J Mater Sci (2007) 42:8517–8522
DOI 10.1007/s10853-007-1747-y

Formation of submicron of periodic structure in high-clean suspensions

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Received: 21 September 2006 / Accepted: 4 April 2007 / Published online: 23 June 2007

Abstract Experimental studies have revealed a dependence of the dimension and texture of supramolecular crystals in clean suspensions (the concentration of inorganic admixtures in dry conglomerates less than 0.4×10^{-4} wt.%) on the width of the counter-ion layer around the submicron spherical silica particles. At pH = 7–10, the pinching-out upward of the 0.5 mm narrow crystals is determined by the interaction of the crystal structural units, which present elongated dipoles due to a great width of the counter-ion layers ($\chi r = 2.5$). At pH < 7, the enlargement of the crystals to 3 mm and the absence of the crystals pinching-out upward is reached by the narrowing of the counter-ion layer ($\chi r = 17.6$) and, as a result, a decrease of the dipole elongation of the crystal structural units.

Introduction

Over the last years, the formation of three-dimensional periodic submicron and micron-scaled structures known as supramolecular crystals (SC) attracts a dramatically increased interest. This is related to the investigation of photonic crystals, whose structures have the permittivity modulation with a period close to the light wave-length. These structures offer enormous potential for their application as the systems with suppressed spontaneous emission in the photon energy gap [1–3]. Gemstone opal presents unique natural analogue of these structures, a mono-dispersed spherical silica particles (MSSP) of diameter 150–400 nm being connected into three-dimensional close-packed lattice [4, 5]. Natural gemstone opal is characterized, as a rule, by a block-cellular structure and numerous defects in regular packing of the MSSP. In natural stone the pores between spherical silica particles are completely or partially filled by silica gel, cementing the stone. Such structures do not suit for technical use.

The gravitational precipitation of the MSSP from the alcohol suspensions containing ammonia hydroxide is a common method for the synthesis of periodic structures. According to Alder [6] and Hoover [7], the phase transition of a disorder system of non-interacting spherical particles into the order state occurs when the particle concentration is about 49 vol.%. It was shown in [8, 9] that the phase transition in MSSP suspensions occurs according to the Alder–Hoover model as well. A polycrystalline agglomerate is formed at the bottom of crystallization vessel, and its separate vertical crystallites pinching-out upward are no more than 0.5 mm large. Despite the essential progress in studying the SC crystallization mechanism [8, 9], the main reasons for the formation of narrow crystallites, pinching-out upward, in alcohol-ammonia suspensions, as well as the deviations from regular packing of the MSSP are still unclear.

The structural units (SU) of the supramolecular crystallization in water-alcohol suspensions are negatively charged ionized MSSP (Si–OH$^-$) surrounded by compensative counter-ion diffusion layer (NH_4^+ in our case). These structural units with double electric layer (DEL), when concentrated at the vessel bottom, interact with each other. According to the theory of stability and coagulation of ion-stabilized dispersed aqueous systems (DLVO theory) [10], the periodic regular structures can form at the interaction of charged constrained particles only at a well-defined ratio of

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repulsion and attraction forces between the SU. The correlation between these two forces is defined by the width of the counter-ion layer around the MSSP. The width is a variable quantity and changes according to the negative charge density at the surface of the MSSP. The latter parameter is specified by the concentration and type of the potential-forming electrolyte in solution. These dependences are represented in Debye parameter

$$\chi = (8\pi e^2 z^2 n / ekT)^{1/2}, \tag{1}$$

where e is electrical charge, z and n present the charge and concentration of counter-ions, ε is the permittivity of liquid, and kT is the thermal motion energy. As the width of the counter-ion layer (δ) is defined as $1/\chi$, then the SU diameter in suspension will be presented as $d_{su} = d_0 + 2/\chi$ (d_0 is MSSP diameter). The $r/\delta = \chi r$ relation is the main structural characteristic of the SU [8, 9].

