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Structure and Dynamics of Aqueous Dispersions

Tatiana Yakhno and Vladimir Yakhno

Abstract

The content of the chapter summarizes the long-term studies of the authors of the structure and dynamics of aqueous dispersions, including model protein-salt solutions, blood serum of healthy and sick people, food microdisperse systems. The data are considered in the context of the existing scientific literature on the stated problem. One of the important issues is the phase transitions of the protein when the ionic strength of the solution changes. To observe these processes, a drying droplet model, optical and atomic force microscopy are used. Based on the observations, a model of a cascade of phase transitions of a protein, from micelles to gel, was created. Parallels are drawn with the violation of these processes based on the results of the study of blood serum in seriously ill people. It is also shown that in the free volume of microdisperse systems there are near-hour oscillatory processes associated with the aggregation - disaggregation of the microdispersed phase. The surface tension of solutions, the mechanical properties of liquids, and the morphological characteristics of dried drops also fluctuate simultaneously. A model of self-oscillatory processes in such systems is presented, consistently describing the observed phenomena.

Keywords: aqueous microdisperse systems, drying drops model, protein phase transitions, ionic strength, free and bound water, nearhourly fluctuations

1. Introduction

The entire world around us, including the “starry sky above us,” is an innumerable set of different-scale dispersed systems. The main feature of such systems is a large specific interfacial area, which provides them with excess energy. It is this excess energy that is the driving force that determines the structure and dynamics of dispersed systems. A dispersed system usually consists of two or more phases that practically do not mix and do not chemically react with each other. In the typical case of a two-phase system, the first of the substances (dispersed phase) is distributed in the second (dispersion medium). The result of the physical interaction of the lyophilic elements of the dispersed phase with the liquid dispersion medium is the formation of solvation shells around the dispersed particles, which is accompanied by a decrease in interfacial tension and an increase in the aggregate stability of such systems. In the case of aqueous dispersions, as a result of the physical interaction of hydrophilic particles with the environment, the particles acquire hydration shells from ordered layers of water molecules with a special spatial structure that differs from the structure of the bulk phase of water. In this paper, we will focus on the microstructure of aqueous solutions and microheterogeneous dispersions, as well as spontaneous and induced dynamic processes in them.

2. Processes in sessile drying drops of aqueous dispersions

An evaporating droplet sitting on a solid wettable substrate is a convenient model for observing phase transformations in aqueous colloidal dispersions. The shape of a sitting drop in the form of a truncated ball ensures the appearance of temperature gradients on its surface and the development of flows of thermocapillary nature: centrifugal flow and Marangoni flow (**Figure 1**).

Since the thinnest layer of liquid is located at the three-phase boundary, solid-state microdeposits are formed there first of all, ensuring the attachment of the droplet to the substrate. Further evaporation is accompanied by flattening of the droplet dome while maintaining its area. In this case, capillary forces arise, which ensure the predominant evaporation of water through the edges of the drop [1–5]. It is shown that the direction of the flows depends on the ratio of the thermal conductivities of the liquid and the substrate material [6]: if this ratio does not exceed 1.57, then the Marangoni flow promotes the removal of the colloidal phase to the edge of the droplet. If it exceeds, then the direction of the flow changes sign, and the colloidal phase is “swept away” to the center [7]. The ratio of thermal conductivity of glass and water is ~ 0.6 . Therefore, when a drop of hydrocolloid dries up, the remaining solid sediment on the glass has the shape of a saucer with a volumetric rim along the edge. The same phenomenon is associated with the “effect of a coffee drop” - the formation of a colored rim along the periphery of the drop (**Figure 2**).

More complex and interesting processes take place in drying droplets if the water-colloidal system contains salt (for example, human biological fluids). **Figure 3** shows fragments of the drying process of a drop of a protein - salt solution, in which the ratio of total protein to salt corresponds to that in human serum (7% in BSA in 0.9% NaCl). At the beginning of drying (**Figure 3a–c**) the visible dynamics of the process is the same as in the salt-free solution. However, further (**Figure 3d–f**), salt crystallization begins in the center of the drop, and the final picture of the drop acquires a specific image [8, 9].

Let us take a closer look at the structure of the light circle that appears on the inner side of the protein roller (**Figure 3f**). In **Figure 4** it can be seen that this ring is composed of individual micron-sized protein aggregates. Closer to the center of the drop, the layer of protein structures transforms into a homogeneous layer of the protein gel, inside which salt crystallizes.

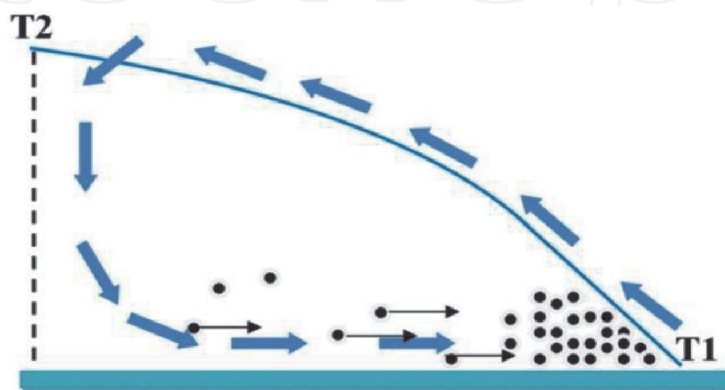


Figure 1.

Scheme of flows in a drying drop of an aqueous colloidal solution sitting on a glass substrate (a half of the 2D image). Capillary flow (black arrows) and Marangoni flow (blue arrows) promote the removal of the colloidal phase (black balls) to the periphery of the drop. $T_1 > T_2$.

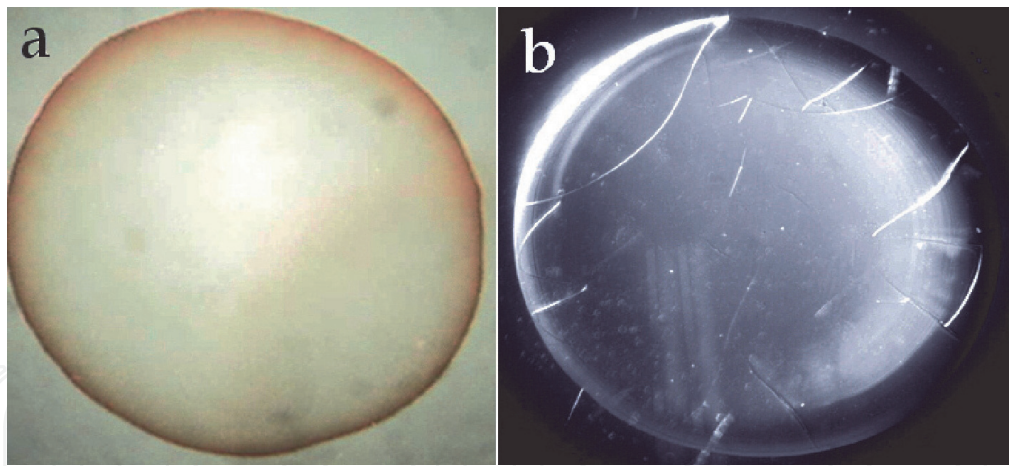


Figure 2.
Dried drops (5 μ l volume) of an aqueous solution of coffee (a) and a 7% solution of bovine serum albumin (BSA) in distilled water (b). Formation of the roller of the colloidal phase along the droplet periphery.

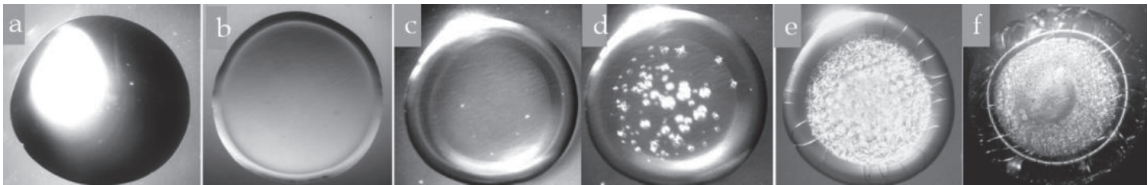


Figure 3.
Consecutive fragments of the drying process of drop of 7% BSA in a 0.9% NaCl physiological solution: (a-c) - redistribution of the colloidal phase and the formation of a protein roller; (d-f) - the process of salt crystallization in the protein matrix and the formation of the final image of the drop (f).

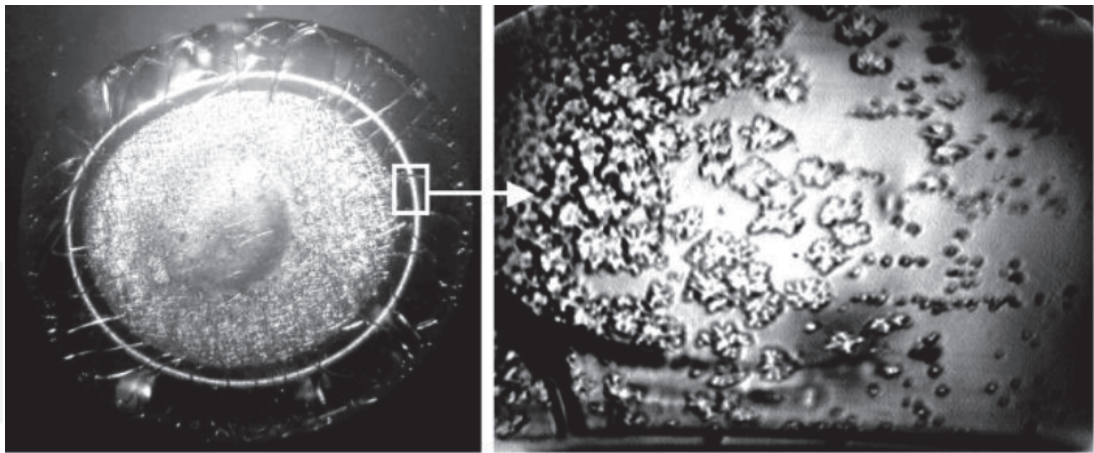


Figure 4.
Dried drop of protein-salt water solution (left) $\times 10$. Light-diffusing circle is a place of protein structures formation. Right picture shows protein structures evolution from separated precipitates (right) to protein clusters that transform into gel. Magnification: $\times 280$ [10].

With the help of physical modeling, it was found out how the ratios of the components in a protein-salt solution, drying in the form of a drop on a glass slide, change (Figure 5).

The protein roll formation time for a 3 μ L drop is 4-6 minutes. During this time, the liquid part of the droplet loses $\sim 30\%$ of water (evaporates) and 70% of albumin (is carried out to the periphery of the droplet and becomes solid). As a result, the initial ratio of the components in the remaining solution changes, causing coacervation of albumin. The mechanism of these events is associated with the competition for hydration between colloidal particles and salt ions. The concentration of salt

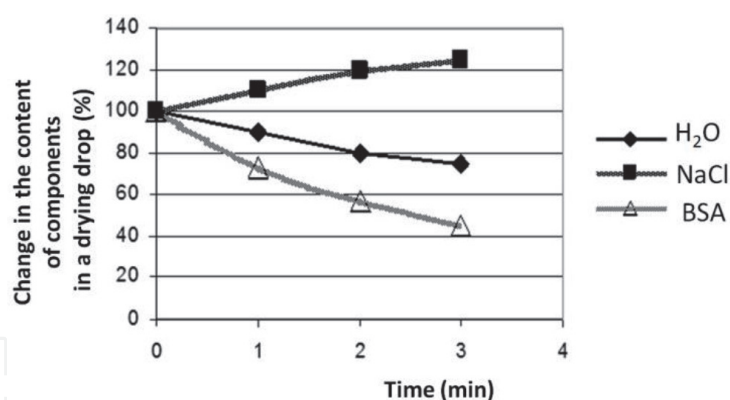


Figure 5.

Change in the relative content of components in the protein-salt solution when it dries in the form of a drop on a glass substrate (according to materials in [10]).

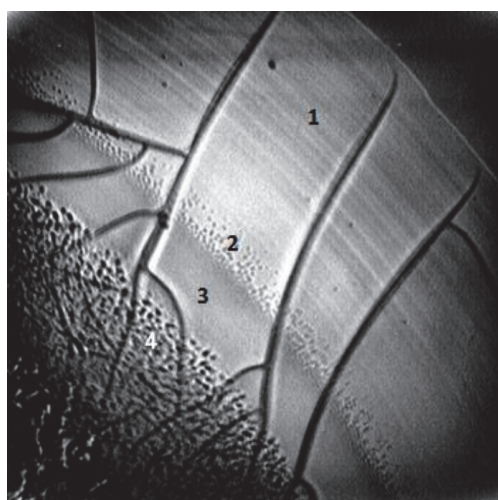


Figure 6.

