \frac{\tau_{f_c}}{\tau_i}\right]^2\right\}^{1/2} - \frac{d}{h}\left(\frac{\eta_0}{\eta_1}\right)^2 \frac{\tau_{f_c}}{\tau_i}. \tag{48a}$$

Here, τ_B, τ_{fc} and τ_i are the characteristic times of the corresponding microprocesses (see above), h is the distance between the particle surfaces in the quasi-lattice, $\eta_1 = \eta$ at $\varphi = 0$.

If $h = d$, this equation is transformed into the expression reported in the studies.[88, 89] It should be noted that at $\eta_{ef} \sim \eta_0$, the general expression (48) and its special analogues (see Refs 87 and 89) provide a satisfactory description of the dependence $\eta_{ef}(\dot{\varepsilon})$ with $\dot{\varepsilon} \to 0$ regardless of the concentration, whereas at $\dot{\varepsilon} > 0$, the deviation of the theoretical curve described by Eqn (47) from the experimental data increases with increasing φ. As $\dot{\varepsilon}$ and φ increase, the $\Delta\eta_{ef}/\Delta\dot{\varepsilon}$ ratio sharply increases. This fact is taken into account in the theory developed in the studies.[30, 62] According to this theory, the effective viscosity depends on the rate as follows:

$$\frac{\eta_{ef}}{\eta_1} \sim \frac{1}{(\tau\dot{\varepsilon})^n}. \tag{49}$$

This formula describes satisfactorily all steps of destruction of an aggregated suspension with increasing $\dot{\varepsilon}$ (or P), which was confirmed by comparing the calculated and experimental data for dispersions formed by monodispersed particles of poly(methyl methacrylate) in decalin stabilised by a monolayer of dihydrostearic acid (Fig. 7, curve *1*). Each step of destruction has a particular prevailing characteristic time of a microprocess τ and the corresponding Debora number [30, 62, 76]

$$D^* = \dot{\varepsilon}\tau.$$

For the region A in Fig. 7 (curve *1*),

$$\eta_{ef} \sim \eta_0,\ \dot{\varepsilon} < \frac{1}{\tau_\mu \exp(-\tau_B/\tau_\mu)},\ D^* \sim \dot{\varepsilon}\tau_B,\ \dot{\varepsilon}\tau_\mu.$$

For the region B corresponding to destruction into superaggregates,

$$\eta_{ef} < \eta_0,\ \frac{\eta_{ef}}{\eta_1} \sim \frac{1}{(\dot{\varepsilon}\tau_B)^{3/5}};\ \frac{1}{\tau_\mu} \ll \dot{\varepsilon} \ll \frac{1}{\tau_B};\ D^* \sim \dot{\varepsilon}\tau_B,\ D^* = \dot{\varepsilon}\tau_{f_c}.$$

For the region C corresponding to destruction of superaggregates into aggregates,

$$\eta_{ef} \ll \eta_0,\ \frac{\eta_{ef}}{\eta_1} \sim \frac{1}{(\dot{\varepsilon}\tau_B)^{1/2}};\ \frac{1}{\tau} \ll \dot{\varepsilon} \ll \frac{1}{\tau_\mu},\ D^* = \dot{\varepsilon}\tau_\mu.$$

For the region D corresponding to complete deaggregation,

$$\eta_{ef} \sim \eta_1\left(\frac{1}{\tau_B}, \frac{1}{\tau_\mu} \ll \dot{\varepsilon} \ll \frac{1}{\tau_1}\right);\ D^* \sim \dot{\varepsilon}\tau_i.$$

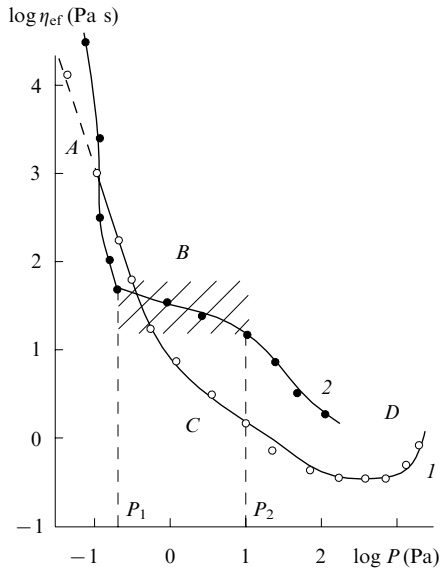


Figure 7. Complete flow curve of a suspension of poly(methyl methacrylate) in decalin.[68]
The solid curve represents the results of calculations by Eqn (49), the points correspond to the experimental values; the concentration of the suspension (%): (*1*) 59.5, (*2*) 60.1; the portion of the flow curve corresponding to a plateau, which is not exactly reproduced, is dashed.

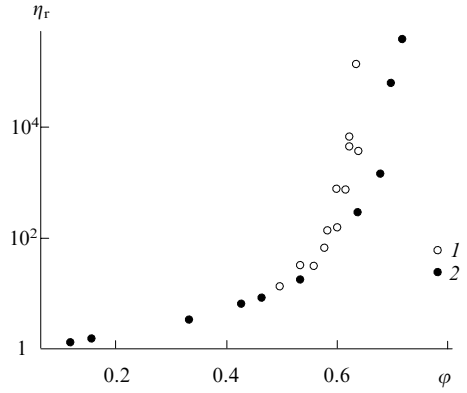


Figure 8. Dependence of the relative viscosity η_r on the concentration of a dispersed phase [monodispersed particles with a diameter of 129 (*1*) and 84 nm (*2*) of poly(methyl methacrylate) in decalin].[69]

Finally, in going to the dilatancy region accompanied by percolation of an adsorption layer,

$$\frac{\eta_{ef}}{\eta_1} \sim \dot{\varepsilon}\tau_i,\ \dot{\varepsilon} \gg \frac{1}{\tau_i},\ P > \frac{r^* h_i}{d^2} P_L\ ,$$

where r^* is the local radius of curvature in the zone of contacts between particles with diameter d, h_i is the thickness of the adsorption layer on their surface, P_L is the strength of the adsorption layer.

Therefore, for lyophilic disperse systems formed by monodispersed spherical particles at a concentration $\varphi < \varphi_c$, destruction of a coagulation structure is isotropic in character; at $\dot{\varepsilon} \sim \dot{\varepsilon}_\infty$, complete deaggregation and the corresponding limiting isotropic dynamic state with maximum fluidity are achieved.

When creating a controlled isotropic dynamic state in dispersions under continuous shear deformation, it should be taken into account that flow curves are completely reversible. The reversibility was confirmed by the fact that the effective viscosity levels and the corresponding degrees of isotropic destruction depending on $\dot{\varepsilon}$ and P throughout the range of their changes in rheological measurements are the same irrespective of whether these levels are attained with increasing or decreasing $\dot{\varepsilon}$ and P (*i.e.*, when moving in upward or downward directions). This indicates that rheological flow curves obtained under purely homogeneous shear are completely reversible.

However, in attempting to construct flow curves for the same systems at concentrations $\varphi > \varphi_c$ (*i.e.*, at $\varphi > 60\%$) in compliance with all the above-mentioned conditions and, correspondingly, to use Eqn (49) for their theoretical description, it was found that the calculated data differ substantially from the experimental results and the flow curves, which were measured in upward and downward directions (see Fig. 7, curve *2*), were poorly reproduced. The degree of these deviations, which is manifested in the presence of a plateau in the flow curve $\eta_{ef} = f(P)$, increases as φ increases in the region $\varphi > \varphi_c$.[89,90]

Such plateaus in the flow curves were found, in particular, in the studies.[71,90] However, the reasons for their appearance were considered to be an artefact[91] or were not discussed at all. The fact that the flow curves are irreproducible in the plateau region is unambiguously indicative of the violation of the isotropic character of a dispersion flow in this region.

At the same time, analysis of theoretical dependences of the strength of a dispersed structure on its porosity (see Fig. 2)[23,24] and experimental data[92,93] on the dependence of the relative viscosity on the effective concentration of a dispersed phase for monodispersed spherical particles of poly(methyl methacrylate) in decalin (Fig. 8) demonstrated that the region $\varphi = \varphi_c \approx 60\%$ corresponds to the onset of a sharp increase in the strength and viscosity with increasing φ. It is this limit, where the inhomogeneity of the structure becomes observable.

An analogous phenomenon, which takes place in going to the region $\varphi \geqslant \varphi_c$, was reported in monograph.[94] Apparently, the authors of the cited monograph were the first to interpret the anomaly of the flow process, which is characterised by a sharp jump (drop) of the shear stress P when its critical value is reached with increasing $\dot{\varepsilon}$, and an ambiguous dependence of the viscosity on the shear stress as a consequence of the appearance of local discontinuity.