It was shown in [11], besides the potential-forming electrolyte (NH_4OH in our case), soluble salts in the dispersed medium significantly influence the χr value. By the data of [8], a block-cellular texture of gemstone opal is formed exactly due to a high concentration of soluble salts in natural solutions. At present the real contribution of soluble salts to the SC crystallization in water-ammonia suspensions is unknown, because the investigations have been made so far without the control of the soluble salts concentration in suspension.

This work presents the results of studies of the main processes of supramolecular crystallization (the SU precipitation rate, the crystallization rate, textural peculiarities of crystallites) at pH = 5–10 in high-clean suspensions (the concentration of inorganic admixtures in dry conglomerates less than 0.4×10^{-4} wt.%).

The high purity of suspensions allowed us to investigate the peculiarities of the SC crystallization in a wider pH range of suspension. The crystallization at pH < 7 was not studied so far, because, in acid medium, the MSSP surface gradually loses the charge, the suspension becomes unstable and coagulates at a slight increase of the salts concentration in solution. The SC crystallization in this pH range is interesting, because it proceeds at maximal χr value.

Experimental

The supramolecular crystallization was conducted in the alcohol suspension with the MSSP diameter of 230 ± 5 nm. Under gravitation the dispersed system in vessel is divided into four visually distinguishable layers: (1) clear dispersed liquid; (2) white layer of SU precipitates of low concentration; (3) white dense suspension of high concentration (‘‘dense liquid’’ [6, 7] with the SU concentration close to critical value C_{cr} = 45–50 vol.%); (4) the layer of supramolecular crystals with the SU concentration equal to C_{cr} in the growth interface. The crystallization begins at the vessel bottom, with subsequent upward movement of the growth front. If the MSSP diameter lies in the region of the visible light wavelengths, the fourth layer is seen by its bright colors, appearing due to the light diffraction on the ordered SU layers. The crystals color depends on the period size of their lattice, which is defined by the d_{su} value.

The MSSP suspensions were prepared according to Stober and Fink method [12] by hydrolysis of tetraethoxysilane $Si(OC_2H_5)_4$ in the ammonia-containing water solution of ethanol with pH = 9. The ethanol was twice sublimated, and tetraethoxysilane was twice purified by method of [13]. We used an extra pure ammonia solution with the admixture concentration less than 1×10^{-3} wt.%. The MSSP diameter, determined from scanning electron microscope images, was 230 ± 5 nm.

The counter-ion width ($1/\chi$) was determined from the SU diameter value, which was defined through the expression $d_{su} = 0.6124(\lambda_{max}/n)$ [14], where λ_{max} is maximal wavelength of the light diffracted on the regular SU layers in the crystals; n presents the refraction coefficient of silica particles.

For approximate calculation of d_{su} we use $n = 1.41$, taking into account that the space between the particles in the SC is filled with liquid medium. λ_{max} was determined visually by the colour of the SC in transmission light. At pH = 7–10, the colour of the SC is red-purple, which corresponds to the λ_{max} = 770 nm. At pH = 6.5–5, the colour of the SC is green-yellow, which corresponds to the λ_{max} = 560 nm. The order of calculated $1/\chi$ values (Table 1) was in agreement with the values in [15], obtained by the Eq. 1.

The pH value of the alcohol suspension was increased by the addition of NH_4OH to the prepared MSSP suspension. The decrease of pH value to 7 was achieved by the precipitation of the MSSP at 1/3–1/4 height of the vessel with subsequent evacuation of clarified liquid above the dispersed medium and dilution of the suspension by pure ethanol up to the initial volume. The procedure was repeated until the required pH value is obtained. Acid medium of the suspension was obtained by the acidification of neutral suspension by hydrochloric acid. We succeeded in preparing the solutions acidified to only pH = 5. At higher acid concentration in the suspension the SU lost their discontinuity and quickly transformed to lumpy precipitates.