Zones in dried drop of BSA-salt solution: 1 – homogenous protein film (colloidal glass); 2 – zone of protein precipitates, from single ones to their clusters; 3 – gel; 4 – zone of salt structures in shrinking protein gel. Magnification: $\times 70$.

per unit volume of protein increased greatly, which led to the loss of its aggregate stability and the beginning of the coagulation process. **Figure 6** shows the zones of different phase states of the protein, formed in the gradient of increasing salt concentration.

The cascade of protein phase transitions, according to the authors, can be represented as follows (**Figure 7**).

To examine the bottom adsorption layer in a dried drop of 7% BSA solution in saline NaCl, the top of the dried protein roll was carefully removed with a scalpel, as shown in **Figure 8**.

Investigation of the lower adsorption layer of a dried drop of a protein-salt solution using an atomic force microscope in zone 2 in **Figure 6** showed the presence of protein precipitates corresponding to the structures of the second order in **Figure 7**. Investigation of the lower adsorption layer of a dried drop of a protein-salt solution using an atomic force microscope in zone 2 in **Figure 6** showed the presence of protein precipitates corresponding to the structures of the second order in **Figure 7** (**Figure 9**).

At a lower concentration of protein in physiological saline solution, the coacervation process begins earlier, which confirms the author's opinion about the nature of the observed phenomenon (**Figure 10**).

Thus, due to protein redistribution during drop drying, protein deposits on the drop edge and protein in the middle part of the drop are in different conditions, and

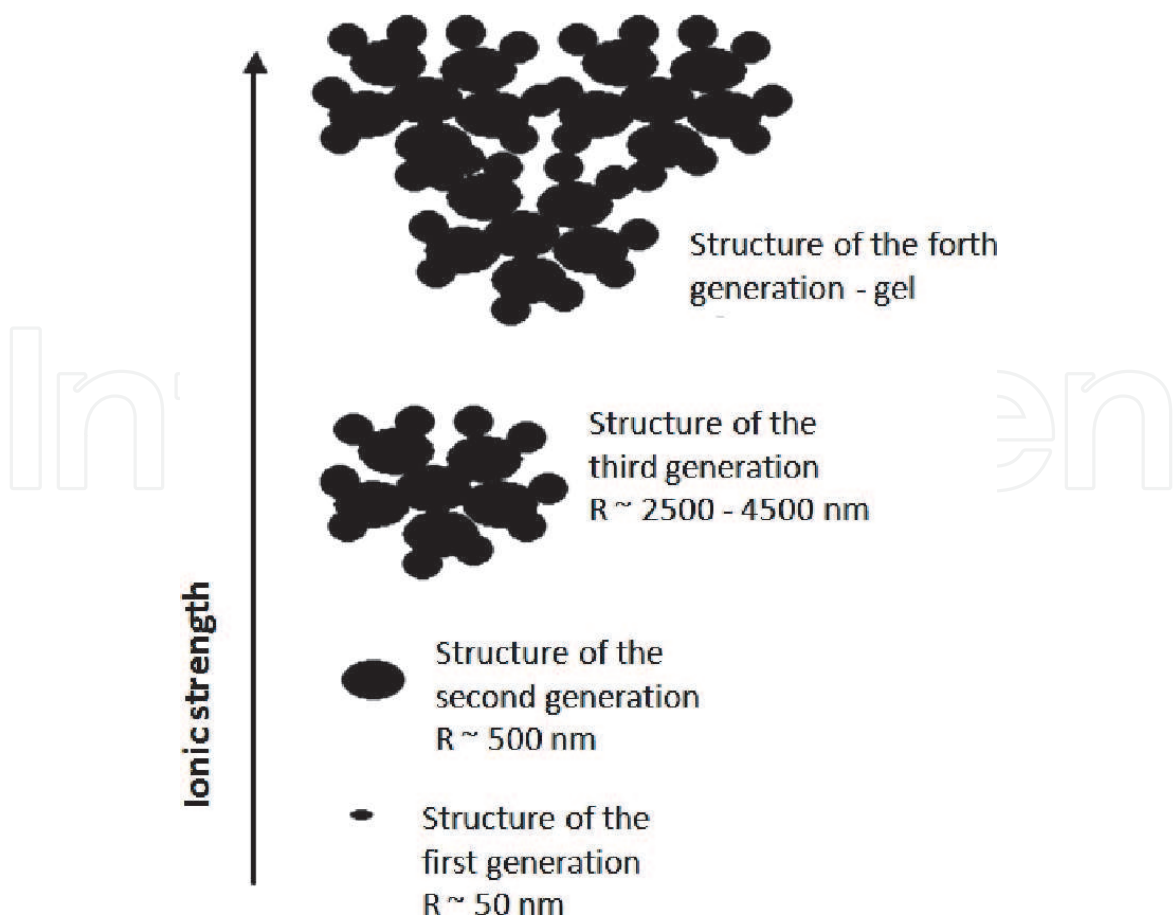


Figure 7.
Protein phase transitions in fluid part of a sessile drying drop of protein-salt-water solution. R is a radius of the structure [10].

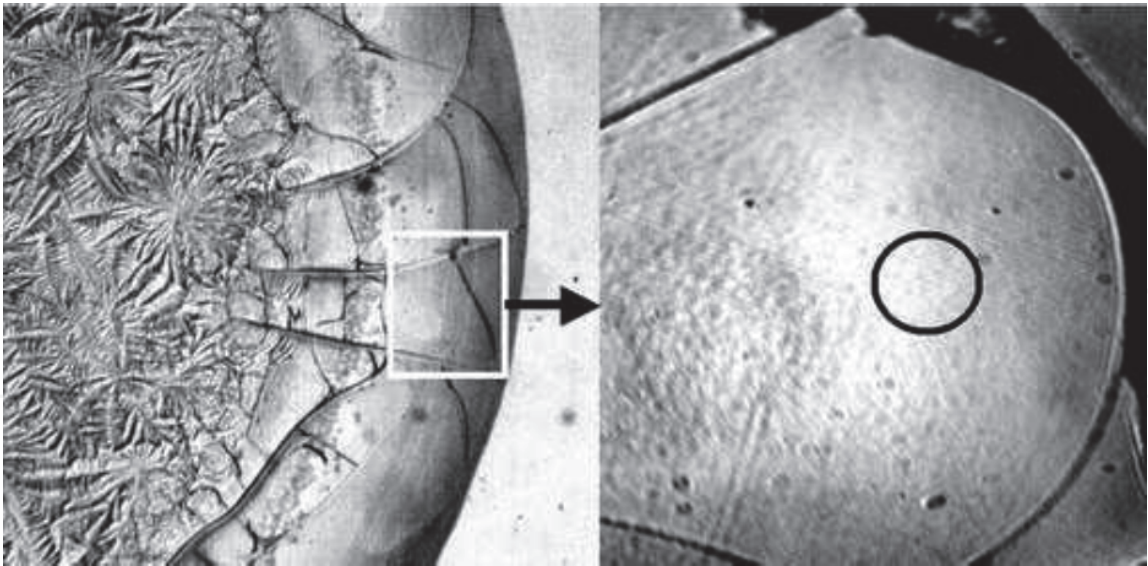


Figure 8.
Fragments of dried drops of 7% BSA in 0.9% NaCl water solution. Left – zone of protein ring (in a white rectangle) before removing; right – the same zone after removing the upper film. Black circle shows the area of bottom protein adsorption layer is used for AFM investigation.

form materials with different properties. The authors [11] argue that colloidal particles can form different structures: from colloidal glasses with very high volume fractions and low strength of interparticle attraction to colloidal gels with very low volume fractions and strong attraction between the particles (**Figure 11**). Before gelation, colloidal particles form fractal clusters, which turn into space-filling

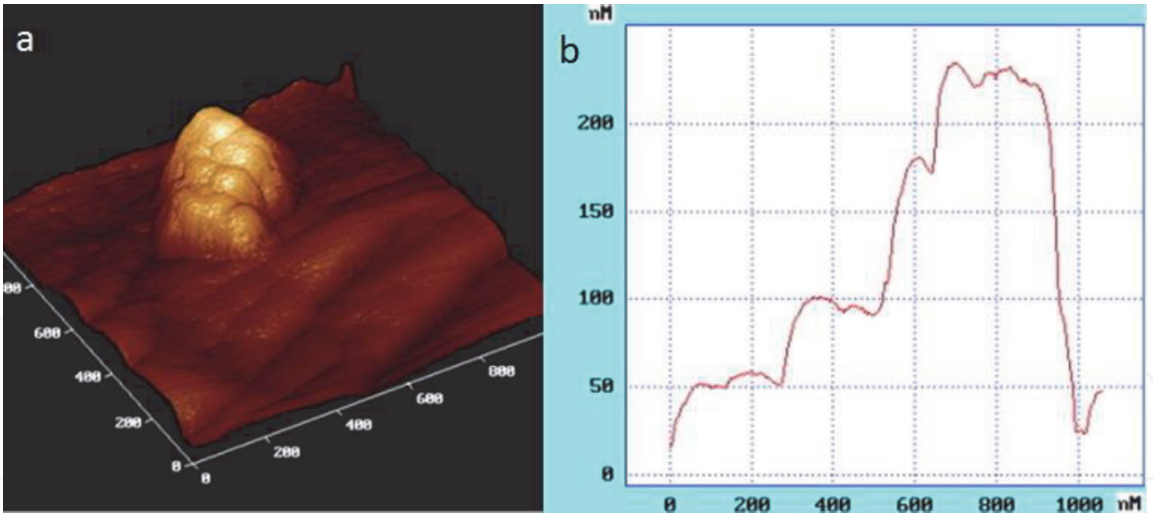


Figure 9.
AFM data: single protein precipitate (structure of the second generation) lying on the protein film in dried drop of BSA-salt – water solution. It consists of some subunits (structures of the first generation), which admittedly represents consolidated micells. (a) three-dimensional image; (b) precipitate profile.

