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Self-organisation processes in the chemistry of materials

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Abstract. The review concerns conservative and dissipative self-organisation phenomena in those physicochemical systems, whose evolution involves formation of diverse chemically complex products, including functional ceramics, supramolecular compounds, and nanocomposites as well as fractal, template and epitaxial structures. It is demonstrated that the use of nonlinear dynamics approaches facilitates organisation of the reaction zone during the synthesis of materials under nonequilibrium conditions in an optimum manner and that biomimetism and biomineralisation processes open up new prospects for materials design. The bibliography includes 308 references.

I. Introduction

Design of advanced functional and structural materials is a critically important research field.[1] Attempts at employing basic research methods in materials design have long been undertaken. It is sufficient to remind readers of an approach proposed by the author of this review nearly two decades ago; this strategy was then successfully applied to the chemistry of magnetic dielectrics and semiconductors as well as materials with ionic and electron-ionic conduction.[2,3] However, modern chemistry of materials is still characterised by the predominance of intuitive approaches and experimental screening techniques that underlie the combinatorial chemistry (the development of this research field is associated with the development of fast screening techniques).[4–6]

Methods for the design of advanced materials can be conventionally divided into two groups:

— techniques involving variation of the composition of the precursor system and

— methods involving variation of processes (including synthesis) and conditions for subsequent treatment (*e.g.*, heat treatment).

Often, the role of the temporal evolution of a system during the preparation of a certain material becomes so important that one should use the *TTT* (Temperature – Time – Transition) diagrams.[7,8] In particular, this approach has proved itself in determining the nature of changes in the critical temperature (T_c) of the neodymium/barium cuprates that are characterised by very low rate of cation ordering.

While on the subject of a material's structure, one should keep in mind different levels of structural organisation of matter, from the structure of a unit cell to the polycrystalline structure exhibiting specific defects including domain boundaries, pores and cracks (Fig. 1). At the same time, interrelations between different levels of structural organisation of a material should also not be overlooked, though this does not imply the possibility of controlling the situation. The diversity of manifestations of synergism as an effect of co-operative behaviour of certain elements (such elements exhibit a chaotic behaviour at the microlevel) of a complex system is often analysed in the framework of the nonlinear dynamics paradigm.[9–12]

II. Nonlinear behaviour of physicochemical systems during the preparation of materials

Considering the chemical complexity of a precursor system, one should take into account the nonlinear character of the physical response. The nature of this nonlinearity is not known with certainty; it is determined by both thermodynamic and kinetic factors.[2,3,13,14] Methods for improving the properties of a material by successively complicating its chemical composition and structure are not necessarily efficient. This can be exemplified by the dependence of the superconducting transition temperature (critical temperature) of cuprates belonging to the $HgBa_2Ca_{n-1}.Cu_nO_{2n+2+x}$ homologous series on the number of CuO_2 layers (Fig. 2).[15]

When preparing homogenenous chemically complex products, the best precursor systems are either true or colloidal solutions, melts or gaseous mixtures with the highest possible (ideally, atomic or molecular) degree of mixing of the material-

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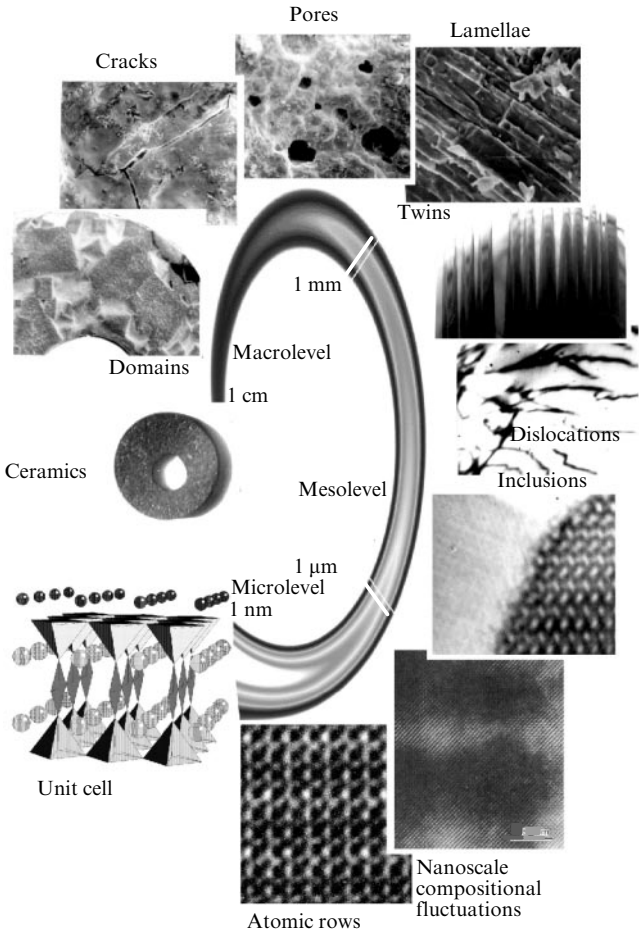