The SU precipitation rate (V_p) in suspensions having various pH was determined simultaneously in graduated cylinders (25 cm^3) by the movement of the boundary between clear dispersed medium and white suspension

Table 1 The characteristics of supramolecular crystals (SC) and structural units of crystallization (SU) at different pH of suspension

pH of suspension	Width of SC (mm)	Colour of SC	λ_{max}, nm	d_{su}, nm	$1/\chi$, nm	$\chi \times 10^{-5}$, cm^{-1}	χr
7–10	0.1–0.5	Red-purple	770	334	52	1.9	2.4
6.5–5	0.5–3.0	Green-yellow	560	243	6.5	15.3	17.6
4.5	Aggregation of particles, quick precipitation of SU aggregates (2–3 h)						

along the scale points till the end of the precipitation. The SC crystallization rate (V_{cr}) for all suspensions was estimated by the movement of the phase boundary polycrystalline sediment—white concentrated suspension (''dense liquid''), observed with horizontal microscope. The boundary separated the vertical brightly colored pillar crystals and white concentrated suspension. The metering was made once a day. In this work we present the typical values of V_p and V_{cr}, obtained after the SU sedimentation was completed.

The silica concentration in the solutions for all suspensions was 4 vol.%. All the MSSP growth and supramolecular crystallization experiments were conducted at 24 ± 5 °C in the air bath.

Results and discussion

The SU characteristics and maximal wavelength of the visible light diffracted on the periodic SC lattices, formed at different pH values, are given in Table 1. At pH = 7–10, the SU diameter remains constant and corresponds to 340 nm (red-purple color of the crystals). At pH = 6.5–5, the wavelength of diffracted light shifts to the short-wave region by 210 nm. The crystals become green-yellow, i.e. at equal MSSP diameter the SU dimension decreases appreciably in acid medium and corresponds to 243 nm.

The V_p and V_{cr} values are constant within the whole alkaline range and increase only in acid medium (Fig. 1). The polycrystalline conglomerate changes from thin crystallites, pinching-out upward at pH > 7, to larger unbroken single crystals in acid conditions (Fig. 2). The ordering of the SU hexagonal packing in acid medium is more perfect than that in alkaline medium of suspension (Fig. 3).

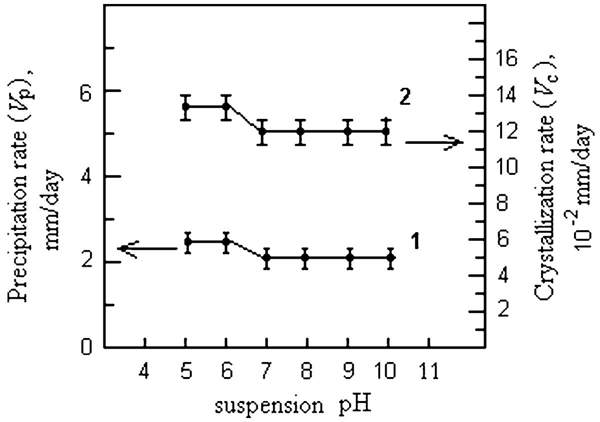


Fig. 1 The dependence of the SU precipitation rate (1) and the crystallization growth rate (2) on pH of the MSSP suspension (for the particles diameter 230 ± 5 nm)

Consider the peculiarities of the SC crystallization in alkaline and acid medium.