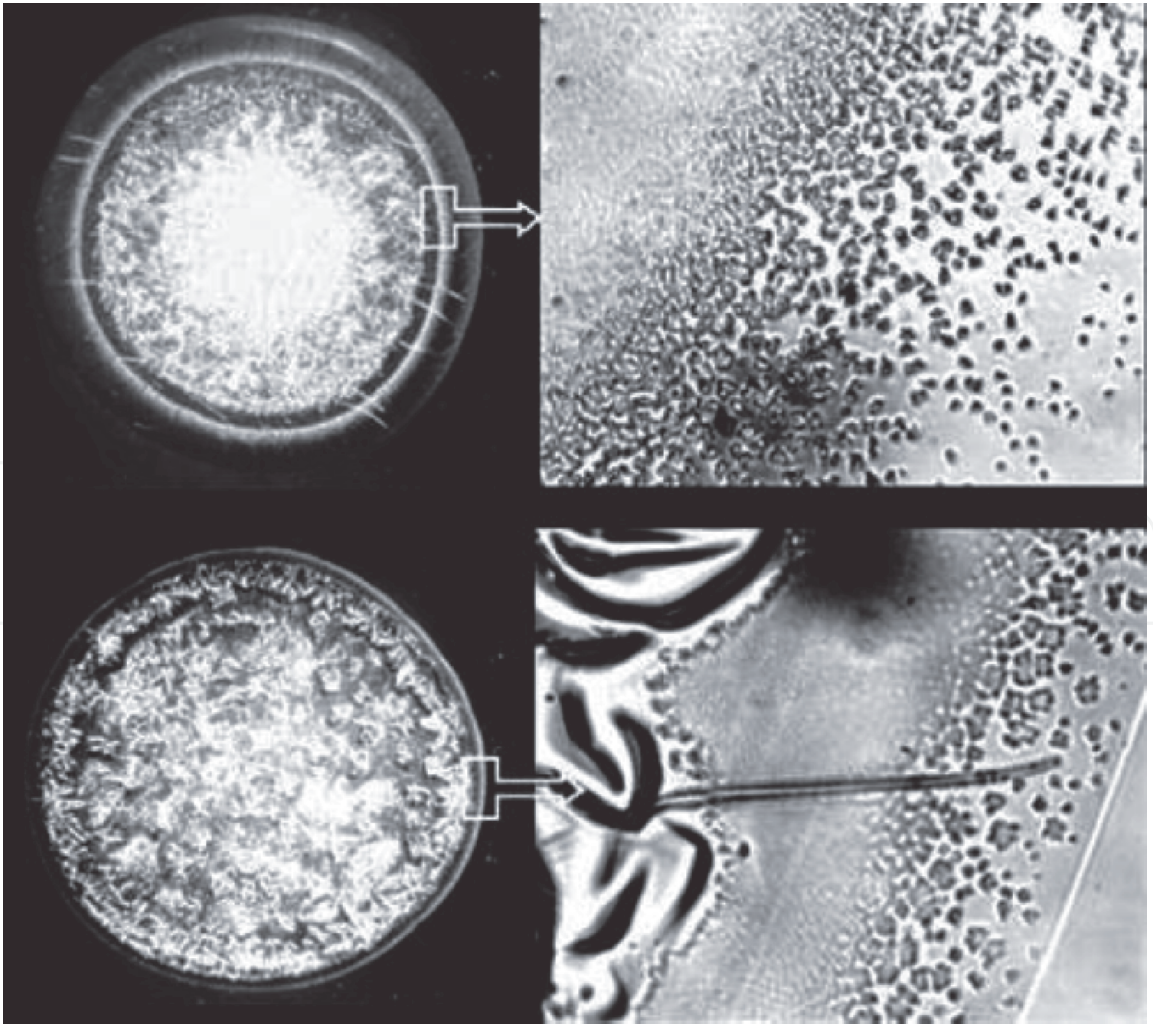


Figure 10.
Dried drops of protein-salt solutions: 7% BSA in 0.9% NaCl (above), and 2.5% BSA in 1.8% NaCl (bottom). Light-diffusing ring of protein structures has different positions (see the text). Magnification: left – $\times 10$; right – $\times 70$.

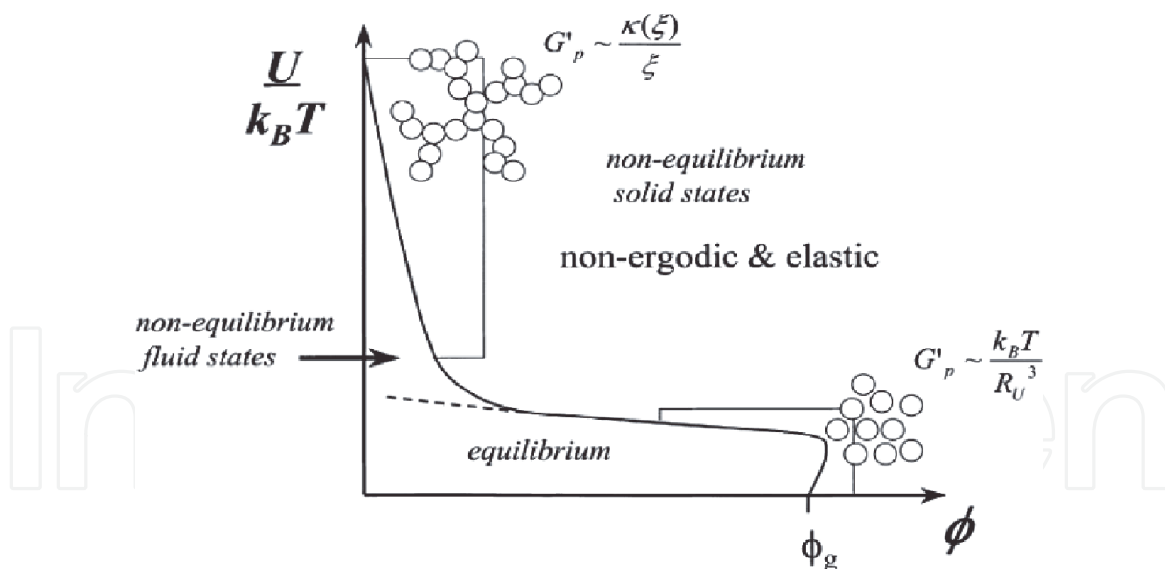


Figure 11.
 Schematic state diagram of colloidal particles with short-range potentials, after V. Trappe, R. Sandkuhler [11].
 Φ – volume fraction of colloid phase; U – strength of the interparticle attraction.

networks. Current investigations show that a drying drop of protein–salt aqueous solution is an excellent illustration of this dynamics. Taking into account hydrodynamic motion of the colloidal phase to the drop periphery and its rapid consolidation there, we suppose that this solid phase really represents the protein glass transition: it is transparent and extremely fragile. In contrast to the drop periphery, low protein volume fraction and high ionic strength in liquid residuals in the middle part of a drying drop stimulate liquid–liquid separation and further cascade of protein phase transitions leading to gel formation. Thus, protein gel probably forms only inside the protein glass ring of a drying drop.

More detailed information on the processes in drying drops of protein-salt solutions can be obtained in publications [12–22].

When working with biological fluids of healthy and sick people, it was noticed that in the case of severe diseases, the processes of protein structuring are disrupted, which is revealed in experiments with drying drops [23, 24]. **Figure 12** shows dried drops of blood serum of women after delivery at term and premature birth. Noteworthy is the significant expansion of the zone of protein structures and the formation of larger precipitates.

It is surprising that in some cases, in seriously ill people, regardless of the nature of the disease, micron-sized protein precipitates can be observed already in liquid blood serum (**Figure 13**).

The magnitude of the osmotic pressure created by the solution depends on the amount, and not on the chemical nature of the substances dissolved in it (or ions, if the molecules of the substance dissociate), that is, the osmotic pressure is a colligative property of the solution. The higher the concentration of a substance in a solution, the greater the osmotic pressure it creates. The volume and mass of a colloidal particle is much larger than the volume and mass of a molecule of low-molecular substances. At the same mass concentration of a substance, a unit volume of a sol contains significantly fewer particles than a unit volume of a true solution. Therefore, it is generally accepted that the osmotic pressure of colloidal solutions is negligible compared to that in true solutions. However, there is an opinion that a relatively small number of particles, much less than required by the “usual” colligation law, can create a high osmotic pressure if they have extensive hydrophilic surfaces [25]. Since, in addition to salts, blood serum contains other osmotically

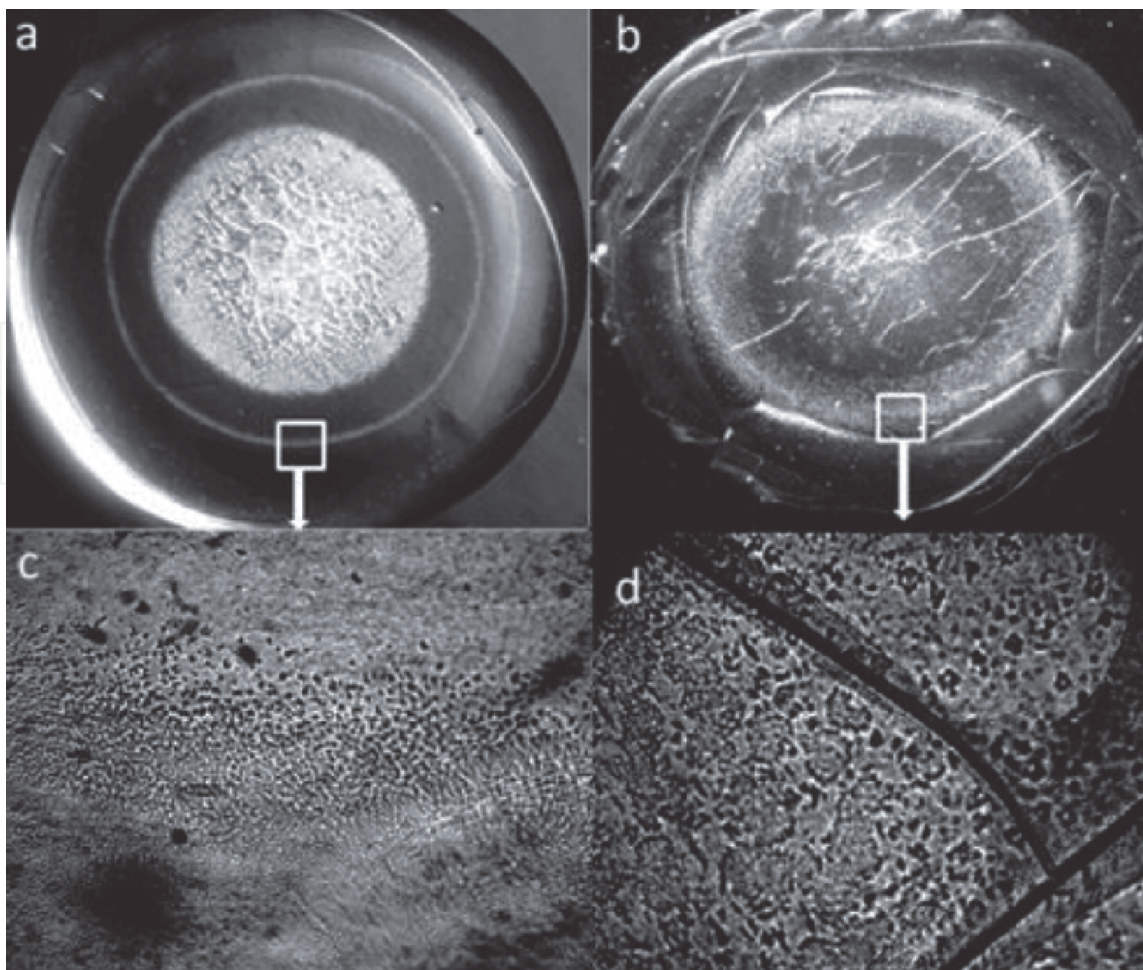


Figure 12.

Dried drops of serum of women in early afterbirth period: (a) is in-time birth (40 weeks); (b) is premature birth (34 weeks). Narrows show ring of micelles; (c) and (d) are selected by tetragon regions in more enlargement. Magnification: 15×40 .

active components, it is customary in clinical practice to operate with the concept of “osmolarity,” meaning the sum of the concentrations of cations, anions and non-electrolytes, that is, all kinetically active particles in 1 liter of plasma or serum. The osmolarity of biological fluids is a fairly strict indicator of homeostasis. So, the osmolarity of blood plasma in normal conditions can vary in the range of 280-300 mosm/l [26] (1).

$$\text{Osmolarity} = 195.1 + 0.74 \times \text{sodium} + 0.25 \times \text{urea nitrogen} + 0.03 \times \text{glucose} \quad (1)$$

where 195.1 is a free member; 0.74; 0.25; 0.03 - empirically found coefficients in the equation; sodium - in mmol/l, urea nitrogen and glucose - in mg%.

Calculations showed that in the examined patients with burn disease, the plasma osmolarity averaged 301.6 ± 6.56 mosm/l, fluctuating within the range of 286.16-320.01 mosm/l. However, in patients, the content of both total protein and albumin was decreased. That is, against the background of normal ionic strength of the solution, there was an average decrease in the mass fraction of albumin [27]. Violation of the protein-electrolyte balance led to coacervation of albumin in the liquid phase of the serum. In the course of successful treatment of the underlying disease, the disturbance of this balance began to decline, and coacervation in the liquid serum was not observed.