This phenomenon, its possible variations and reasons for its occurrence both in well-characterised disperse systems and systems formed by polydispersed (in some cases, anisometric) particles of dispersed phases in liquid media were analysed in-depth.[2,76]

The interpretation assuming discontinuity at $\varphi > \varphi_c$ is supported by the results of studies of dispersions formed by monodispersed spherical particles with lyophilic surfaces (see, for example, Refs 90, 91 and 95).

The theoretical description of this phenomenon[30,62,68] was based on the comparison of the following three relaxation times of the processes, which together determine the discontinuity condition: τ_1, the time of elastic energy release under deformation; τ_2, the time of formation of a new surface due to the development of a macroscopic crack, *i.e.*, a slip zone with an inhomogeneous structure; τ_3, the time of mass transfer to the discontinuity zone as a result of vacancy drift, *i.e.*, the time of the possible 'healing' of the structure under shear deformation.

The structural discontinuity occurs if the following inequality is fulfilled:

$$\frac{1}{\tau_1} \gg \frac{1}{\tau_2} + \frac{1}{\tau_3}\ . \tag{50}$$

The discontinuity can take place in a broad range limited by the initial (P_1) and final (P_2) shear stresses

$$P_1 \sim P_c \left(\frac{d}{\varepsilon_i}\right)^{1/2},$$

$$P_2 \sim P_c - \frac{d\eta}{h\tau_B} \ln \frac{d}{\lambda h}, \quad (51)$$

where P_c is the flow limit of a disperse system, ε_i is the size of the structure inhomogeneity, λ is the parameter determined from Eqn (48a) and h is the average distance between the particles in the structure.

From a comparison of the available experimental[90,91] and calculated[30,90,91] data, it follows that a change from $\varphi = 59\% - 60\%$ to higher concentrations is accompanied by substantial changes in the flow mechanism of dispersions. The threshold concentration corresponds to a random cubic packing,[27,28] in the case of which the flow of a dispersion consisting of monodispersed spherical particles is isotropic in character under conditions of purely homogeneous shear. However, at concentrations higher than this threshold value, islands, *viz*., elements with a denser hexagonal packing, appear inside dispersions with a random cubic packing. As φ increases in the region $\varphi > 60\%$, the concentration of such islands increases, which is equivalent to the appearance and an increase in the number of inhomogeneity elements of the structure. Their coalescence gives rise to macroinhomogeneities, when a particular critical concentration is reached in the course of deformation. Apparently, a concentration jump in the vicinity of macroinhomogeneity boundaries is responsible for the appearance of local slip zones, which are equivalent to discontinuity, under shear in the range $P_1 \leqslant P_i \leqslant P_2$. The higher the concentration of a dispersed phase in a dispersion medium at $\varphi > \varphi_c$, the higher is the probability of this flow mechanism.

This mechanism of formation and development of discontinuities was confirmed in a computer simulation of the behaviour of an ensemble of monodispersed spherical particles in a Newtonian liquid under shear (Fig. 9).

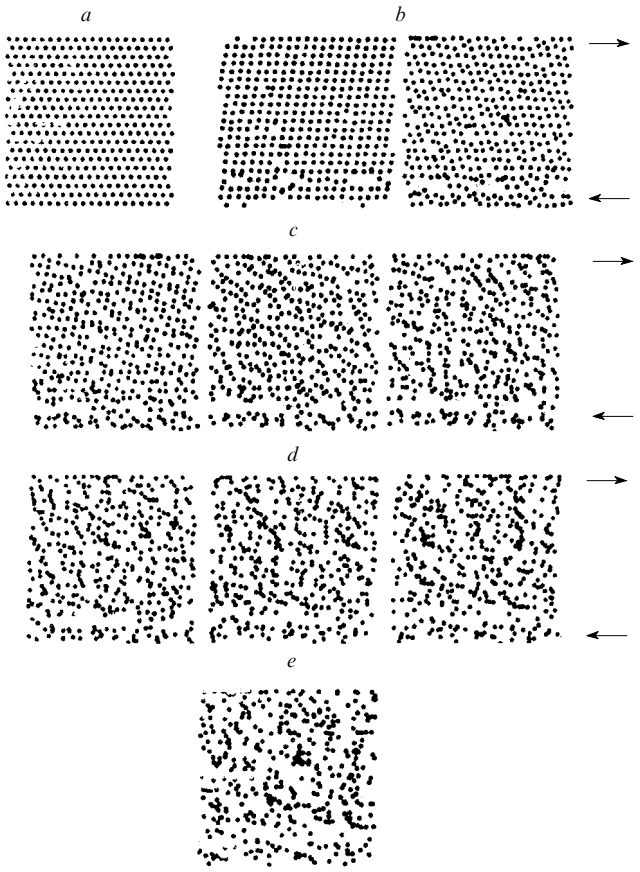


Figure 9. Results of computer simulation of the flow process for suspensions of monodispersed quartz particles with a diameter of 1 μm in water with discontinuity[96] in static conditions (*a*) and under continuous shear at different rates (*b*–*e*).
$\dot{\varepsilon}$ /s^{-1}: (*b*) 10^{-1}, (*c*) 50, (*d*) 100, (*e*) 150.

It can be assumed that this flow mechanism is even more probable for real disperse systems containing polydispersed and anisometric particles, because there are more possibilities for a local increase in the concentration of a dispersed phase in a dispersion medium, particularly, on going to $\varphi > \varphi_c$. This was shown by analysis of the complete rheological flow curve of aqueous dispersions of bentonite at a concentration $\varphi = 20\%$ (for this system, it is higher than φ_c).

The S-shaped flow curve shown in Fig. 10 *a* illustrates an ambiguous dependence of the viscosity η_{ef} on the shear stress P. Such a curve is characteristic of structured dispersions, whose deformation is accompanied by discontinuities.[76]

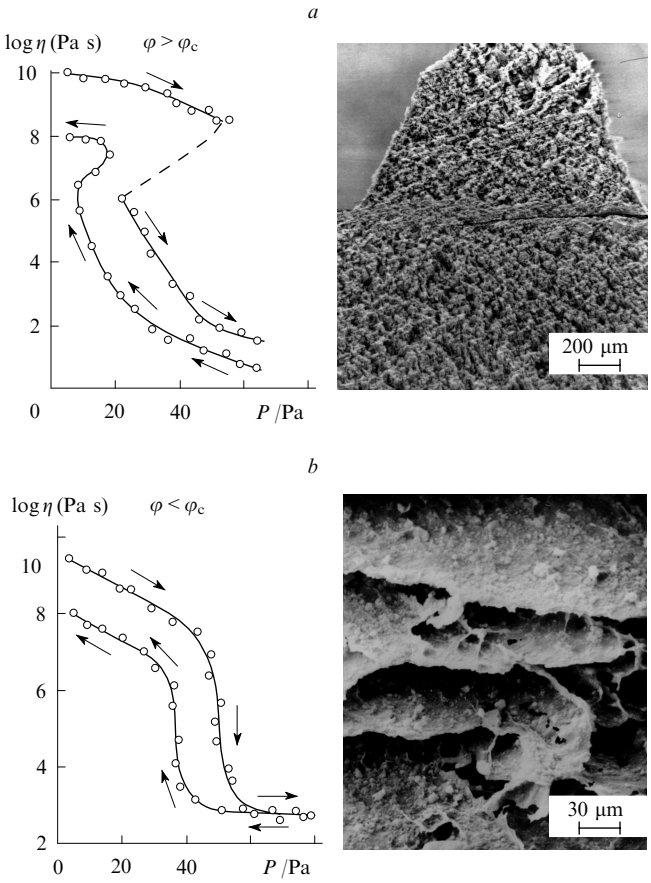


Figure 10. Complete rheological flow curves for aqueous dispersions of calcium bentonite (S_{BET} = 70 m^2 g^{-1}).[68,76]
(*a*) For a system with $\varphi = 20\%$ ($\varphi > \varphi_c$), (*b*) for a system with $\varphi = 11\%$ ($\varphi < \varphi_c$). Solid and dashed lines represent the results of measurements under increasing and decreasing shear stress, respectively; scanning electron micrographs were taken using a specially designed procedure.[62,95]

The hypothesis of discontinuity is supported by photomicrographs taken in the course of deformation of these dispersions (to the right of Fig. 10 *a*,*b*). It can be seen that the discontinuity is developed inside the structure subjected to deformation ($\varphi > \varphi_c$). Its appearance and subsequent development under shear deformation excludes shear propagation in the bulk of the structure outside the discontinuity zone.

All subsequent measurements at an increasing shear rate lead to complete violation of the isotropic character of destruction and a distortion of the results of measurements. Hence, it is impossible to construct flow curves under continuous shear. This is confirmed also by the fact that the flow curves measured in downward and upward directions are irreproducible.