Alkaline medium of suspension (pH > 7)

According to DEL theory, the increase of the concentration of potential-forming electrolyte (NH_4OH) in suspension must lead to an increase of Debye parameter (Eq. 1) and, accordingly, to a decrease of the width of counter-ion layer around the MSSP. In the work [8] this factor is used to explain the appreciable changes in V_p and V_{cr} at pH = 7.5–10. In presented experiments at pH = 7–10 we do not observe the correlation between the χr value and the concentration of electrolyte: the V_p and V_{cr} values are constant in the whole alkaline range (Fig. 1). The color of the crystals at the vessel bottom also remains the same

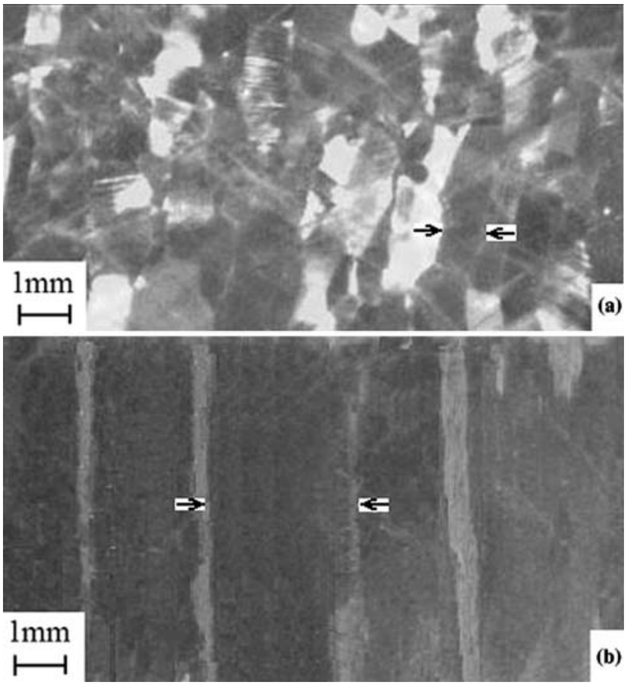


Fig. 2 Texture of polycrystalline precipitates, formed in suspensions with the particles diameter 230 ± 5 nm at: pH = 9 (**a**); pH = 5 (**b**). Arrows indicate single SC

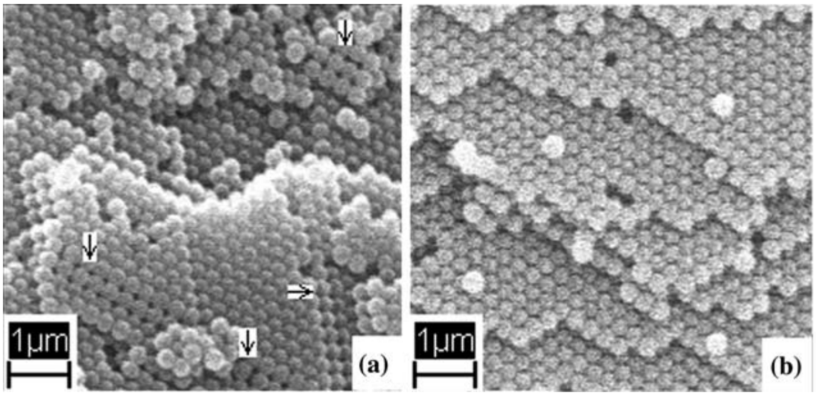
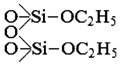


Fig. 3 SEM images of periodic layers in SC, formed in suspensions at: pH = 9 (**a**), arrows indicate the main defects of hexagonal packing; pH = 5 (**b**)

(red-purple) (Table 1). This is possible only at fairly close χr values.