In this brief review, the phase transformations of protein in droplets of protein-salt solutions drying on glass were examined, and analyzed the cause-and-effect

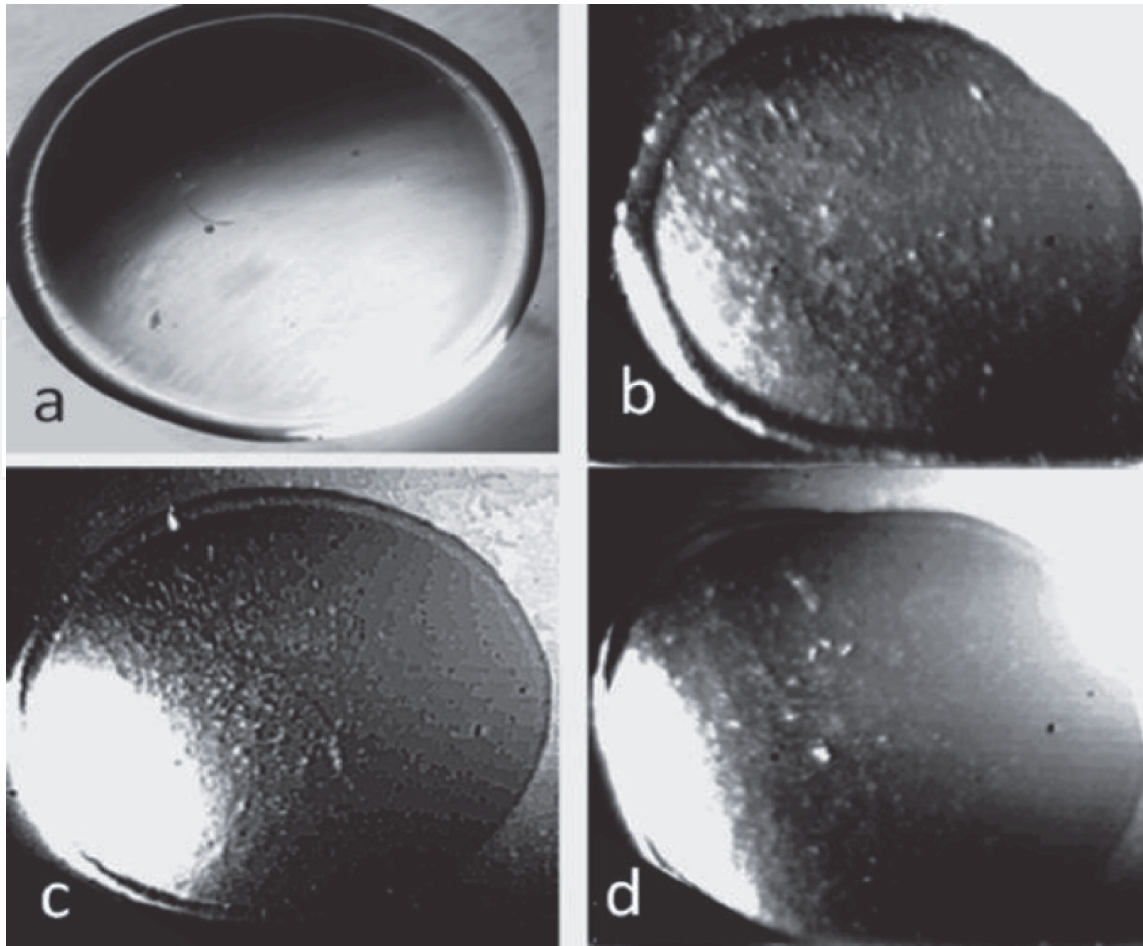


Figure 13.

The initial drying process of blood serum drops is the formation of a solid rim along the periphery of the drops: (a) - norm, (b) - chronic hepatitis B + C; (c) - burn disease; (d) - coxarthrosis. In the liquid phase of the patient's serum, micron-sized protein precipitates are visible. The initial volume of each drop is 3 μ l.

relationships of these transformations. Also similar processes occurred in real human biological fluids was found. In this regard, it would like to note the amazing results of the successful treatment of hundreds of cases of serious diseases of a different nature, obtained by the Soviet doctor A.S. Samokhotskiy, which were carried out according to the method developed by him [28, 29]. Here is the conclusion of one of his articles [30]:

1. The concentration of electrolytes (sodium, potassium, calcium, magnesium) in the blood serum changes in a wide variety of diseases, but the ratios of these electrolytes can be similar in different diseases and different in the same disease in different people, as well as in one person for different stages of the painful process.
2. The use of medicinal compositions containing electrolytes, the concentration of which in the blood serum is relatively low, naturally increased their content and improved the patient's condition.
3. The use of medicinal compositions containing electrolytes, the concentration of which in the blood serum is relatively high, naturally increased their content (increased the gap in the ratios) and worsened the patient's condition. The deterioration usually was significant.

4. Very small doses of these elements are useful to normalize the ratios of sodium, potassium, calcium and magnesium in the blood serum and improve the patient's condition.

Unfortunately, after the death of the author in 1986, his work was not continued. Current investigation shows that continued research in this direction is very promising.

2.1 Materials and methods used when working with drying drops

7% w bovine serum albumin solution (BSA, 68 kDa, Sigma, USA) in distilled water or in physiological salt solution (0.15 M NaCl, chemically pure, "Reactiv, Inc.," Russia) were used. All solutions were prepared without buffering, a day prior to experimentation, refrigerated overnight and allowed to come to room temperature before testing. The samples under study were placed, using micropipette, onto clean glasses in the form of drops of volume of 3 μ l (6-8 drops for each sample), and let for drying at room conditions. Morphological observations were carried out during drying, and 2-3 days after placing on the glasses, using LUMAM-I-3 microscope and video camera – computer setup. Dried drops also were investigated by means of atom force microscope (AFM) "Smena" NT-MDT (Russia), Russia, using a sensor CSG11. Samples of blood plasma and serum were obtained from 30 clinically healthy donors (the material supplied by Hemotransfusion Station, Nizhny Novgorod); 18 patients with viral hepatitis B and C in acute stage (the material supplied by the Hepatological Center, Nizhny Novgorod); 30 patients with burn disease, and 8 patients with diseases of articulations of inflammatory and degenerative character (supplied by the Federal Burn Treatment Center, Nizhny Novgorod Research Institute of Traumatology and Orthopedics); 40 women after normal or premature (second- and third-trimester) childbirth (supplied by the maternity and child-welfare services of Nizhny Novgorod).

3. Structure and dynamics of water microdispersed systems

Due to the thermodynamic instability of colloidal solutions, aggregation and disaggregation processes continuously occur in them, leading to a change in the number of osmotically active particles per unit volume, and, consequently, in the osmotic pressure. With an increase in the average radius of the particles of the system, as a result of their coagulation and the formation of aggregates, the osmotic pressure should drop very strongly. On the contrary, with the disintegration of aggregates into primary particles, the osmotic pressure should increase strongly. Since the phenomena of aggregation and disaggregation in colloidal systems very easily occur under the influence of sometimes even very weak external influences, the variability of the osmotic pressure of lyosols and their dependence on the prehistory of the solution becomes clear [31]. In recent years, evidence has appeared in the literature about the inhomogeneity of water and aqueous solutions at the micro level. For the first time, as far as we know, giant (millimeter-sized) clusters in a thin layer of water were detected using IR spectroscopy [32]. An assumption was made about their liquid crystal nature. As a result of the study of solutions of NaCl, citric acid, glucose, urea, vinegar and ethanol using static and dynamic light scattering, it was concluded that the dissolved substances in liquid media are distributed unevenly: areas with low and high concentration provide a contrast in light scattering during experimental observation. There are separate domains, close to spherical in shape, with a high density relative to the surrounding

fluid. Their size can reach hundreds of nanometers [33]. Investigation of suspensions of fluorescent polystyrene microparticles ($d = 1 \mu\text{m}$, $C = 0.2\%$ in highly purified water) using a confocal laser scanning microscope for several hours allowed the authors to observe the appearance and growth of “voids” inside the colloidal phase [34]. According to the authors, the reason for this is the attraction initiated by counterions between like-charged particles [35]. The ability to move a particle forcibly placed in the resulting voids was severely limited in comparison with particles located in adjacent areas with a high packing density [36]. The addition of salt to the solution reduced the distance between the colloidal particles, but after reaching a certain limit, the “colloidal crystal” melted.

The results of experiments on determining the size distribution of optical inhomogeneities (clusters) in bidistilled water by the method of small-angle light scattering are presented [37]. The measurements showed the presence of a spectrum of cluster sizes in the water in the range $(1.5\text{--}6.0) \mu\text{m}$. With the help of laser interferometry, the formation of supramolecular water complexes with linear dimensions of $30\text{--}100 \mu\text{m}$, distributed in continuous water, was shown [38, 39]. A critical review of modern water purification methods [40] states that water is easily contaminated with chemicals, gases, vapors and ions that are washed out of pipelines and containers. These can include sodium and silica from glass, plasticizers and ions from pipes, microbial particles and their endotoxins, and contaminants. Soluble organic contaminants can even be introduced from deionizing resins used during processing, especially if inadequate resins are selected or the resins have previously been contaminated. No cleaning method is perfect.

In our previous works it was also shown that water and aqueous solutions are microdispersed systems [41, 42]. Upon evaporation of free water, structures ranging in size from ten to hundreds of micrometers remain on the substrate, which are aggregates of a microdispersed phase (**Figure 14**). The aggregates do not evaporate at room temperature, have a viscous consistency and “melt” when the osmotic pressure rises. The unit of the microdispersed phase is NaCl microcrystals surrounded by a thick hydration shell. The water of hydration shells evaporates at a temperature of $> 200^\circ \text{C}$ and accounts for $\sim 20\%$ of the dry sediment mass [43].

The hydration shells of hydrophilic microparticles are denser liquid crystalline water, which forms a zone around the particle, displacing all impurities, including ions, from its volume — Exclusion Zone (EZ) [45]. The microheterogeneous structure of water was investigated using a conventional light microscope in the

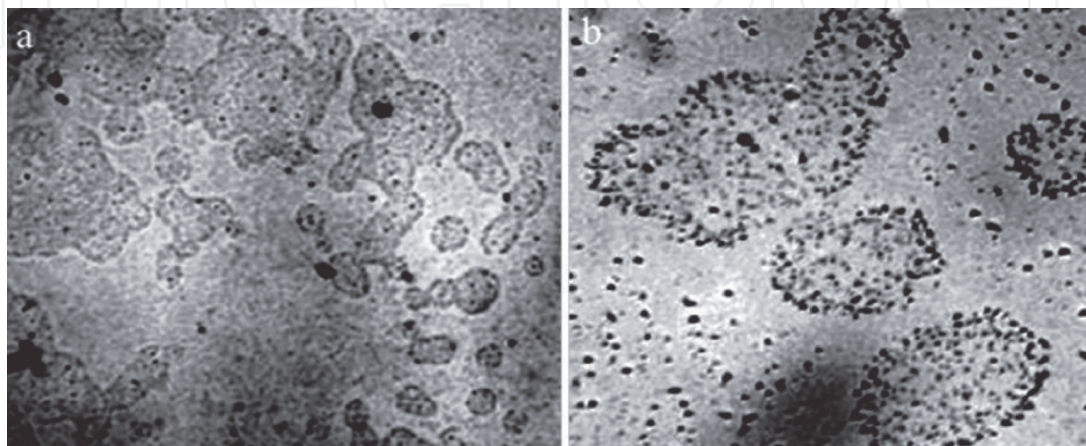


Figure 14.
Fragments of microstructure aggregates: (a) - dry white wine, in a thin layer of liquid ($8 \mu\text{m}$), frame width - 2.4 mm ; (b) in the precipitate of a NaCl solution on a substrate after evaporation of free water, the frame width is 1 mm [44].

preparation between the slide and cover glass (layer thickness $\sim 8 \mu\text{m}$), as well as in a drop of water placed in a hole in a plastic plate 0.5 mm in diameter (**Figure 15**).

The dry residue mass after evaporation of free water from these liquids was 0.25%, 0.48% and 2.5% of the initial mass, respectively.

Now, when it became known that water and aqueous solutions are not homogeneous media, but are microheterogeneous dispersions with their characteristic dynamic processes, facts that previously did not have an adequate explanation become clear. For example, oscillatory processes in liquids revealed by different physical methods of analysis: determination of enzyme activity [46–48]; dynamic light scattering [49, 50], IR spectroscopy, Raman spectroscopy, UHF radiometry and NMR [51]. Continuous multi-hour studies of autonomous oscillatory processes in a number of beverages (tea, dry red wine [52], instant freeze-dried coffee [53, 54]), were conducted registering several parameters simultaneously: the dynamics of the complex mechanical properties of drying drops of these liquids, the dynamics of the surface tension of the solution, and the width of the edge roller for drops dried on glass. For periodic registration of complex mechanical characteristics of drying drops, a method developed by us earlier was used.

3.1 Methods used for studying dynamical processes in water microdispersed systems

3.1.1 Drying drop technology (DDT)

To monitor fluctuations of physicochemical properties of colloidal systems the DDT method was used based on acoustical impedancemetry developed in our laboratory earlier [55, 56]. Here only its main features would be explained. A coffee drop (volume of 3 μl) without any pretreatment dries on a polished end of a quartz plate. The quartz oscillates with a constant frequency of 60 kHz, which is equal to the resonance frequency of unloaded resonator. Acoustical – Mechanical Impedance (AMI) of the drop during drying is displayed as a curve on a screen (**Figure 16**). The parameter BS_2 reflects the dynamics of complex mechanical properties of the drying drop deposit (mechanical stress) and is calculated automatically by the software. In the same environment this parameter depends strongly on liquid composition and structure. The diagrams were built for temporal fluctuations of BS_2 parameter using Excel.