The measured shear stress describes, in essence, only friction between layers bounded by discontinuity zones and the possible partial destruction in the regions adjacent to the discontinuity surfaces.

Taking into account the above notions, it could be assumed that the bulk character of destructions without discontinuities would be observed at lower concentrations of a dispersed phase in the region $\varphi < \varphi_c$. This assumption is supported by the shape of the flow curve of a dispersion at $\varphi = 11\%$, which reflects an unambiguous dependence of η_{ef} on P (Fig. 10*b*). However, the photomicrographs of the structure (to the right of Fig. 10*b*) are indicative of the opposite phenomenon: the appearance of not one (like at $\varphi > \varphi_c$), but even numerous discontinuities with the formation of periodically repeating dense structured layers, which are oriented along the shear direction and are separated by a dispersion medium. It should be noted that the concentration of a dispersed phase in these layers is as high as 60%, *i.e.*, is several times higher than the volume-average concentration before deformation (11%). Correspondingly, the strength and viscosity of the structure should increase many-fold [see Eqns (19) and (20); Figs 2 and 8]. The flow curves for the same compositions as those reported in the studies [1, 75] were reproduced in experiments.

The possible mechanism of such a sharp increase in the density of a structure in solid-like layers is associated with the effect of inertial coagulation of anisometric particles, the probability of which increases as the rate of movement of the layers with respect to each other increases [see Eqns (28) – (32)].

As mentioned above, the critical rate of inertial coagulation for anisometric particles can be many times lower than that for spherical particles. This is also favoured by the slip of a liquid with respect to the particle surface,[48] which was taken into account in the study.[12]

Therefore, inertial coagulation can give rise to structures stable to an extent that they cannot be destroyed even at high shear rates corresponding to $\dot{\varepsilon}_\infty$. This becomes even more favourable if the particle surfaces have lyophobic regions with a small radius of curvature, at which selective inertial coagulation with fixation of particles in the short-range potential well is substantially facilitated.[50]

Consequently, the commonly accepted notions of the attainment of the lowest viscosity level of an 'ultimately destroyed structure' $\eta_{ef} \approx \eta_{min}$ at $\dot{\varepsilon} \to \dot{\varepsilon}_\infty$ (see Refs 1, 75 and 97) can be assigned not to the structure as a whole but only to low-concentration (in essence, structureless) layers oriented along the shear direction. Moreover, it can be assumed that it is this portion of the flow curve corresponding to $\eta_{ef} \approx \eta_{min}$, where high-viscosity and dense (and, hence, particularly stable) structures can form, which is very typical of systems containing anisometric particles.

Periodically repeated structure layering was revealed (from a change in the density) in the course of sedimentation in highly disperse systems formed by particles, whose surface is characterised by lyophobic – lyophilic mosaicity (Fig. 11). This was demonstrated [62, 98] using an annihilation gamma probe. Apparently, layered sediments are formed according to this mechanism. This mechanism is responsible for natural phenomena, such as landslides and landslips of bottom sediments of rivers, lakes, *etc*.

Under dynamic conditions, the formation of layered structures is favoured by possible changes in the sedimentation rate V_1 and the rate of increase in the sediment density (V_s) depending on the shear rate in a flow and, hence, on the effective viscosity.

The drops of the shear rate $\Delta\dot{\varepsilon}$, which are characteristic of both natural phenomena and a series of industrial processes (chemical engineering and pipeline transportation) involving structured dispersions, inevitably lead to changes in V_1 and V_s and variations in the sediment density $\Delta\rho$. In the theoretical study,[9] this dependence was revealed on assumption of the aggregation mechanism of destruction of a coagulation structure under shear and the dependences of the size D and the density of aggregates ρ_a on $\dot{\varepsilon}$. The above dependence is expressed by the equation

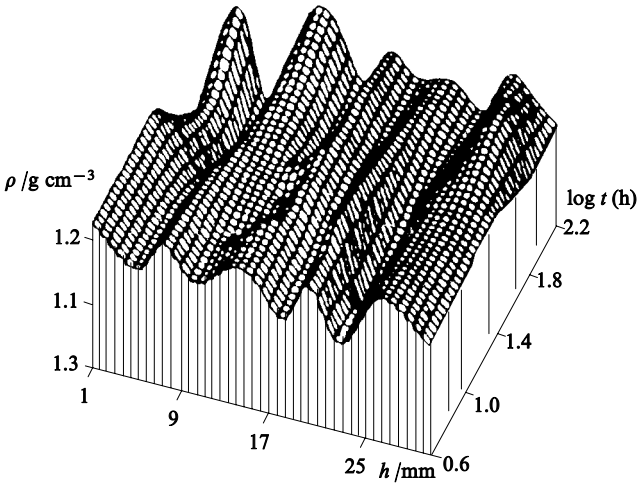


Figure 11. Periodic layers of different densities formed in the course of sedimentation in an aqueous suspension of technical carbon (d = 42 nm, φ = 28%).[98]

$$V_1 = \frac{(1-\varphi_{max})D^2 g \Delta\gamma_1}{12\lambda z \eta_1 \varphi_{ext}} \left(\frac{\eta_1 \varphi_{ext} \dot{\varepsilon}}{2.7 P_m}\right)^{1/2}, \qquad (52)$$

where φ_{max} is the maximum concentration of the dispersion in a sediment, η_1 is the viscosity of the dispersion in an interaggregate space, φ_{ext} is the concentration of the dispersed phase in an interaggregate space, $\Delta\gamma_1$ is the difference between the average densities of the aggregates and the suspension between the aggregates, λ is the dimensionless parameter, P_m is the strength of the aggregate structure

$$P_m = z_1 \frac{4 f_c}{n d^2},$$

z_1 is the number of bonds per particle on the aggregate surface, n is the number of particles in the aggregate.

According to Eqn (52), the rate V_1 is proportional to $(\dot{\varepsilon})^{1/2}$. The rate of sediment growth is related to V_1 by a simple equation

$$V_s = V_1 \varphi_{max}.$$

Hence it follows that any change in $\dot{\varepsilon}$ leads to changes in the rates of these processes. Since $\Delta\gamma_1$ also varies with V_1, the probability of the formation of layered sediments increases as $\Delta\dot{\varepsilon}$ and the frequency of its change increase. This is illustrated in Fig. 12, which displays the dependence of V_1 on $\dot{\varepsilon}$ and the corresponding change in η_{ef} for a concentrated aqueous carbon suspension.

An analogous result for suspensions of monodispersed spheres was obtained in the study.[98] The effect of layering of dispersions was mentioned in the studies.[99, 100]

Therefore, the appearance of structure macroinhomogeneities under dynamic conditions (including discontinuities, along which shears occur in structured disperse systems) results from the fact that the critical concentrations of not only a dispersed phase in a dispersion medium φ_c but also, in a more general case, of microinhomogeneity elements in the bulk of the structure are attained and exceeded. What this means is discontinuities in disperse systems formed by anisometric particles with lyophobic – lyophilic surface mosaicity can appear at concentrations $\varphi < \varphi_c$ (see Fig. 10*b*).

As a consequence, the limiting isotropic dynamic state and the corresponding condition for true ultimate destruction, *i.e.*, η_{ef} (with $\dot{\varepsilon} \to \dot{\varepsilon}_\infty$) = η_{min} in the bulk of the system subjected to deformation, cannot be attained under shear deformation.

Let us consider the mechanism of destruction of disperse systems with $\varphi < \varphi_c$ and analyse the data obtained for a model

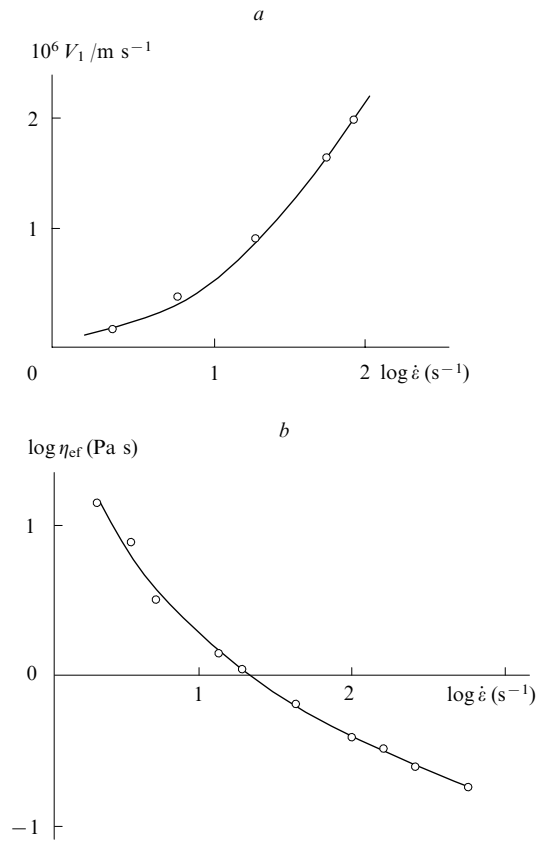


Figure 12. Plots of the sedimentation rate (*a*) and effective viscosity (*b*) *vs.* the shear rate for an aqueous carbon suspension ($\varphi_m \approx 60\%$).[68]

system of a dispersion of spherical polystyrene particles ($d = 70$ nm) in a gelatin gel in the presence of stabilisers [additives of a NaCl electrolyte and an anionic surfactant, *viz.*, aliphatic alcohol (Fig. 13)].