Consider in detail the surface of the MSSP, formed in pure ethanol-ammonia suspensions at pH = 9. By the data of [11], the silica particles in commercial ion-stabilized water sols are surrounded by a close 2.4 nm wide counter-ion layer (Huy layer). Such a layer can be formed onto a rather highly charged surface of the particles (more than 2 OH^- groups per 1 nm^2 of the particle, the theoretically possible charge density being 5.5 OH^-/nm^2). An appreciable width of the counter-ion layer around the MSSP (52 nm) indicates to its diffusive character (Shtern layer) and, correspondingly, to a low charge density on the MSSP surface. In the presence of potential-forming electrolyte the ionicity of the particles surface is influenced by the admixtures of soluble salts. According to the data of [11], the increase of the NaCl concentration from 10^{-4} to 10^{-1} N at pH = 9 (with NaOH as potential-forming electrolyte) the OH^- number increases from 0.25 to 1.8 per 1 nm^2 of the silica particle. It should be expected that the charge density at the MSSP surface in the initial suspension will be lower than the presented minimal value (0.25), because of low dielectric qualities of ethanol and the use of weak electrolyte—NH_4OH as a stabilizer. Therefore, a high purity of the ethanol-ammonia suspension determines a low charge density on the MSSP formed at pH = 9. The question arises what is the reason for the permanency of ionicity of the MSSP surface and, correspondingly, of the width of diffusive counter-ion layer around the MSSP at different ammonia concentrations in suspension.

Experimental dispersed systems are characterized by a high stability in the whole alkaline range. At repeated crystallization and subsequent dilution of the SC by the dispersing solution the structure units of crystallization become discrete, forming a dispersed system with the properties of the initial suspension. At low ionicity of the MSSP surface one could expect a steric factor to govern the SU stability in suspensions [11]. In this case, the contact between the particles is prevented by the inert compounds, for example hydrocarbon chains, bounded to the particles surface. Because of incomplete hydrolysis of $Si(OC_2H_5)_4$ at the MSSP surface, the latter is covered by the alcohol radicals to some extent [5]:



The high extent of the surface etherification of the MSSP, prepared in pure alcohol-ammonia solutions, is confirmed by the fact that, at thermal treatment of dry conglomerates of crystallites in hermetic vessels at 300–500 °C, the MSSP surface is carbonized during the pyrolysis of residual ethoxy-groups, which leads to the intensive nigrescence of the samples at full depth.

In the work [16] it is has been found that the oxygen atoms in the surface ensembles $Si–OC_2H_5$, screened by the bent groups $–C_2H_5$, are inaccessible for several chemical reagents due to steric factor. Thus, the permanence of the SU structural characteristic ($\chi r = 2.4$) in the whole alkaline range of crystallization may be caused by the screening of the MSSP surface by the hydrocarbon chains, preventing the interaction with dispersed medium at the change of NH_4OH concentration. The obtained results confirm the data of [11, 17] about some limitations of the application of DEL theory for a number of liquids.

The results, obtained at the SC crystallization in high-clean alcohol-ammonia suspensions, show that, in such conditions, the SU are highly stable particles with constant charge density of the surface and constant large width of the diffusive counter-ion layer around them in a wide range of pH from 7 to 10. Therefore the concentration of the potential-forming electrolyte in such suspensions cannot be used as a control factor of the SC texture.

Acid medium of suspension (pH = 5–6.5)

The shift of the crystals color to the short-wave region (green-yellow) at the transition to acid medium is related to a significant decrease of the width of the counter-ion layer around the MSSP to 6.5 nm (Table 1). This value approaches the width of counter-ion Huy layer at a high ionicity of the silica particles surface in alkaline medium (2.5 nm) [11]. The decrease of viscous braking of the less polarized SU with $\chi = 17.6$ at the downward movement in the dispersed medium is revealed by the increase of V_p (Fig. 1). However, the reason for such a drastic decrease of the width of the counter-ion layer around the MSSP in acid medium principally differs with the formation of Huy layer at a high charge density on the particles surface in alkaline medium.