3.1.2 Optical investigation of coffee ring width fluctuations

The experiments were carried out using water solutions of the Nescafe Gold sublimated instant coffee bought in a store, with a concentration of 2.50 g/100 ml,

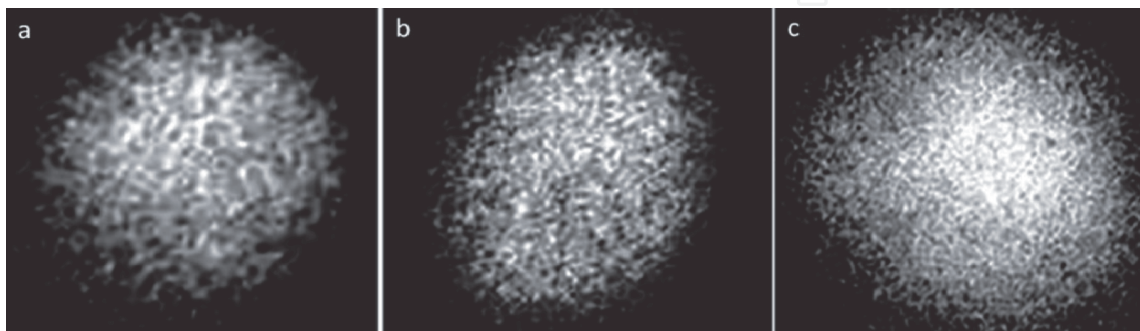


Figure 15.

Microstructure of liquids in the “hanging drop” preparation. Liquid placed in a hole in a plastic plate with a diameter of 0.5 mm: (a) - distilled water; (b) - tap water; (c) - water from the Black Sea. The drops were looked via microscope right through.

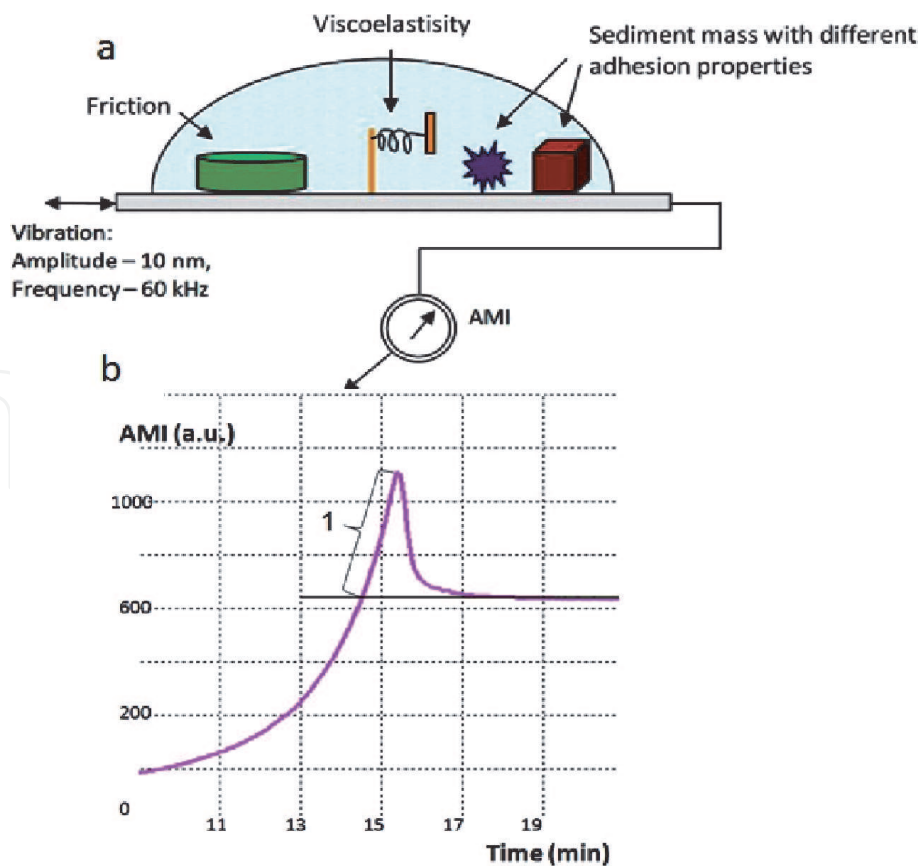


Figure 16.
DDT scheme: (a) – a drop as an object having a set of unique physical properties is drying on the surface of oscillating quartz resonator; (b) – typical AMI curve for drying drop of coffee: 1 – portion of the curve measured by total derivative (parameter BS_2).

at $T = 22\text{--}23^\circ\text{C}$ and $H = 64\text{--}65\%$. A dry coffee sample was placed in a chemical glass, filled in with hot tap boiled water, and mixed by a glass stick until the coffee dissolved. Sampling was begun after cooling of solution to room temperature, at 9 o'clock Moscow time. Sampling was made each 30 minutes from the same glass of coffee solution standing on a table, using the zone equidistant from the center and edges of the glass, from the depth of about 2 cm by a microdispenser with removable tips. Such 30 minute intervals were stipulated by the duration of one test (20 min) and quartz treatment procedure. In some experiments we added to the colloidal system surfactant sodium dodecyl sulfate (SDS) with a concentration of 0.2% w. Ten repeated experiments were made for every type of investigation. The tests were carried out simultaneously with BS_2 parameter measurements. For every 30-minute counting we took four drops having a volume of $3\text{ }\mu\text{l}$: one drop for BS_2 parameter measurement, and 3 drops for coffee ring width measurements. Those 3 drops were placed on a new (without any treatment) microscope slides ApexLab, 7 countings of each slide (**Figure 17**), up to 22 countings.

The preparations were drying in horizontal position under room conditions, and were investigated the next day. Coffee ring width was measured using the

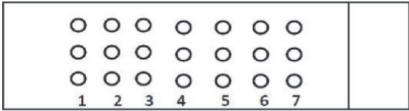


Figure 17.
Arrangement of drops on a glass for drying and microscopy.

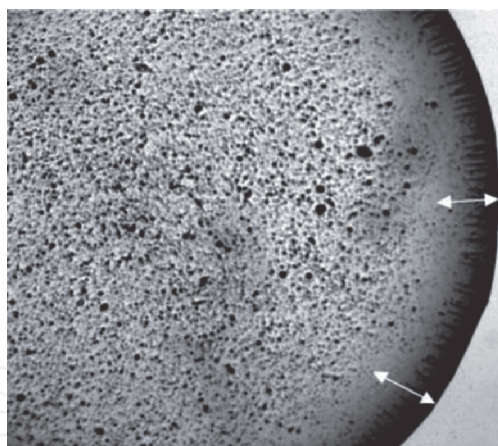


Figure 18.
Measurement of coffee ring width under microscope.

Levenhuk ToupView program in 3 positions into every drop (**Figure 18**), so for each 30-minute account 9 measurements were made. Arithmetic mean and standard deviation were calculated for further analysis.

3.1.3 Optical investigations of liquid samples

The microscopy investigation of coffee solution was carried out in freshly prepared samples by the method of “flattened drop.” For this purpose a drop with a volume of 5 μl was placed on a new (without any treatment) microscope slide ApexLab (25.4×76.2 mm) then the drop was covered with a cover glass 24×24 mm in size (ApexLab), avoiding formation of air bubbles, and was studied under microscope Levenhuk with a digital camera connected to a computer. We made 10 pictures for every 30-minute step with the same magnitude and analyzed them later using the Levenhuk ToupView program. Morphometric measurements (diameters of avoids in the pictures) were made for every 30-minute step. Statistical analysis (calculation of mean and standard deviation) were made by Excel program. In some experiments, in parallel with the flattened drop, freshly prepared smears (without cover glass) were also examined under a microscope in polarized light.

3.1.4 Surface tension fluctuations detection

For detecting surface tension temporal changers we used a set of certified glass capillaries (10 μl Drummond Microdispenser, 100 Replacement Tubes, made in the USA by Drummond Scientific Company. Cat.# 3-000-210G). Each capillary was used once. A new dry capillary was submerged into liquid at regular intervals to a certain mark on a capillary and liquid raising level was measured. Simultaneously, the fluctuations of BS_2 were usually measured. Diagrams and calculations of the correlation coefficient were done by means of Excel program.

3.2 Results and discussion

3.2.1 Dynamic processes in liquid media

Figure 19 shows joint temporal fluctuations of parameter BS_2 and coffee ring width. Direct linear correlation between them at significant value $p = 0.005$ was 0.7 ± 0.16 . This testified to a causal relationship between these parameters.

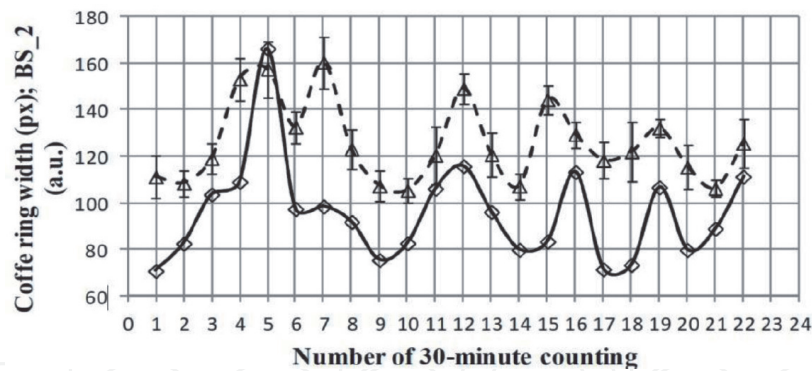


Figure 19.
Joint dynamics of parameter BS_2 (solid line) and coffee ring width (dashed line) in coffee water solution (2.5 g/100 ml).

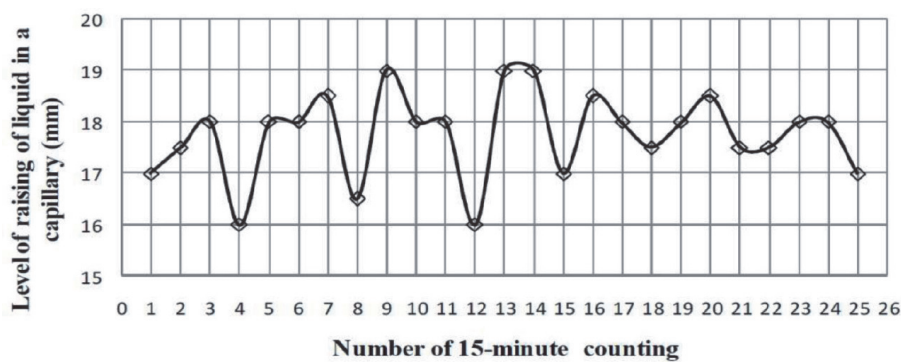


Figure 20.
Fluctuations of surface tension in coffee water solution (2.5 g/100 ml).

Fluctuations of surface tension in the same coffee solution could be measured more frequently. It was shown that one period took 30-40 minutes (**Figure 20**). Correlation coefficient between BS_2 and surface tension fluctuations in one and the same experiment was 0.8 ± 0.2 ($p = 0.01$) (**Figure 21**). It is interesting to note that fluctuations of these parameters did not disappear either on the third day of stay of this liquid in the same glass without cover on the table in laboratory. Despite a long

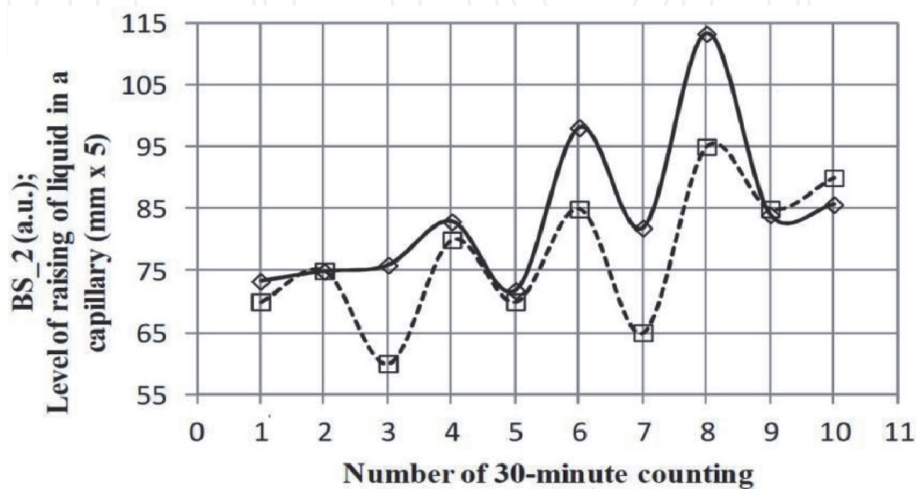


Figure 21.
Joint dynamics of parameter BS_2 (solid line) and level of rising of liquid in a capillary (dashed line) in coffee water solution (2.5 g/100 ml).

period of storage, fluctuations of parameters persist, and direct correlation link between them remains high ($r = 0.7 \pm 0.2$, $p = 0.01$).