Destruction of a coagulation structure under shear leads to its decomposition into aggregates, which appear when the yield stress

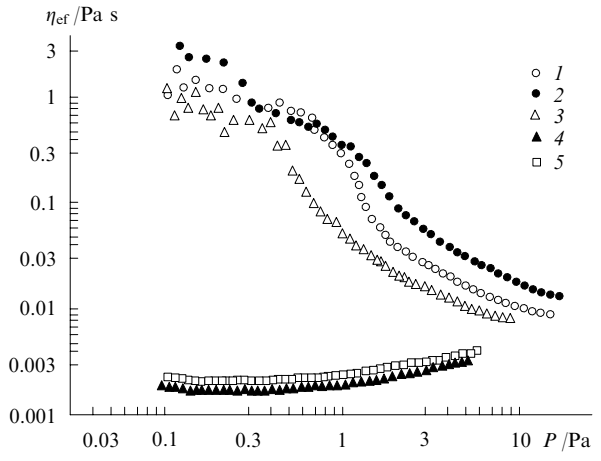


Figure 13. Complete flow curves for a suspension of polystyrene particles in gelatin gel ($\varphi = 4.8\%$).[101]
(*1*) A suspension of particles without additives, (*2*) a suspension of particles with an NaCl additive (0.02%), (*3*) a suspension of particles with an additive of an aliphatic alcohol (0.1%), (*4*) a liquid dispersion medium, (*5*) a theoretical curve under the condition of complete deaggregation.

P_c of the system is reached with increasing shear stress.[2] The characteristic size of aggregates in this region can be calculated by the equation [68]

$$D_a = \left(\frac{\alpha A^* z r^2}{16 P_c h^2 \varphi}\right)^{1/3}, \qquad (53)$$

where $A^* \approx 7 \times 10^{-20}$ J; h was varied from 60 to 100 nm, $r = 35$ nm and $z = 3$. The calculated values D_a varied with the temperature of the system from 300 to 1000 nm. The measurements of the rheological properties of these dispersions showed that even in the region of very high shear rates (as high as $\dot{\varepsilon} \approx 1300$ s^{-1}), the level $\eta_{ef} \approx \eta_{min}$ is more than 30 times higher than that found from the condition of complete destruction for $\varphi = 4.8\%$ according to Batchelor's formula [102]

$$\eta_{ef} \approx \eta_1(1 + 2.54 + 6.25\varphi^2),$$

where η_1 is the viscosity of a dispersion medium. Hence, not individual particles but their aggregates, whose effective concentration is 35% – 60% (*i.e.*, is approximately an order of magnitude higher than the concentration of polystyrene particles), serve as kinetic units at $\eta_{ef} \approx \eta_{min}$.

The above-described mechanism of destruction is even more strongly supported by the results of analysis of the structural and rheological properties of a dilute dispersion formed by monodispersed spherical SiO_2 nanoparticles ($d = 14$ nm) in ester.[103]

Lyophobic interactions in this dispersion give rise to a fractal structure formed by aggregates of particles. The complete flow curve (Fig. 14) shows two pronounced Newtonian viscosity levels, *viz.*, the highest level $\eta_0 \approx 10^8$ Pa s and the lowest level $\eta_{min} \simeq 10^{-1}$ Pa s. Therefore, the effective viscosity drop is nine orders of magnitude. Taking into account that the level attained at $P = 10$ Pa remains virtually the same as P increases to 100 Pa, it can be assumed that this level should actually correspond to the lowest viscosity of the ultimately destroyed structure.[1]

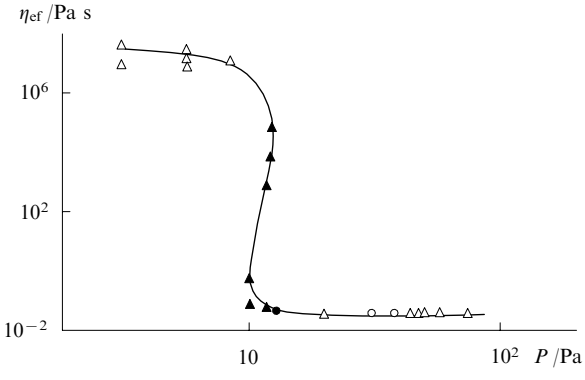


Figure 14. Complete flow curve for a suspension of SiO_2 ($d = 14$ nm) in ester ($\varphi_{ef} = 2.5\%$).[103]
Different triangles and circles correspond to different geometries of a measuring cell.

The validation of this assumption is substantially facilitated by the fact that the dispersed phase consists of monodispersed spherical particles and its volume content in the dispersion medium is < 3%. Therefore, the Einstein equation can be used for the description of the region $\eta \approx \eta_1(1 + 2.5\varphi)$ (see Refs 104 and 105) on condition that complete deaggregation of the dispersion in this region is attained.

However, a comparison of η and η_{ef} demonstrated that the latter values are tens of times larger. Consequently, the experimental values of η_{ef} do not correspond to the condition of true ultimate destruction, but they correspond to bulk thickening of a dispersion medium with kinetic structural elements ($\varphi_{ef} \gg 3\%$) retained at $\eta_{ef} \approx \eta_{min}$. Therefore, the Einstein equation is inappli-

cable for the estimation of the real volume concentrations of these elements, and the equations derived by Patel and Russel[78] or Frankel and Acrivons[86,106] should be used. According to these equations, φ_{ef} for aggregates is $\sim 49\%$. The initial size of these aggregates at the shear stress $P = P_c = 10$ Pa, which corresponds to the onset of a sharp decrease in the effective viscosity, can be determined by Eqn (53). The value calculated by Eqn (53) is 1500 nm, which was confirmed by direct measurements of the average size of aggregates by neutron diffraction ($D_a \approx 1560$ nm).[68]

As a further development of the concepts reported in the study,[107] it was demonstrated that the flow process of such colloidal disperse systems as fractal gels analogous to those described above can be considered as a flow of a system consisting of 'solid-like' and 'liquid-like' components, whose viscosities differ by many orders of magnitude ($\eta_{ef1} \sim 10^8$ Pa s and $\eta_{ef2} \sim 10^{-1}$ Pa s, respectively), and the corresponding relaxation times are $\tau_1 \sim 10^5$ s and $\tau_2 \sim 10^{-4}$ s.

It should be noted that the flow giving rise to alternating 'solid-like' and 'liquid-like' quasi-phases, which form layers oriented along the shear direction, was interpreted[107] as the most probable process in the context of thermodynamics of non-equilibrium processes.

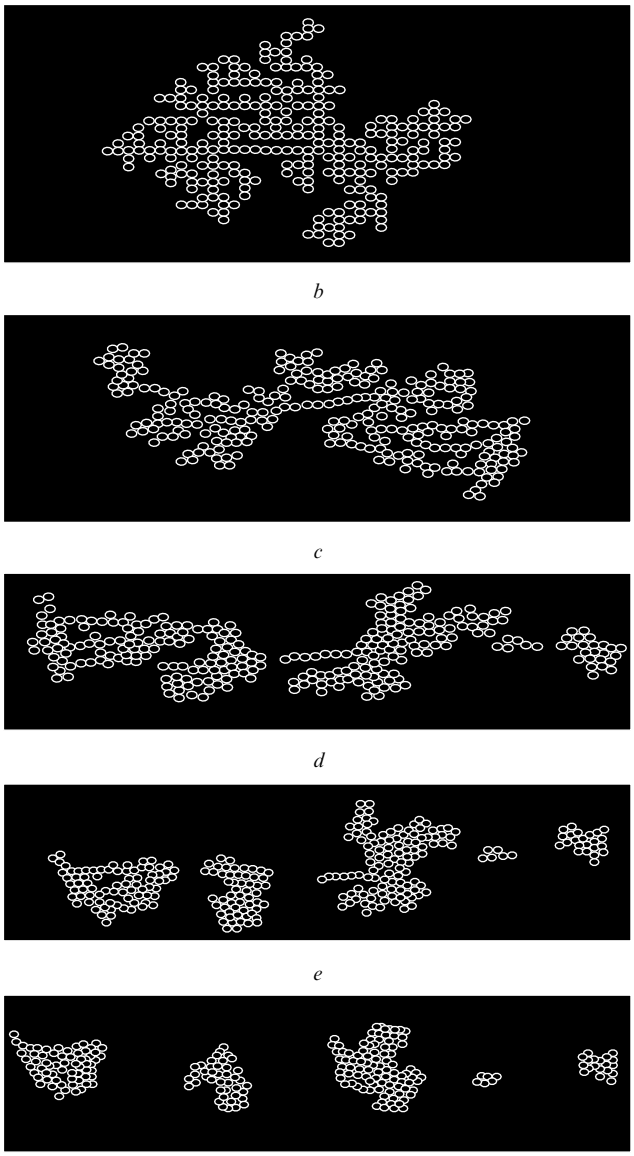


Figure 15. Evolution of a superaggregate in the course of shear deformation (computer experiment).[68]
$\dot{\varepsilon}$ /s^{-1}: (*a*) 0, (*b*) 0.3, (*c*) 1, (*d*) 10, (*e*) 50.