It is known [11] that, with an increase of acidity of colloidal dispersed systems, the ionicity of surface groups Si–OH decreases, the micelles lose negative charge and tend to zero charge, which is achieved at pH = 2. The interaction energy of the particles with uncharged surface approximates the first minimum on the potential curve of pairwise interaction of the particles (Fig. 4), which is evidenced by the particles flocculation leading to the formation of shapeless aggregates. In the presented experiments the loss of the SU aggregative stability at acidification of the suspension proceeds far before the achievement of zero charge on the particles. The MSSP flocculation at $d_0 = 230$ nm was observed already at pH < 5 (Table 1). At acidification of neutral suspension the increase of ionicity of the silica particles results from the interaction of acid proton and hydroxyl group on the MSSP surface: $H^+ + OH^- = H_2O$. Simultaneously the counter-ions remained on the MSSP surface to pH = 7 bind together: $NH_4^+ + Cl^- = NH_4Cl$. Thus, the decrease of the width of the SU counter-ion layer in acid medium is caused by its destruction at simultaneous decrease of the surface ionicity. The state of such dispersed systems may be characterized as a metastable aggregative stability, which is easily disturbed at slight changes of the suspension purity and other unfavorable conditions.

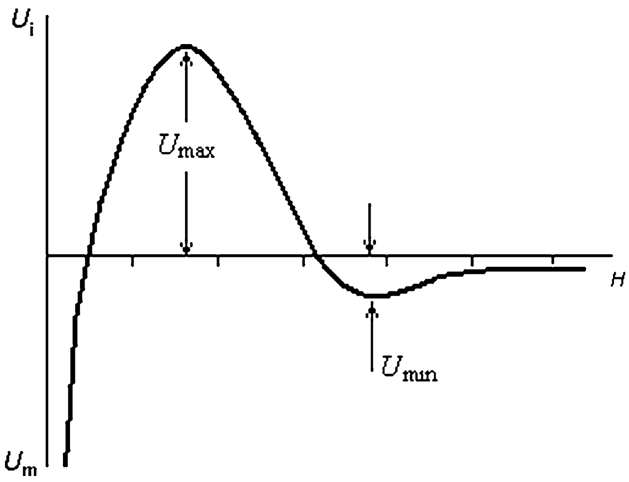


Fig. 4 Potential energy of the interaction of two colloidal particles versus the distance between them (*H*)

Texture of the crystals

In the conditions of terrestrial gravity the periodic systems are formed under the influence of two main forces: the external gravitational forces and the internal electrostatic repulsion (U_i) and molecular attraction (U_m) between the SU [8–10]. We do not consider here the role of gravitation onto the crystallization process, which is discussed in detail in [8].

The periodic systems are formed provided that the potential curve of pairwise interaction of the particles contains, in addition to the large repulsion maximum (U_{max}), a secondary minimum (U_{min}) associated with far interaction between the SU (Fig. 4) [10]. The molecular forces of attraction of spherical particles are determined by the equation: $U_m = -Ar/12H$, where A is Hamaker constant, r is MSSP radius, H is the distance between the surfaces of the silica particles. From this formula it is seen that the molecular forces of attraction depend on the distance and, by the data of [10], arise only at $H < r$. In the ‘‘dense liquid’’ layer with SU concentration close to C_{cr} the distance between the MSSP surfaces must exceed 2δ and amount no less than 116 nm, taking into account the 10% liquid layer, displaced out of the ion-solvation sphere at the transition disorder–order. At $r = 115$ nm (MSSP diameter is 230 ± 5 nm) the forces of molecular attraction between the SU are absent or negligibly small. This conclusion is confirmed by the calculations [8] showing that, at $r = 125$ nm and $H = 90$ nm, the molecular attraction energy corresponds to $U_m 10^{15} = -11.6$ mkJ. The energy of electrostatic repulsion of the SU ion spheres, determined in [8] by the formula $U_i = 1/2\varepsilon r\varphi^2 \ln(1 + e^{-\chi H})$ [9], where φ_0 is surface potential of the particles, corresponds to $U_i 10^{15} = 260–270$ mkJ.

The given analysis of the SU interaction energies for alkaline conditions denotes the absence of far interactions in these systems. In this case, the potential curve of pairwise interaction between spherical particles does not contain the second minimum. Therefore, the formation of periodic structures without additional forces, compensating for the low-energy molecular attraction between the SU, is theoretically improbable.