It is important to note that when the concentration of coffee in the sample was halved, the amplitude was halved, and the period of oscillations doubled [53]. This makes it probable that oscillatory processes in liquids are associated with aggregation - disaggregation of the microdispersed phase.

A very important problem for the theory and practice is the development of methods for increasing the stability of colloidal systems. Such tasks can be decided in particular by means of adding surface modifying polymers [57] and a literature there]. In our research it was important to find out how addition of surfactant influences parameters of fluctuations and structurization of the drops drying on a glass support. According to **Figure 22**, SDS adding drastically reduced BS_2 value (mechanical stress during drop drying). It occurred due to decrease in interaction between colloidal particles as well as between the particles and quartz surface.

Diameter of the dried drops considerably increased, and the relief of their surfaces became smooth (**Figure 22**, drops 12, 13). Drops 5 and 6, corresponding to one of maxima of fluctuations of the BS_2 parameter before SDS adding were characterized by the relief coffee ring and presence of fragments of reticular structures on the surface. Drops 4 and 7, corresponding to the minimum BS_2 values,

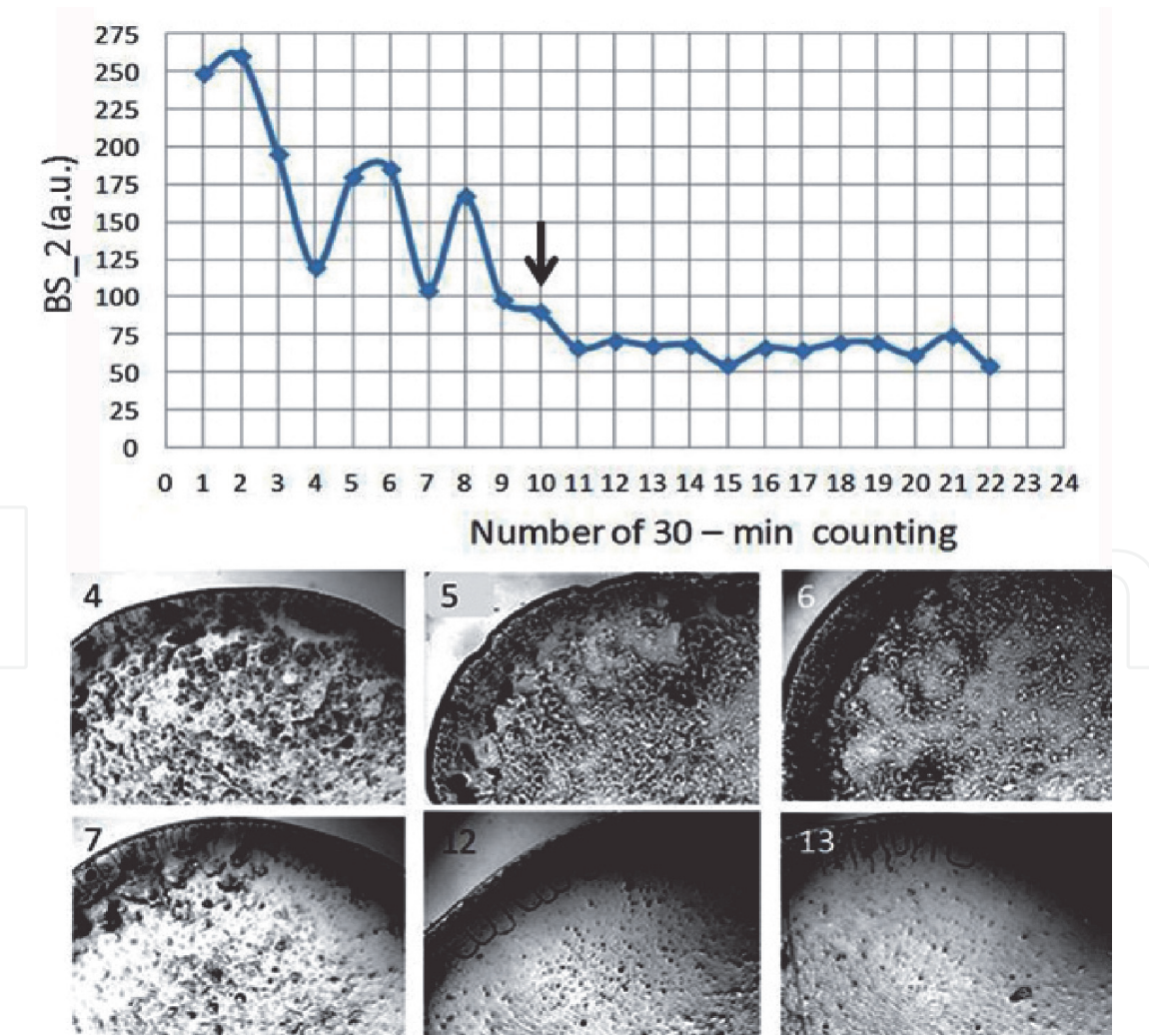


Figure 22. Fluctuations of the BS_2 parameter in the drying drops of coffee solution (2.5 g/100 ml) before and after SDS addition (the moment of addition is specified by an arrow). From below - photos of the dried drops of coffee solution on glass support taken from total volume in different phases of the process (numbers of photos correspond to numbers of counting in above diagram).

had more flat coffee ring and did not contain the reticular structures. Instead of them separate clumps on a surface of the drops were observed. Our data agree with results of the work [58], showed that the interactions of colloids with (and at) liquid-solid and liquid-gas interfaces as well as bulk particle-particle interactions affect the morphology of the deposit. Now we can add that such interactions influence also the mechanical properties of dried materials from these colloids, which may be represented quantitatively. After surfactant addition the area of drops considerably increased, formation of the coffee ring has been complicated and structurization was suppressed, which corresponds to results of the research [59]. Thus, it can be stated that autonomous temporal fluctuations of mechanical properties of drying drops of colloidal suspensions revealed by us earlier [43, 52, 53], are also followed by coordinated fluctuations of surface tension. The authors will try to disclose the internal mechanism of these fluctuations looking directly into a liquid phase.

Observation of colloidal systems under optical microscope followed the same scheme: samples from one and the same volume of coffee solution were taken in certain periods of time and investigated them by the method of flattened drop. Perfectly shaped circles contoured by colloidal particles, sitting close to each other were observed everywhere (**Figure 23**). The circles were sitting on a glass substrate. Commonly it could be possible to find one central particle in each circle. Those round figures could associate, forming large – scale agglomerates [54].

It seems that growing “circles” pushed back colloidal particles, creating conditions for their convergence and coagulation. The size of the particles observed by us was not less than $1\text{ }\mu\text{m}$ so they did not participate actively in Brownian motion. Therefore during creation of spatial reticular structures their passive crowding due to the growing external structures seems to us more convincing than their active movement at the expense of the long-range attraction forces. **Figure 24** shows stages of temporal evolution of round structures in bulk, from small to big, and the remains of arches from colloidal particles after collapse of “round structures.” Similar arches after collapse of round structures could be observed for some time in free floating (**Figure 25**).

The dynamics of growth and destruction of such round structures and their associates is shown in **Figure 26**. On the ascending and descending parts of the curve, size distribution of structures became bimodal due to the presence in the field of view, along with round structures, their large associates (see **Figure 23**, left). Nevertheless, our observations have revealed the rhythmic nature of formation and

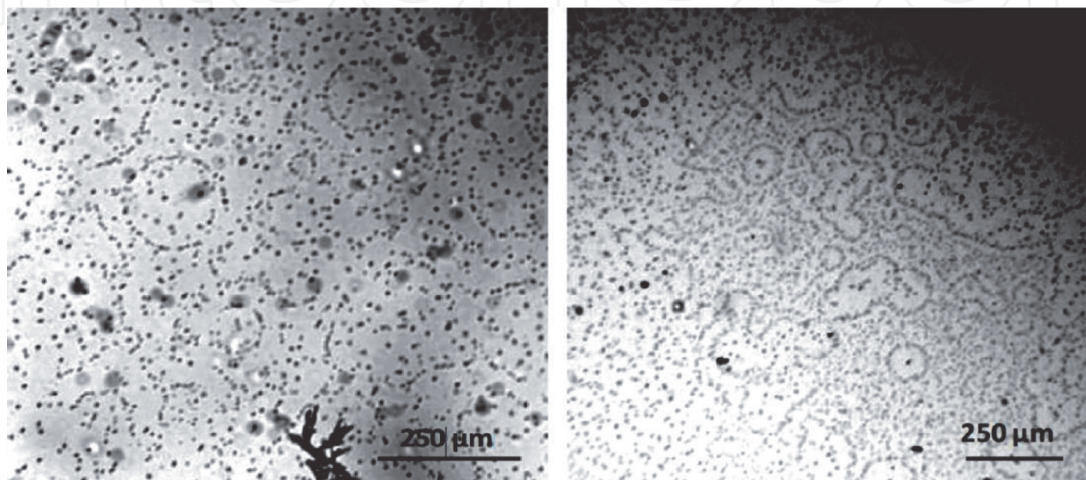


Figure 23.
Microphoto of water solution of coffee. Round figures and associates of round figures.

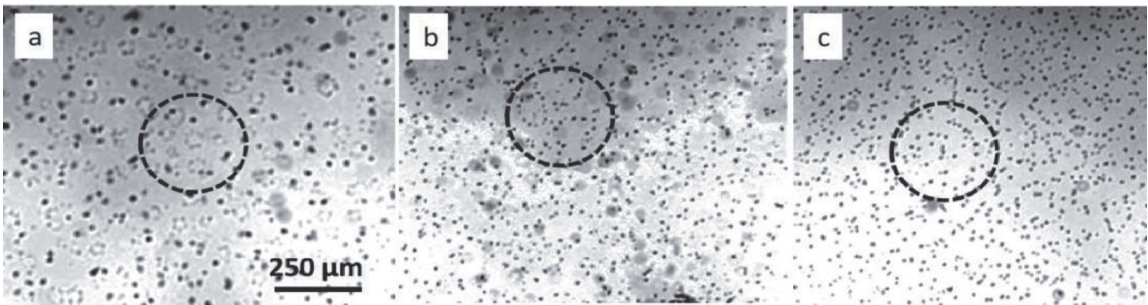


Figure 24.
Microphoto of water solution of coffee. Temporal evolution of round structures in bulk. Some structures in every picture are encircled (as a guide for eyes). Sampling time from the solution: (a) – 12:50, (b) – 13:30, (c) – 14:00.

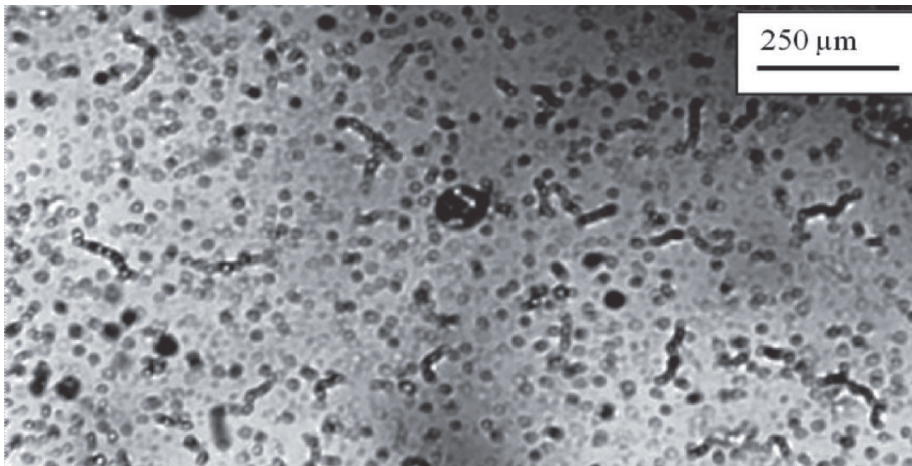


Figure 25.
Water immersion. Microphoto of water solution of coffee. Remainders of arches floating in solution after destruction of round structures.