The results of computer simulation of the structure evolution of aggregated disperse systems with increasing shear rate (Fig. 15) are also indicative of the formation of smaller aggregates, which are characterised by an increasing density and, correspondingly, increasing strength and viscosity, against the background of destruction of superaggregates under deformation. This effect follows from the theory of destruction of aggregated dispersions under shear deformation. The aggregate radius R_a is related to the particle radius by the equation[19,30,62]

$$\frac{R_a}{r} \sim n^{1/f}, \tag{54}$$

where n is the number of particles involved in the aggregate and f is its fractal dimensionality. Then, the concentration of particles in the aggregate φ_{int} also increases with increasing shear rate $\dot{\varepsilon}$

$$\frac{\varphi_{int}}{\varphi_{max}} \sim \left(\frac{r}{R_a}\right)^{3-f}, \tag{55}$$

where φ_{max} is the maximum particle concentration in a particular disperse system.

Aggregates form a chain (layer) oriented along the shear direction. It can be stated that this mechanism, which combines destruction and formation of dispersed structures with a higher strength, excludes the possibility of attaining the true and complete destruction, and, hence, the limiting dynamic state even at very high $\dot{\varepsilon} \to \dot{\varepsilon}_\infty$ in the region of $\eta_{ef} \approx \eta_{min}$.

4. Dynamic state of disperse solid phase – liquid medium systems under combined action of shear and orthogonal oscillation

Anisotropic destruction of dispersed structures oriented along the shear direction, which is accompanied by decomposition into aggregates and formation of new more stable aggregates through inertial coagulation, excludes the attainment not only of an isotropic dynamic state but also of equivalent aggregation dynamic stability of disperse systems.

Consequently, to attain the limiting isotropic dynamic state, it is necessary to subject a disperse system to action in such a way as to either exclude the formation of structure inhomogeneity elements as aggregates and structured layers or achieve their ultimate destruction. For this purpose, the energy delivered to a disperse system and imparted to particles fixed in a structural network should be higher than the binding energy with adjacent particles.

As mentioned above, until the binding energy of a particle (whose size is smaller than 1 μm) in contact with adjacent particles is lower than $(10-15)kT$, the structure can be destroyed through thermal motion (random Brownian oscillations) of particles. In all cases of lyophobic interactions between particles, the total energy of their binding with adjacent particles in a structure is, generally, much higher than $(10-15)kT$, and destruction *via* Brownian motion becomes impossible.

Besides, it can be suggested that just as particles of sizes larger than 1 μm in aggregation-stable colloidal disperse systems undergo random oscillations under the action of thermal impacts of molecules of a dispersion medium, so can such particles in structured dispersions if they are subjected to forced oscillations using an external source. The necessary condition for the attainment of aggregation dynamic stability of such systems in the case of their complete deaggregation is that the energy of forced oscillations should be higher than the total energy (U_c) of binding of particles with adjacent particles in a structural network (taking into account z). It can also be assumed that forced oscillations play a decisive role in destruction under combined action of continuous shear and oscillations, whereas the mass transfer of elements of the destroyed structure proceeds under continuous shear.

The destruction under shear involves two main steps, *viz.*, destruction of a continuous structural network to form layers and/or aggregates of particles and destruction of aggregates as such. Correspondingly, the results of an external oscillation action first on a continuous structure and then on the aggregate structure should be considered with the aim of determining the parameters necessary for complete destruction of a coagulation structure. Various aspects of this problem were considered in-depth.[2, 30, 62]

Assuming that particle oscillations are excited with an external source through a medium, the rate of particle motion in the vicinity of the aggregate surface can be taken as

$$V(t) = V_0 a \sin \omega t.$$

Here, V_0 is the maximum rate of particles under oscillation, a is the oscillation amplitude and ω is the oscillation frequency. In the case of such harmonic oscillations, a particle undergoing forced oscillations with a frequency ω comparable to the eigenmode frequency can escape from a structural network. The eigenmode frequencies at which the particle can escape from long-range ($i = 1$) and short-range ($i = 2$) coagulation sites are determined, respectively, by the equations

$$\omega_1 \sim \frac{1}{r}\left(\frac{B}{\rho h_2^4}\right)^{1/2} \sim \frac{10}{r}, \qquad \omega_2 \sim \frac{1}{r}\left(\frac{A^*}{10\rho h_1^3}\right)^{1/2} \sim \frac{10^2}{r}. \tag{56}$$

For a comparative numerical analysis, let us assume that $\eta_1 \sim \eta = 10^{-1}$ Pa s, $A^* \sim 10^{-19}$ J, $B = 10^{-28}$ J m, $h_2 \sim 5 \times 10^{-8}$ m, $h_1 \sim 10^{-9}$ m, $\rho = 1000$ kg m^{-3}.

As expected, the results of numerical estimates differ sharply (by several orders of magnitude) and depend on r and h. Thus, the frequency increases by five orders of magnitude as r decreases from 10^{-4} to 10^{-7} m and, particularly, as h_i decreases from 5×10^{-8} to 10^{-9} m.

From this it follows that it is worthwhile to combine low-frequency mechanical oscillations and ultrasonic oscillations, particularly, in the case of destruction of colloidal disperse systems. It should be emphasised that it is technically quite possible to expose dispersed structures to oscillations with such parameters. This was demonstrated, in particularly, in the studies,[7, 62, 108] where structures were destroyed in the course of compaction of finely dispersed powders as well as of highly filled suspensions containing ultra-dispersed aerosil particles ($s_{BET} \approx 400$ m^2 g^{-1}).[62]

The effect of oscillations on a disperse system at $\eta_{ef} \to \eta_0$ can be expressed by the simple equation

$$\frac{\eta_{ef}}{\eta_0} \sim e^{U_c/\Theta} \tag{57}$$

where

$$\Theta = kT + m(a\omega)^2.$$

The first term of the latter equation takes into account the possible contribution of thermal motion. The second term accounts for the kinetic energy imparted to a system subjected to oscillation with an amplitude a and a circular frequency ω.

This approach to estimations of oscillation action on disperse systems was also used in the study.[109]

The second step of destruction of dispersions is associated with aggregate disintegration under combined action of oscillation and shear. In these conditions, the effective viscosity of a dispersion consisting of aggregates can be expressed as follows:[30, 61]

$$\eta_{ef} \sim \eta_{ef}^0 \frac{L}{d^*} \sim \eta_{ef}^0 \left[1 + \frac{1}{a\omega L/z_a\eta + (\dot{\varepsilon}/\dot{\varepsilon}_a)^{1/2}}\right]. \tag{58}$$

Here, η_{ef}^0 is the highest effective viscosity, d^* is the average distance between the aggregates, L is the distance between the centres of the aggregates ($L = D + d^*$, D is the diameter of the aggregate) and z_a is the coordination number of the aggregate,

$$\dot{\varepsilon} \approx \frac{z_a P_c}{\eta_{ef}^0}.$$

Equation (58) was derived from the condition that the parameter L/d^* is expressed as follows

$$\frac{L}{d^*} \sim \frac{z_a \eta}{\rho a \omega L},$$

where ρ is the density of particles of a solid phase.

It is worthwhile to represent the dependence of the effective viscosity on the oscillation intensity

$$I \approx a^2\omega^3.$$

This parameter determines the oscillation power per unit oscillating mass. In essence, this parameter can be considered as a 'vibrotemperature',[30] an increase of which leads to an increase in the intensity of motion of kinetic units (particles or aggregates), much as an increase in the temperature in colloidal systems leads to intensification of Brownian motion.

The dependence of the effective viscosity on this parameter can be described by the following equation:[30, 62]

$$\eta_{ef} \sim \eta_1 \left(\frac{z_a h}{a\omega\rho D} + 1\right) \sim \eta_1 \left[\frac{z_a \eta}{\rho L}\left(\frac{\omega}{I}\right)^{1/2} + 1\right], \tag{59}$$

where h is the distance between particles in an aggregate.