The dipole interaction of the colloidal systems, caused by the mobility of the micelle counter-ion layer, is prevalent in nature [10]. At that, the range of the inductive electric field (U_d) produced by the dipole, is noticeably larger than the range of energy of the particles with rigid DEL. The authors of [9] point to the possibility of appearance of fluctuating momentary dipoles in a concentrated SU layer at high pH of suspension.

The ''dense liquid'' layer in the experimental suspensions does not exhibit even weak opalescence, which could evidence for the appearance of three-dimensional ensembles of several SU with short range ordering. In this layer a spherical form of the SU with the χr value close to 1 will determine a low value for the molecular force of attraction between the particles U_m ($H > r$). The primary fixation of the SU always proceeds first near the vessel wall, which provides along with the vessel bottom two limiting planes. This is evidenced by the first appearance of diffracting zones near the vessel walls, with further spreading across the bottom toward the centre. Such fixation of the first SU near the vessel walls will lead to the shift of mobile diffusive counter-ion layer around the MSSP from the wall to the centre of a vessel. Such fixed elongated SU will already present stable dipoles, inducing the dipole moment μ in adjacent SU ($\mu = Qh$, where Q is the charge of the MSSP surface, h is the range of the possible MSSP shift relative to the SU centre within the ion layer having the width δ [9]). In extreme case the h value tends to the δ value. The energy of interaction of such dipoles is approximated as $U_d = B/\chi r \cdot (Qh)$, where B is aspect ratio which increases along with $\delta = 1/\chi$. The dipoles appeared near the wall will determine further SU interaction, which is no a weak molecular attraction (U_m), but a stronger polarized interaction (U_d).

According to the data of [10], the formation of periodic colloidal systems with elongated dipoles is accompanied by the shift of periodic layers relative to each other. This is because the electrical fields of the SU dipoles in periodic lattices are mutually neutralized, thus defining the total dipole moment of the SC structure to be zero. A quick accumulation of shear defects in the SC, formed during the dipole–dipole interaction between the SU, may result in the formation of narrow crystallites, pinching-out upward, in alkaline medium at the χr values close to 1 (Fig. 2). The polycrystalline precipitates, prepared in alkaline conditions, are thixotropic, i.e. they are easily destroyed at shaking and restored again at their dilution in dispersed medium and recrystallization.

In acid conditions, the minimal liquid interlayer between the MSSP ($\chi r = 17.5$) and low ionicity of the particles surface result in the increase of U_m and the decrease of U_i. Such energetic state of the SU is realized in a rigid fixation of the SU in periodic layers of the crystals. In this case, the polycrystalline precipitates are not thixotropic.

As in alkaline medium, in acid suspension the primary fixation of the SU begins near the vessel walls with further spreading toward the centre. Due to a negligible width of the ion-solvate layer around the MSSP, the SU structure is less polarized and is almost spherical. The ordering of the SU packing in periodic lattices at these pH conditions is probably related to a slower accumulation of the shear and other defects (Fig. 3).

Conclusions

1. At the reconstruction of the mechanism of SC crystallization in the alcohol-ammonia suspensions it is necessary to take into account the influence of soluble salts in the dispersed medium onto the SU interaction.
2. Under the gravitation forces the supramolecular crystallization is realized provided the energy of electrostatic repulsion between the SU is compensated by the molecular attraction and/or polarizing interaction between the SU.
3. The polarizing interaction between the SU is one of the possible factors, which determine the defects formation and the upward pinch of the polycrystalline precipitate in the alcohol-ammonia suspensions. This should be taken into account at the synthesis of matrixes for photonic crystals as well as at preparation of any other periodic structures.
4. The width of the SU counter-ion layer is the main parameter, which controls the SC texture. A significant increase of the width and vertical size of the SC proceeds at $\chi r \gg 1$.

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