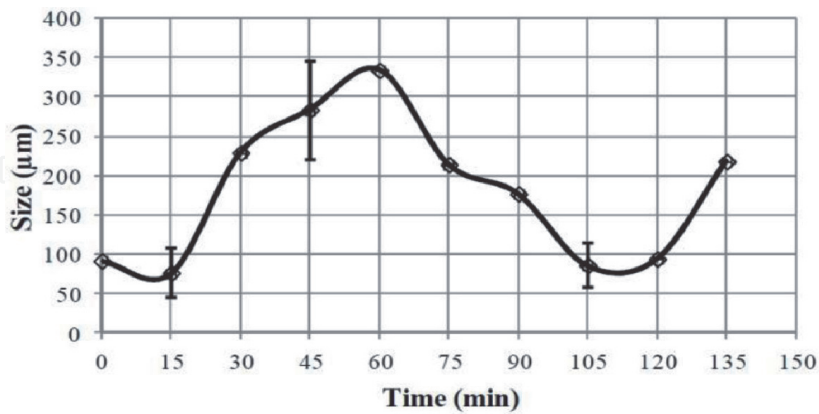


Figure 26.
Dynamics of growth and destruction of “round structures” in coffee solution (2.5 g/100 ml).

destruction of round structures, similar to a rhythm of fluctuations of physico-chemical parameters of this colloidal system. Our equipment allowed observing events only in two-dimensional option. Therefore, circular structures can be a projection of the balls on the plane. Data obtained by means of a laser scanning microscope manifestly showed spherical cavities in latex suspension (**Figure 2** in

[34]). Unfortunately, the authors did not pay attention to their shape. Those cavities looked empty, but now we believe that they were filled by transparent liquid crystal water. If so, then it is easy to explain the restricted movement of the particle placed in such media [16]. This assumption is confirmed by our observations of freshly prepared smears of coffee solution (**Figure 27c and d**). We could see real agglomerates of liquid crystal water. In a flat variant (between substrate and cover glasses), these agglomerates consist of round structures, which have visible borders due to adsorbing colloid particles (**Figure 27a and b**).

The mechanism of particle interaction in solution is currently actively discussed. Attraction of like charged gel beads with a diameter of 400-650 μm spaced several hundred micrometers apart in water was described in [60]. The authors measured the charge distribution around the beads with a pH sensitive dye and conjectured that the cause of the long-range attraction was a shell of multilayer structured water, formed around beads' hydrophilic surface. Here we can see the analogy with our experiment, where colloidal particles rather than gel beads interact. Moreover, their interaction is caused by spatial convergence which is due to the growing spheres of the liquid crystal water. In soft matter and nano-science, critical Casimir forces attract an increasing interest thanks to their capability of reversible particle assembly [61–67]. These forces are the thermodynamic analogue of the quantum mechanical Casimir force arising from the confinement of vacuum fluctuations of electromagnetic field. In its thermodynamic analogue, solvent fluctuations confined between suspended particles give rise to an attractive or repulsive force between them. Due to its unique temperature dependence, this effect allows in situ control of

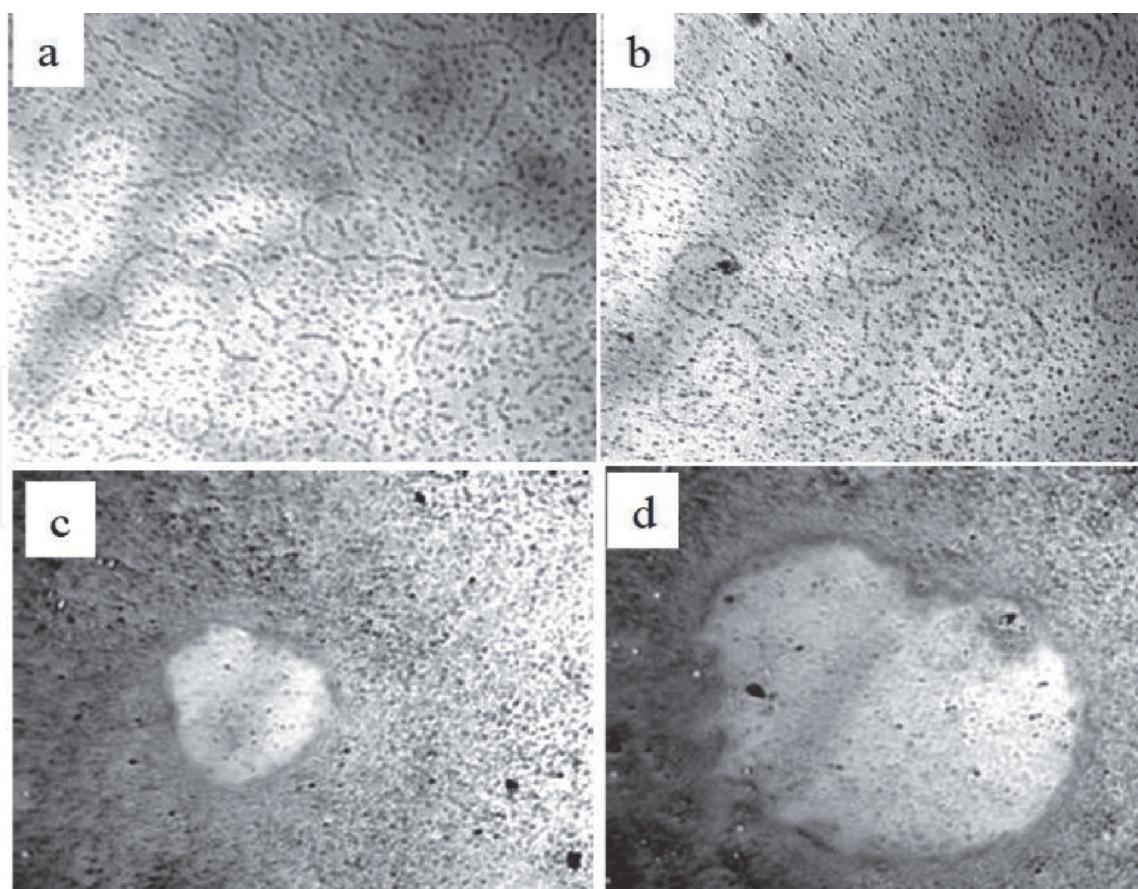


Figure 27.
Microphoto of water solution of coffee (a, b) prepared by the method of flattened drop; (c, d) – agglomerates of microdispersed particles with hydration shells of liquid crystal water (smears of the same coffee solution in polarized light). Each frame width is 1700 μm .

reversible assembly [63, 64]. The authors of [62] showed that in the system with negligible van der Waals forces a simple competition between repulsive screened Coulomb and attractive critical Casimir forces can account quantitatively for the reversible aggregation. Above the temperature T_a , the critical Casimir force drives aggregation of the particles into fractal clusters, while below T_a , the electrostatic repulsion between the particles breaks up the clusters, and the particles resuspend by thermal diffusion [62]. If the gap between the interacting surfaces is filled with a specially designed substance, the attraction between the surfaces can change their repulsion. If such interaction of surfaces with a dielectric constant ϵ_1 or ϵ_2 , respectively, occurs in a medium with a dielectric constant ϵ_3 , they will be attractive at $(\epsilon_1 - \epsilon_3)(\epsilon_2 - \epsilon_3) < 0$, and repulsive at $(\epsilon_1 - \epsilon_3)(\epsilon_2 - \epsilon_3) > 0$. These interactions are extremely sensitive to temperature, chemical composition of the medium and its physical characteristics [65, 66]. According to our data, the observed process is characterized by cyclic changes both in liquid solute concentration due to displacement of the ions and particles from Exclusion Zones (EZs) to the bulk, and in particle surface properties due to EZ shell growth around them. As these zones routinely generate protons in the water regions beyond, unequal proton concentrations in the respective areas may be responsible for creating both the pH and potential gradients, which may be ultimately responsible for the osmotic drive [30]. On the other hand, the surface water has different water activity and chemical potential to the bulk, leading to differences in osmotic pressure and other colligative properties [25]. When this increase in osmotic pressure next to the surface reaches a threshold, the mechanical instability of the system sharply grows, velocity of microstreams enhances, and aggregates of EZ spheres start to collapse. They break into small pieces and melt. Solute concentration and osmotic pressure decline. Free colloidal particles are distributed uniformly. Chains of particles coagulated on the surface of the water balls remain in solution. Growth of EZ balls begins again and the process recurs (**Figure 28**). As similar events (EZ growth) are registered for other polar liquids, we believe that the autonomous fluctuations based on rhythmic formation and destruction of liquid crystal spheres are the universal law of the nature. The considered processes have been used for creation of a phenomenological model showing a possibility of the existence of self-oscillatory modes in similar systems.

3.2.2 Model of dynamic processes in microdispersed water media

Let the volume of a colloidal system be a cube with edge length L . Let this cube house N_1 hydrophilic particles – seeds around which liquid crystal water spheres

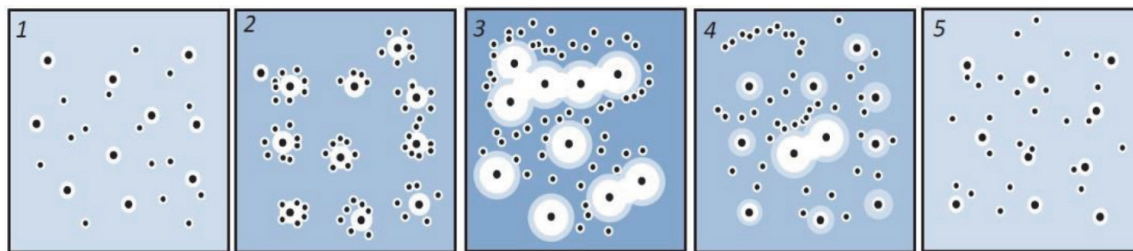


Figure 28.

Scheme of cyclic physicochemical transformations in colloidal system. Background coloring intensity corresponds to the concentration of ions and particles in dispersive phase 1 – Initial state, quasi-homogenous distribution of particles with small EZs; 2 – EZs growth around some particles is more intense than around others; 3 – giant EZ-balls aggregate and begin destruction due to high osmotic pressure; chains of particles coagulated on the surface of water balls remain in solution; 4 – destruction process continues, osmotic pressure decreases progressively; 5 – EZs are ready to grow again.

(EZ) are formed. Let n be the number of ions and colloidal particles determining osmotic pressure P at the interface between water spheres of radius r and dispersive medium. V is the amplitude of mean speed of microflows with a characteristic lateral dimension smaller than πr . This corresponds to the excited mode of mechanical instability for the sphere surface: $2\pi r/m$, where $m = 2, 3, 4, 5 \dots$. The estimated equations for integral processes in such a system can be written down in the following form: EZ growth near a seed particle can be described as (2).

$$dr/dt = l_0/\tau_{gr}(1 - V/V_{crit}) \quad (2)$$

where V is the average velocity of microstreams in bulk near the water balls; V_{crit} is the critical velocity of microstreams in bulk with sufficient energy for destruction of external borders of the water balls; l_0 is the increment of EZ shell thickness around a hydrophilic particle during time τ_{gr} . From the works [68, 69] and our own experiments we know that $l_0/\tau_{gr} \approx 1 - 10 \mu\text{m}/\text{sec}$. Formation of microstreams near the interface between the EZ shell and free water on achieving critical osmotic pressure P_{crit} can be described as (3)

$$dV/dt = -V/\tau_{visc} + 4\pi r^2 \cdot \gamma_m \cdot P \cdot F_{[x]} \cdot [P - P_{crit}] \quad (3)$$

where τ_{visc} is the characteristic time of reduction of microstreams velocity due to solution viscosity; $\tau_{visc} \approx \text{const}$; γ_m is the coefficient characterizing average change of destruction force depending on the created mode of spatial nonuniformity on the destroyed external border of EZ; $F_{[x]}$ is the step-type function equal to zero if $x = P - P_{crit} \leq 0$, and equal to 1 if $x = P - P_{crit} > 0$.