Figure 1. Structural levels of a material (bulk ceramics). Macroscopic level (10^{-3}–10^{-2} m): pores, cracks, domains, ceramics; mesoscopic level (10^{-6}–10^{-3} m): inclusions, dislocations, twins, lamellae; microscopic level (10^{-10}–10^{-6} m): the unit cell, atomic rows, nanoscale compositional fluctuations. Ceramics is the visual appearance of a sample of the high-temperature superconductor $RBa_2Cu_3O_x$; domains are macroscopic pseudo-single-crystal regions of the superconductor; cracks are macroscopic cracks developed as a result of thermal shock; pores are channels formed as a result of exchange of the superconductor matrix with oxygen from the gaseous atmosphere during the melting–crystallisation process; lamellae are intergrown plate-like crystallites; twins are defects formed as a result of oxidation of the superconductor; dislocations are a network of dislocations; inclusions are associated with boundaries between the particle of the normal phase (Y_2BaCuO_5) and the superconducting matrix; nanoscale compositional fluctuations are microscopic inhomogeneities of the chemical composition of the superconductor; atomic rows are the rows of atoms constituting the unit cell of the crystal along a specified direction; and the unit cell is a fragment of the crystal structure.

forming components. However, even in these cases there are basic obstacles associated with the incongruence of virtually all multicomponent systems (different compositions of the coexisting phases).[16, 17] Hence one should carry out thorough studies of phase equilibria and use equilibrium or quasi-equilibrium processes. The field of application of such processes is of crucial importance but limited to the growth of perfect single crystals from solutions and melts[18] and the preparation of thin films by the chemical vapour deposition technique.[19]

Another approach, which seems to be the simplest one, involves the use of individual oxides or salts of oxygen-containing acids as precursors. Mixtures of these compounds are transformed into the target product as a result of solid-phase reactions.[13] For

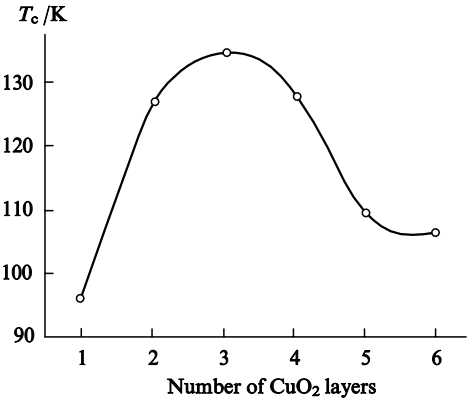


Figure 2. Superconducting transition temperatures (critical temperatures) of cuprates $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ plotted *vs.* the number of CuO_2 layers.[15]

instance, magnetic ceramics based on yttrium orthoferrite are synthesised by the reaction

$$\frac{1}{2}Y_2O_3 + \frac{1}{2}Fe_2O_3 = YFeO_3\,.$$

The small driving force of this and similar reactions ($-\Delta G^\circ_{1273\,K} \approx 20-30$ kJ mol^{-1}) and low solid-phase diffusion coefficients ($D < 10^{-12}$ cm^2 s^{-1}) preclude preparation of single-phase chemically complex oxides and the more so highly homogeneous products. Diffusion limitations are usually eliminated by using intermediate grinding levels (degrees of mixing) or by increasing the reaction temperature; however, both methods give rise to some additional difficulties. These are uncontrollable contamination of the product with particles of the abraded container in the former case and evaporation of the most readily volatile oxide components (*e.g.*, ZnO and alkali metal hydroxides), dissociation of readily reducible oxides (CuO, Fe_2O_3) and formation of non-stoichiometric (first of all, with respect to oxygen) complex phases of uncontrollable composition in the latter case.[20]

The driving forces of solid-phase processes can be not only the chemical potential gradient, as in the case of the reaction of yttrium orthoferrite formation

$$\Delta G^\circ = \Delta\mu^\circ = \frac{1}{2}\Delta\mu_{Y_2O_3} + \frac{1}{2}\Delta\mu_{Fe_2O_3}$$

but also the temperature and pressure gradients (for oxides, the gradient of the partial pressure of oxygen is most often used), as well as the mechanical strain (in compaction and sintering of ceramic powders) or electrochemical potential gradients (in solid-phase galvanic cells). Often, these forces exhibit synergistic effects. For instance, intense sonication of heterophase systems gives rise to cavitation due to the simultaneous appearance of very large temperature and pressure gradients and mechanical strain.[21]

Nonequilibrium processes can occur in both isolated (or closed) and open systems, which differ from one another in character of response to external conditions and in evolution pattern. For any system, the total change in entropy can be written as the sum

$$dS = d_eS + d_iS,$$

where d_eS is the entropy change due to exchange with the environment and d_iS is the entropy change within the system under study (for the nonequilibrium state, this term is always positive).

For an isolated system (no exchange of matter and energy with the environment), one has $d_eS = 0$ and $dS = d_iS > 0$. Hence, the spontaneity of a process in the isolated system is governed by the trend towards an increase in the system's entropy, which reaches

its maximum value in the equilibrium state. In other words, the evolution of an isolated system causes the disappearance of the reasons that gave rise to the evolution.