It was demonstrated[62, 68] that the results of calculations by Eqns (57)–(59) are in good agreement with the results of studies of the rheological properties of concentrated suspensions of aluminosilicates in water subjected to oscillation. The selected parameters of these suspensions are as follows: $\varphi \sim 0.46$–0.6; $A^* \sim 10^{-20}$ J; $h = 1$–10 nm; $(R/r)_{min} \sim 10$. Under conditions of continuous shear, irreversible macroscopic discontinuities appear at $P = P_c$ or $\dot{\varepsilon} \approx \dot{\varepsilon}_c$. The possibility of the occurrence of these discontinuities is completely eliminated under combined action of continuous shear and orthogonally directed oscillation with a frequency $f_v^* = 50$ Hz ($\omega = 2\pi f_v^* = 300$ s^{-1}) and with increasing intensity (Fig. 16). In particular, this is evidenced by a relatively

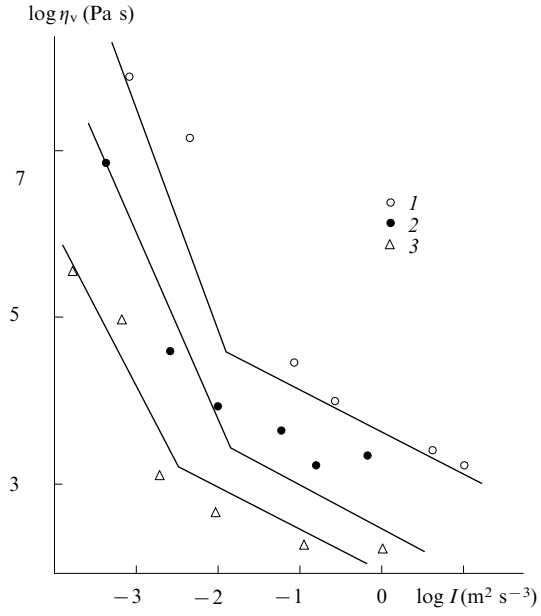


Figure 16. Vibrorheological curves of aqueous suspensions of aluminosilicates.
Circles and triangles represent experimental data;[2] curves show the results of calculations by Eqns (58) and (59); $\varphi = 0.6$ (*1*), 0.53 (*2*), 0.46 (*3*).

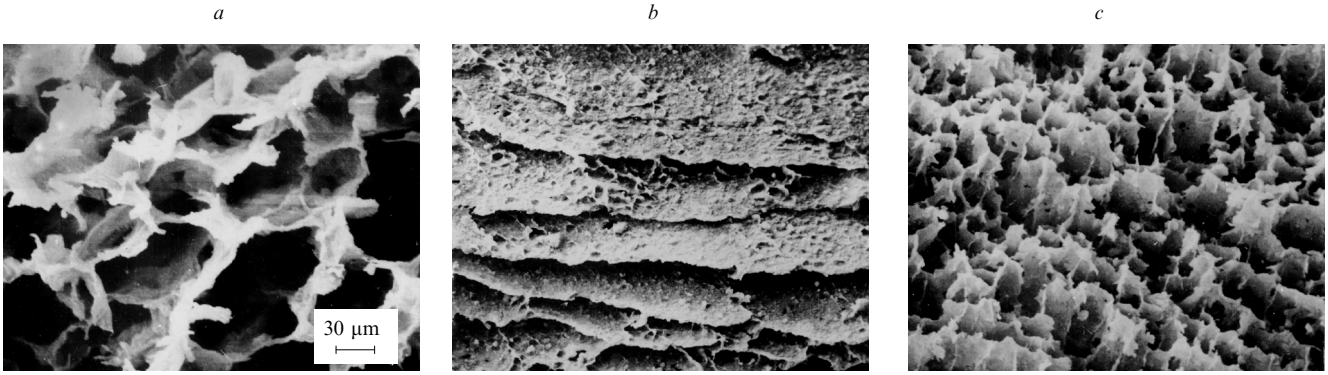


Figure 17. Characteristic features of destruction and formation of coagulation structures for aqueous dispersions of CaB, $\varphi_{max} = 11\%$ ($\times 1000$). (*a*) A structure before deformation (static conditions), (*b*) a structure under conditions of continuous shear ($\dot{\varepsilon} = 0.3\ s^{-1}$), (*c*) a structure under combined action of continuous shear ($\dot{\varepsilon} = 0.3\ s^{-1}$) and orthogonal oscillation ($f_v^* = 50$ Hz, $a = 10^{-3}$ m)

high reproducibility of vibrorheological flow curves (with slight deviations within several percentage) in viscosity measurements in going both from the minimum to the maximum values of I and in the reverse direction.

The flow curves have two main portions characterising various steps of destruction of a coagulation structure (see Fig. 16): the first sharp decrease in the viscosity corresponds to decomposition of a continuous structure into aggregates, whereas the second decrease corresponds to destruction of the latter into aggregates of smaller sizes and individual particles. At the same time, these curves reflect some essential features of destruction under oscillation.

Although eliminating discontinuity and destroying the structure, oscillation does not lead to complete destruction of aggregates, as evidenced by retention of substantial differences in the level of η_v (up to an order of magnitude) at $I \geqslant 1$. Destruction of aggregates of very small sizes is a very energy-consuming process. This is confirmed by the fact that an increase in I by 3–4 orders of magnitude in lower portions of the flow curves leads to a small decrease in the viscosity.

Analogous results were obtained for aqueous suspensions of calcium bentonite (CaB) both for systems with $\varphi > \varphi_c$ and suspensions at concentrations $\varphi \leqslant \varphi_c$. Figure 17 presents scanning electron micrographs of dispersed structures taken with the use of a procedure described in the studies.[62,95] The photomicrographs show successive structural transformations. It can be seen that discontinuities, which appear under continuous shear, are completely eliminated under orthogonally directed oscillation. This important result indicates that a combination of continuous shear and orthogonal oscillation allows one, in principle, to control an isotropic dynamic state. However, the destruction under oscillation and shear is not limiting (although is close to the limiting value) but is characterised by the presence of aggregates throughout the range of changes in $\eta_{ef} = \eta_v$, where η_v is the effective viscosity under oscillation.

Vibrations destroy structures predominantly at weak contacts thus initiating the formation of dense microaggregates, in which particles are fixed in a short-range potential minimum due to inertial coagulation. This fact complicates substantially the attainment of ultimate destruction. In combination with continuous shear, oscillation facilitates mutual dynamic scanning of the surfaces of contacting particles and, in the presence of lyophobic–lyophilic mosaicity of these surfaces in most real disperse systems, leads to a 'manifestation' of mosaicity and selective formation of new strong contacts predominantly in lyophobic regions.[2] This spontaneous formation of microaggregates, in which particles are fixed in sites of short-range coagulation, is manifested as the effect of strengthening of the structure under oscillation.[2] This phenomenon resides in the fact that after cessation of exposure to orthogonal oscillation, the effective viscosity η_{ef} (the effective stress P at $\dot{\varepsilon} = \text{const}$) sharply increases compared to its equilibrium value in a steady shear flow at the same value of $\dot{\varepsilon}$ prior to exposure to oscillation (Fig. 18). Hence it follows that the limiting isotropic dynamic state and, correspondingly, aggregation dynamic stability of disperse systems can be attained only if both inertial (short-range) coagulation and the effect of strengthening due to oscillation (this effect is associated with coagulation and lyophobic–lyophilic mosaicity of the particle surface) are excluded.

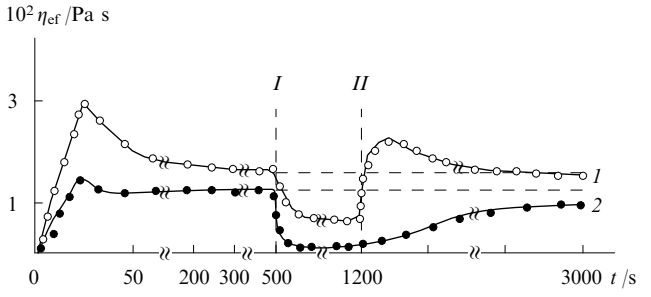


Figure 18. Dependence of the effective viscosity of an aqueous dispersion of CaB ($s_{BET} = 70\ m^2\ g^{-1}$, $\varphi = 0.33$) on the time under continuous shear deformation $\dot{\varepsilon} = 0.3\ s^{-1}$ (see Ref. 2).
(*1*) a dispersion in the absence of surfactant additives, (*2*) a dispersion of particles whose surface was modified with a monolayer of oxyethylated alkylphenol (OP-10); (*I*) the onset of oscillation orthogonal to continuous shear ($f_v^* = 50$ Hz, $a = 5 \times 10^{-4}$ m), (*II*) cessation of oscillation.