We assume that the speed of diffusion of ions and colloidal particles is much more than the growth rate of EZ shell and speeds of delay of microstreams. Then we can use Vant Hoff's law for stationary conditions (4)

$$P = n \cdot R \cdot T/V \quad (4)$$

where R is universal gas constant, T is absolute temperature.

The volume of colloidal liquid except for the volume of water spheres is found from equation (5)

$$V = L^3 \cdot [1 - 4/3\pi r^3 \cdot N_1/L^3] \quad (5)$$

Thus, the status of water spheres in the bulk of the remaining colloidal liquid can be described by Eqs. (2)–(5). We introduce the following notation:

$$\beta = 4\pi N_1/3L^3 \quad (6)$$

$$\alpha = 4\pi\gamma_m \cdot nRT/L^3 \cdot V_{crit} \quad (7)$$

$$\chi = V/V_{crit} \quad (8)$$

and rewrite the above equations correspondingly:

$$\begin{cases} dr/dt = l_0/\tau_{gr}(1 - \chi) \end{cases} \quad (9)$$

$$\begin{cases} d\chi/dt = -\chi/\tau_{visc} + \alpha r^2/1 - \beta r^3 \cdot F_{[x]} \cdot [P - P_{crit}] \end{cases} \quad (10)$$

$$\begin{cases} P = n \cdot R \cdot T/L^3 \cdot (1 - \beta r^3) = (V_{crit}/4\pi\gamma_m) \cdot \alpha/(1 - \beta r^3) \end{cases} \quad (11)$$

On the basis of this system of equations and understanding of the physics of the dynamical process we can distinguish 3 stages of the process:

- a. EZ shell growth around hydrophilic colloidal particles to the size of huge liquid crystal water spheres; osmotic pressure growth in a bulk;
- b. Osmotic pressure growth in bulk over critical value, forming conditions for the development of mechanical instability at the interface between water spheres and bulk (similar to the Rayleigh-Taylor instability [67]); microstream strengthening, causing erosion until complete destruction of water spheres.
- c. Microstreams slowdown due to viscosity and transition of the system to stage 1.

Let us consider the dynamics of the process based on Eqs. (9)–(11) in simplified form.

Stage 1. EZ shell growth around hydrophilic colloidal particles (12)–(14):

$$\begin{cases} dr/dt = l_0/\tau_{gr}(1-\chi), & \chi > 1 \end{cases} \quad (12)$$

$$\begin{cases} d\chi/dt = -\chi/\tau_{visc}, & \chi \approx 0 \end{cases} \quad (\text{at } t = 0) \quad (13)$$

$$\begin{cases} P = (V_{crit}/4\pi\gamma_m) \cdot \alpha/(1-\beta r^3) < P_{crit} \end{cases} \quad (14)$$

Stage 2. Development of instability and destruction of water spheres (15)–(17):

$$\begin{cases} P = P_{crit} \end{cases} \quad (15)$$

$$\begin{cases} r^3 = r_{crit}^3 = 1/\beta [1-(\alpha \cdot V_{crit}/4\pi\gamma_m \cdot P_{crit})] \end{cases} \quad (16)$$

$$\begin{cases} d\chi/dt = (\chi_{max}-\chi)/\tau_{visc}, \end{cases} \quad (17)$$

where $\chi_{max} = \alpha \cdot \tau_{visc} \cdot r_{crit}^2 / (1 - \beta \cdot r_{crit}^3)$. If $\chi \leq 1$, then r continues to grow. According to our observations, $r_{crit} \approx 250 \mu\text{m}$.

Stage 3. Microflows slowdown.

Since turbulent flows are formed at this stage, τ_{gr} may depend on χ and P . However, for our simplified representation, we shall assume that $\tau_{visc} = \text{const}$, as in the case of laminar flow (18)–(21):

$$\begin{cases} P < P_{crit}. \end{cases} \quad (18)$$

$$\begin{cases} dr/dt = l_0/\tau_{gr} (1-\chi), \chi > 1 \end{cases} \quad (19)$$

$$\begin{cases} d\chi/dt = -\chi/\tau_{visc} \end{cases} \quad (20)$$

$$\begin{cases} P = (V_{crit}/4\pi\gamma_m) \cdot \alpha/(1-\beta r^3) < P_{crit} \end{cases} \quad (21)$$

This dynamics can also be represented on phase plane in χ and r coordinates (Figure 29).

4. Conclusions

In this part of work an instant coffee as a sample of complex colloidal system was used. Making long repeated measurements of the dynamics of complex mechanical properties of drying drops by DDT [55, 56] slow periodic fluctuations of the

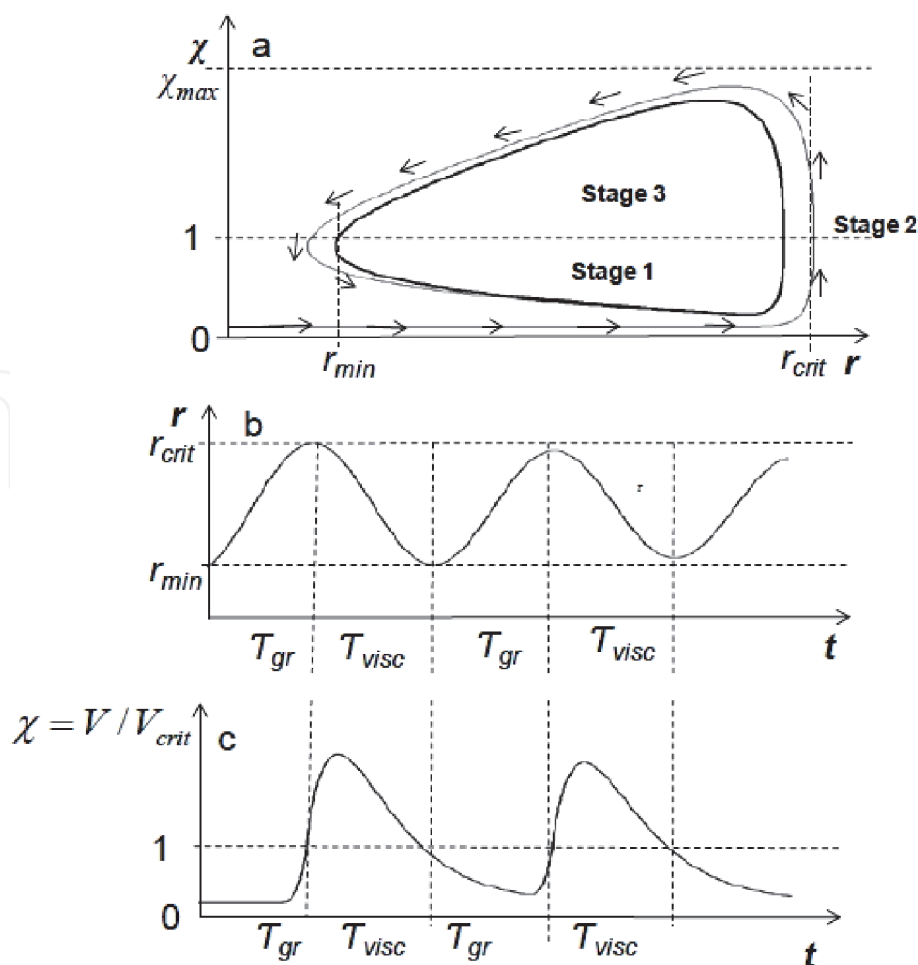


Figure 29. Qualitative description of cyclic changes of variables in the course of growth of water spheres, their destruction and formation of conditions for their new growth: (a) - view of phase trajectories: process begins at the zero point ($\chi = 0$; $r = 0$) and reaches limit cycle; (b) - temporary change of radius of water spheres; (c) - temporary change of velocity of microstreams.

measured parameter were noticed. Additional studies showed that, simultaneously with the above mentioned parameter, there occurred coordinated fluctuations of the surface tension and the character of structuring in drying drops. It had been found earlier that parameters of fluctuations depended on the extent of dilution and did not depend on additional hashing of solution and shielding from external electromagnetic fields [53, 54]. So, it was decided to elucidate the mechanism of such fluctuations in liquid phase. The basis for such a study was, on the one hand, information available on reversible formation of voids inside colloidal dispersions [34–36] and, on the other hand, description of slow fluctuations and inhomogeneity of fluids of different types obtained in the light scattering studies [33, 49, 50]. Moreover, it had been earlier described similar fluctuations of optical density in blood and plasma diluted with physiological saline solution in different proportions [27]. For the liquid phase study, the method of flattened drop and smears of freshly prepared coffee solution were used. The existence of spherical structures in the liquid phase of coffee, their periodical occurrence, growth, destruction and re-emergence, which agreed with fluctuations of physicochemical parameters of the system, was described for the first time. It had been showed morphologically that these spheres are liquid crystal water which forms EZs around hydrophilic colloidal particles. Agglomerates of such crystal water spheres look like voids inside colloidal dispersions under confocal scanning laser microscope. These findings are based on modern and last-century studies of wall layer of water mentioned in the book of Gerald Pollack [45]. We proposed a water-induced mechanism of self-oscillatory

processes in colloidal systems and confirmed the principle possibility of its existence by a simple mathematical model. These data allow a fresh look at the process of aggregation - disaggregation of colloidal particles in the solution. The experiments showed that the growth of water spheres pushes colloidal particles to the borders of the spheres, promotes their crowding and coagulation. On the border of water spheres, the particles form chains (reticular structures) which exist some time in liquid phase after destruction of liquid crystal water shells. Thus, all complex dynamics is controlled by the phase transitions of water – from the free to the bound (liquid crystal) state and back. Osmotic pressure acts as the intermediary messenger and the synchronizer of these transformations in a whole volume of liquid. Actually, these processes are not very sensitive to temperature (unlike the models based on calculation of Casimir forces [61–66]), and do not notably depend on liquid disturbance by hashing. Hashing by a turning of a test tube initiates emergence of streams of liquid with a characteristic size of an order of the size of a test tube (1.5×9.0 cm [53]), when the most part of the brought energy is spent for movement of spheres in bulk. Destruction of water spheres happens at initiation of microstreams of 10-100 μm in size, which correspond to the sizes of the destroyed objects. Osmotic pressure P in accordance with Eq. (3) is proportional to the absolute temperature (≈ 295 K). Possible changing the temperature at a few degrees is negligible to affect the considered processes. For obvious reasons parameters of fluctuations depend on concentration of the components. The described mechanism can explain some phenomena that were not clear before and deserves special research. The authors believe that we deal with a universal phenomenon of undoubted importance for fundamental and applied science. We are sure that our hypothesis will stimulate researchers with other ideas and other tool kits to join this direction of study.

5. Concluding remarks

In this chapter, the authors tried to present their ideas about the structure and dynamics of aqueous microdispersed media, which were developed by them over the course of last 20 years. The authors followed the phase transformations of the protein using the drying drop model; found similar changes in the blood serum of seriously ill people and came to the conclusion that they have a violation of the required proportion between the content of protein and salt components of blood serum; found confirmation of our conclusions in the practical activities of Dr. A.S. Samokhotkiy, who drew the attention to the importance of the problem posed and the prospects of its solution for the drug-free treatment of patients. It has been shown that water and aqueous solutions of salts are also microdispersions. There is no clean water in the world around us. Using instant coffee as an example, we made sure that aqueous dispersions live in their own rhythm, the parameters of which depend on the ratio of the volume of the dispersed phase and the ionic strength of the dispersion medium. These parameters do not depend on the volume and shape of the vessel, as well as on mechanical disturbances. Surfactants reduce the amplitude of oscillations without significantly affecting their phase. In phase with the fluctuations in the mechanical properties of dispersion media, their surface tension and the width of the edge ridge of the drops dried on glass change. The authors associated these processes with the phenomenon of aggregation - disaggregation of the dispersed phase, the elementary unit of which is a hydrophilic microparticle surrounded by a hydration shell of liquid crystalline water. A model of self-oscillatory processes in microdispersed systems, which consistently describes the observed phenomena, was proposed.

The authors regard this work as a stage on the path of knowledge, which must be refined and corrected on the endless path of the development of science.

Conflict of interest

The authors declare no conflict of interest.

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