It was demonstrated[94] that an efficient way for solving this problem consists in combining the exposure of a disperse system to oscillation and the introduction of surfactant additives, which lyophilise the particle surface and create a structure-mechanical barrier (according to Rehbinder). Therefore, inertial coagulation under dynamic conditions is hindered in the presence of a surfactant adsorption layer, which serves as a structure-mechanical barrier. From Eqn (35) it follows, in particular, that the attainment of aggregation stability of dispersions under dynamic conditions requires an increase in the strength of an adsorption layer, particularly, in the presence of asperities with a small radius of curvature on the particle surface. The modulus of elasticity of the layer can be decreased by increasing the thickness of the layer L, the particle size and the distance between their surfaces.

In the presence of an adsorption layer, the critical coagulation rate can be determined by Eqn (34) or from the following relation:

$$V_c^* > \lambda_i \frac{L}{r_{max}} \left(\frac{P_L}{E_L}\right)^{3/2} \left(\frac{E_L\, r^*}{2\rho r_{max}}\right)^{1/2}, \qquad (60)$$

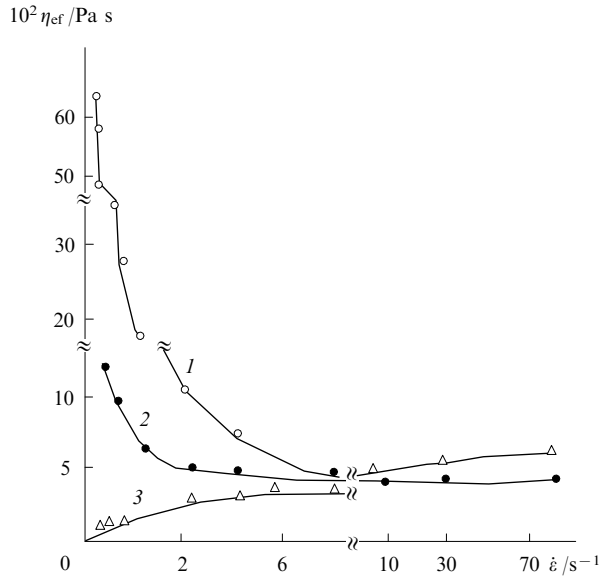


Figure 19. Dependence of the effective viscosity of highly concentrated aqueous carbon suspensions (φ = 72.5%) on the shear rate.[111]
(*1*) In the absence of oscillation action; (*2*) in the absence of oscillation action with an additive of an anion-active surfactant, *viz*., a sulfonation product of oil tars (1% of the mass of the solid phase); (*3*) under conditions analogous to those used in run (*2*) combined with orthogonal oscillation with a frequency of 50 Hz and acceleration $A = 2.5g$.

where the parameter λ_i determines the curvature of the particle surface in the contact zone: for spheres, $\lambda_i = 1$; for particles with a radius of curvature $r^* < r_{max}$, in particular, for two disk-like particles, which collide perpendicular to one another, $\lambda_i = 2(r_{max}/r^*)^{3/4}$. Assuming $L \sim 10^2$ nm for disk-like particles with $r^* \sim 3 \times 10^2$ nm and $r_{max} = 10$ μm, the aggregation stability in dynamic conditions will take place at $E_L \sim P_L > E_{Lc} \sim 10^5$ Pa. For polyvinyl alcohol, this condition is fulfilled [110] at a rather high rate $V_c^* \sim 0.5$ m s^{-1}. The same condition is obviously fulfilled for a polyfunctional anion-active surfactant of a new type, which was prepared starting from dehydrated liquid products of hydrocarbon pyrolysis, which were mixtures of water-soluble salts of sulfonic acids of bicyclic aromatic hydrocarbons (sulfonation product of oil tars).[111] When choosing surfactants, which satisfy the above-mentioned conditions, one should take into account the characteristic features of their micellar structures, because micelles formed in solutions of surfactants can produce a structure-mechanical barrier.[67]

The results of experimental test of the efficiency of a combined action of orthogonally directed oscillation and the presence of surfactants, which create a structure-mechanical barrier on the surface of particles of dispersed phases are presented in Figs 18 and 19.

Upon modification of the CaB particle surface with oxyethylated alkylphenol OP-10, both the depth and the destruction rate under oscillation (a decrease in η_{ef}) increase (see Fig. 18, curve *2*) compared to the analogous values observed under oscillation but in the absence of surfactants (curve *1*). This fact can be attributed to a substantial decrease in the strength and energy of interparticle interactions under oscillation. At the same time, the vibrostrengthening effect completely disappears in the presence of surfactants, and the rate of thixotropic recovery of a structure decreases sharply, which is indicative of the absence of 'breakdown' of the adsorption layer under oscillation and the retention of a structure-mechanical barrier in the course of prolonged (for more than 10 min) high-intensity oscillation.

An analogous effect of a combination of orthogonal oscillation and surfactant additives was revealed in a shear flow of highly concentrated aqueous carbon suspensions (see Fig. 19). A particularly sharp decrease in η_{ef} (by two orders of magnitude) was observed at low shear rates ($\dot{\varepsilon} \leqslant 2$ s^{-1}). The viscosities calculated by the equations reported in the study [30] had close values in this region, which indicates that the ultimate destruction was reached. A slight increase in the viscosity with increasing $\dot{\varepsilon} > 2$ s^{-1} is not associated with the structural effects, but apparently results from turbulisation of a flow under oscillation ('vibrodilatancy'). This is confirmed by full reversibility of the effect. Thus, the viscosity reaches the initial minimum level when $\dot{\varepsilon}$ decreases to 2 s^{-1}. The effect of a decrease in the vibroviscosity and oscillation intensity in concentrated cement aqueous dispersions as a result of the surface modification of cement particles with surfactant additives is illustrated in Fig. 20. This effect is noticeable in the presence of OP-10 (curve *2*) and, particularly, of sodium methylsiliconate (curve *3*). In the latter case, a decrease in η_{ef} amounts to as much as four orders of magnitude and a decrease in the oscillation intensity necessary for the attainment of η_{ef} ranges up to three orders of magnitude.[68] It should be emphasised that both these effects are

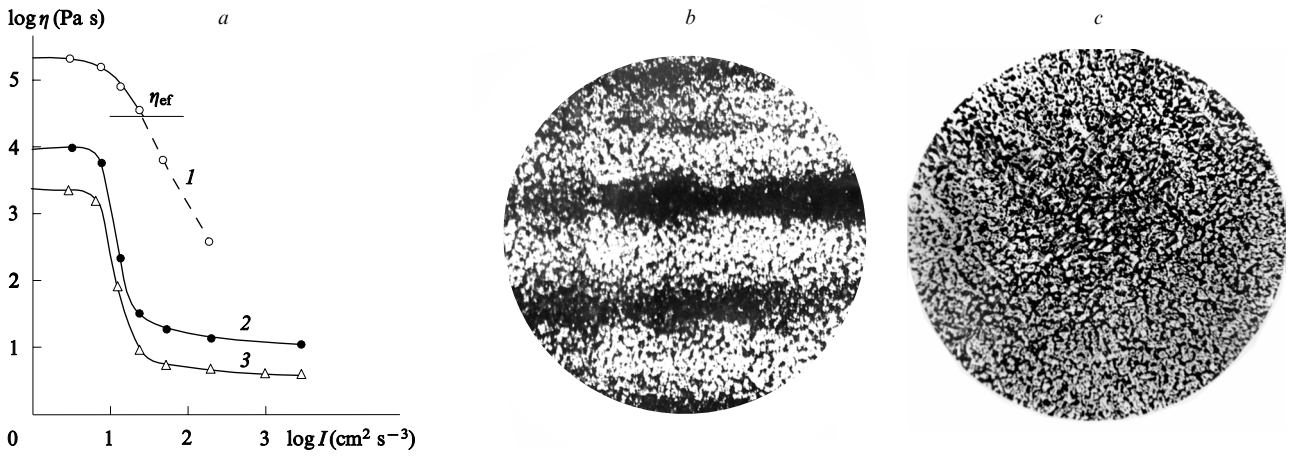


Figure 20. Effect of combined action of shear deformation, orthogonal oscillation and surfactant additives.[68]
The model dispersion is a mixture of tricalcium hydrosilicate and tricalcium hydroaluminate in water (φ = 0.48).
(*a*) rheological flow curves: (*1*) under shear without oscillation (η_{ef}), (*2*) a combination of continuous shear ($\dot{\varepsilon}$ = 0.3 s^{-1}) and oscillation with increasing intensity, (*3*) under conditions analogous to those used in run (*2*) in combination an additive of sodium methylsiliconate (0.3%). Photomicrographs of the structure formed under dynamic conditions: (*b*) under continuous shear for 600 s, (*c*) under combined action of continuous shear, orthogonal oscillation and a surfactant additive (15 s).

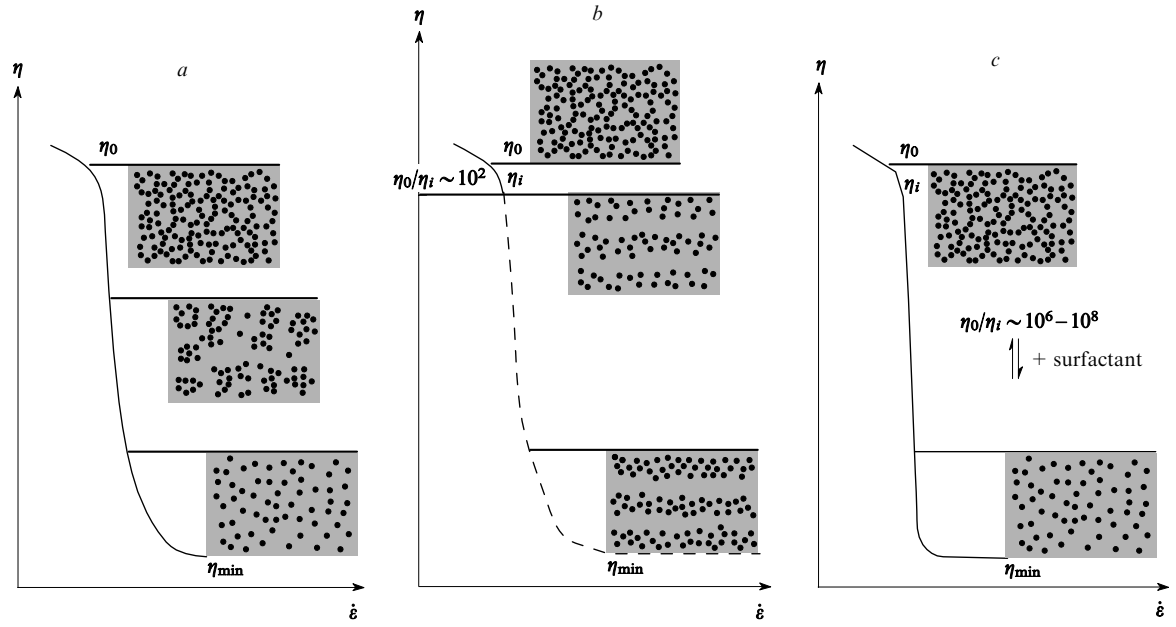


Figure 21. Scheme illustrating the destruction mechanism of coagulation structures in disperse systems under dynamic conditions.[68]
(*a*) Under continuous shear deformation with increasing shear rate (commonly accepted views), (*b*) the real pattern of destruction of dispersions under continuous shear, (*c*) spontaneous ultimate destruction with the attainment of the true maximum fluidity and complete ultimate deaggregation under conditions of an optimum combination of continuous shear and orthogonally directed oscillation in the presence of surfactant additives.

most pronounced in the region of the lowest vibroviscosity levels. This indicates that oscillations suppress the formation of dense and stable microaggregates as a result of inertial coagulation, which is typical of destruction under oscillation in the absence of surfactants. At the same time, this fact is also indicative of isotropic destruction, *i.e.*, of the attainment of the limiting dynamic state in the case of both highly concentrated aqueous carbon suspensions and cement aqueous dispersions.

A combination of orthogonal oscillation and the introduction of surfactant additives can be considered as an efficient way of intensifying processes of wetting and flowing of non-Newtonian structured high-viscosity dispersions as a result of their transformations into low-viscosity Newtonian liquids.[64,65] This phenomenon is of considerable importance in the preparation of composition materials with a binder as a structured dispersion.[62]

The main steps of the generation of a controlled dynamic state of two-phase structured disperse systems of the solid phase – liquid dispersion medium type are illustrated in Fig. 21. The main step involves the construction of complete rheological flow curves describing the overall range of changes in dynamic states, which are determined by the effective viscosity levels corresponding to a given deformation rate. When constructing these curves, it was assumed that a certain equilibrium degree of isotropic destruction (degree of deaggregation) corresponds to each viscosity level, and complete deaggregation corresponds to the lowest Newtonian viscosity level η_{min} (see Fig. 21 *a*). In actuality, the destruction is often anisotropic in character and gives rise to solid-like layers, which are strengthened as the deformation rate increases, are separated by an interlayer of a dispersion medium and are oriented along the shear direction (see Fig. 21 *b*). Consequently, contrary to the commonly accepted views of the flow mechanism of structured dispersions, the true ultimate destruction as well as the maximum fluidity of dispersions are not achieved.

The use of the above-described approaches and methods for creating of the optimum dynamic state in structured dispersions actually allows one to achieve the complete and isotropic destruction with complete spontaneous deaggregation and, correspondingly, to attain true maximum fluidity (Fig. 21 *c*).

IV. Conclusion

The dynamic state of structured disperse systems depends on the degree and conditions of destruction of dispersions. Depending on the type and intensity of external actions, disperse systems in dynamic conditions are characterised by the presence of macroscopic quasi-phases as aggregates consisting of particles and solid-state layers, which are oriented along the direction of the high-intenisty continuous action (for example, shear). The sizes and densities of aggregates and layers depend on the state of the surface, the shape of primary particles and the degree of destruction. The same factors are responsible for the effective viscosity of disperse systems under dynamic conditions. Methods for the creation of a controlled dynamic state of such systems are based on the following two main factors: first, the modification of particle surfaces (their lyophilisation) to form a surfactant adsorption layer serving as a structure-mechanical barrier, which hinders inertial coagulation of particles; second, the complex exposure of a disperse system to continuous shear and orthogonally directed oscillation, whose intensity (in combination with the modification of the particle surface) corresponds to the condition of complete (ultimate) deaggregation.

This level of the limiting isotropic dynamic state corresponds to dynamic aggregation stability and maximum fluidity of structured disperse systems. In essence, the views of the characteristic features and methods for creating a dynamic state and controlling the properties of disperse systems under dynamic conditions provide the basis for physicochemical dynamics of structured disperse systems.

The attainment of the true maximum fluidity of structured disperse systems with complete deaggregation allows one to radically change the conditions for performing various chemical engineering processes, including those for the preparation of dispersed composition materials. It is known that the rate of heterogeneous processes carried out under conditions of forced convective diffusion is inversely proportional to the viscosity. Hence, the attainment of complete destruction, deaggregation of a system and the true lowest Newtonian viscosity by decreasing the effective viscosity of dispersions by 5 – 7 orders of magnitude

provides the possibility of accelerating many heterogeneous chemical engineering processes to the same extent.

Liberation of an immobilised dispersion medium from a structural network and a sharp increase of the 'operating' active interface due to complete deaggregation make it possible to increase the rate and degree of completion of a series of heterogeneous processes by several orders of magnitude.

In the case of complete deaggregation under conditions of attainment of the optimum dynamic state of dispersions, both the dispersity of the solid phase S and its concentration φ increase and, hence, it is possible to pass to the previously 'forbidden' (due to a sharp increase in the viscosity and the limiting shear stress) region of highly concentrated ($\varphi > \varphi_c$) and finely disperse systems, which also allows one to accelerate sharply heterogeneous processes, whose rates are proportional to the areas of operating interfaces.

By attaining the highest degree of homogeneity of phase distribution with a simultaneous increase in their dispersity and concentration in dispersion media, one can prepare both traditional and new types of highly filled dispersed composition materials possessing the desired properties and structures.

Numerous examples of various applications of the principles of the creation of a controlled dynamic state in disperse systems lie at the basis of new methods and high-performance technologies for the production and procession of disperse systems and composition materials.[2, 54, 55, 105, 112–114]

In conclusion, let us formulate briefly the main results of studies carried out in the last 10–15 years, which provide the basis for physicochemical dynamics of disperse systems:

— the dynamic theory of contact interactions was devised;

— the theory of complete rheological flow curves taking into account discontinuities was developed;

— foundations of the theory of the creation of the limiting dynamic state of disperse systems and their maximum fluidity were laid;

— the mechanism of a combined action of oscillation and the introduction of surfactant additives in flow processes of dispersions for the attainment of their maximum fluidity was revealed.

In addition, new characteristic features of sedimentation processes both under static and dynamic conditions were found. The results of these fundamental studies were supported by experimental investigations and have found practical applications in various fields of technology and engineering. Among new promising lines of physicochemical dynamics, let us note the elucidation of the mechanism of flowing of structured dispersions, investigations of the dynamics of three-phase disperse systems and the development of theoretical foundations of new methods for performing various chemical engineering processes in highly concentrated and finely disperse systems.

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