Irreversible processes in isolated systems include mixing, interdiffusion (in the case of, *e.g.*, diffusion welding) and poisoning of ultrapure substances. Strictly speaking, perfectly isolated systems are a kind of idealisation, so we can deal with a certain extent of approximation in such systems.

If isolated systems can exchange energy with the environment (no mass transfer), the spontaneity of processes in such systems is governed by the trend towards a decrease in the Gibbs free energy

$$\Delta G = \Delta H - T\Delta S < 0.$$

For this relationship to hold, the entropy contribution, $T\Delta S$, must be larger than the enthalpy term ΔH. This means that raising the temperature of any isolated system from 0 K causes thermodynamically unavoidable defect formation processes involving different types of disordering [22, 23] and the appearance of nonstoichiometry in binary and more complex crystals with mainly ionic bonding.[24] Here, the source of the increase in entropy is of no concern: it can be the free surface, dislocations or point defects. Depending on particular experimental conditions, the growing crystal acquires those defects that provide a maximum increase in entropy at the lowest energy expenditure.

For instance, hematite α-Fe_2O_3 dissociates to give a black substance, magnetite (Fe_3O_{4+x}), on heating to 1300 °C in air. This transformation is due to a substantial increase in entropy owing to structural (cation vacancies) and electronic disorder intrinsic in magnetite. However, the undesired dissociation can be inhibited by adding titania to hematite. The lattice of the iron titanate (or titanium ferrite) thus obtained can be so easily disordered on heating (in this case, ΔG decreases) that dissociation becomes thermodynamically unfavourable.

Being guided by their intuition, materials scientists have long employed the method of chemical and structural complication of materials in order to improve their chemical stability and mechanical strength. Based on the aforesaid, it becomes understandable why sintering of highly pure polycrystalline alumina does not result in transparent ceramics irrespective of the duration of heating. The reason is that internal pores, intercrystallite boundaries and dislocations are a source of the disorder, which provides a minimum value of the Gibbs free energy. However, transparent yttria-based ceramics were prepared by doping Y_2O_3 with zirconia and thus producing heterovalent defects (the sources of increased entropy). Doping causes formation of a structure with high concentration of point defects (the source of additional disordering).[14]

Taking into account the systems' trend towards a minimum Gibbs free energy and using the equivalence principle of entropy sources, it is an easy matter to understand why a perfect single crystal is thermodynamically unstable and spontaneously tends to acquire defects (formation of dislocations, adsorption of impurity atoms from the environment) on heating provided that no defect structure relevant to the operating characteristics of the material was designed artificially. Clearly, the higher the quality of a single crystal, the more pronounced its ability to spontaneously develop dislocations, form domain structures and adsorb impurity atoms.

Based on the above-mentioned considerations, one can explain such seemingly paradoxical phenomena as an increase in the rates of solid-phase reactions in the presence of a chemically inert component or a decrease in the very small thermal expansion coefficient of quartz upon doping with titania.

An abnormally large jumpwise increase in entropy is observed in some salts and salt-like systems due to a polymorphous transformation giving rise to high ionic conductivity. Noteworthy is that the entropy jump accompanying the solid-phase transformation is comparable with and sometimes greater than the change in entropy upon melting of the crystal. For instance, the transformation of Li_2SO_4 into the highly conducting α-modification at 850 K is accompanied by a jumpwise increase in entropy $\Delta S = 31.9$ J (mol K)$^{-1}$ [*cf.* $\Delta S = 6.7$ J (mol K)$^{-1}$ for melting of Li_2SO_4 at 1130 K]. The substantial increase in entropy is associated with disordering of one sublattice in the crystal structure, which goes to the 'quasi-liquid' state.[25]

Table 1 lists the changes in entropy upon polymorphous transformations and melting of some binary crystals that are used as solid electrolytes or electronic-ionic conductors.

Table 1. Change in entropy upon polymorphous transformations and melting of some crystals.

Crystal	T_{tr} /K	ΔS_{tr} /J (mol K)$^{-1}$	T_m /K	ΔS_m /J (mol K)$^{-1}$
AgI	419	14.5	830	11.3
Ag_2S	452	9.3	1115	12.6
$BaCl_2$	1193	14.4	1233	13.3
LuF_3	1230	20.4	1457	20.8
YF_3	1350	24.0	1428	19.6

Chemically complex crystals (*e.g.*, ferrites, aluminates, manganites and cuprates) having two or more cation sublattices often exhibit the so-called antistructural disorder on heating. In binary crystals this is possible if the atoms of the constituent elements have similar characteristics (Cu – Sn bronzes). The existence of antistructural disorder in superconducting cuprates was proved taking $Nd_{1+x}Ba_{2-x}Cu_3O_7$ ('123' phase) as an example. In this compound, mutual substitution in the Nd and Ba positions can occur despite different stable oxidation states of these elements.[26, 27]

III. Conservative and dissipative self-organisation

As the temperature of an equilibrium or near equilibrium isolated system decreases, some ordering processes called conservative self-organisation [28] occur spontaneously. Though the term 'conservative self-organisation' was introduced in connection with the development of supramolecular inorganic chemistry, it has a much broader sense and covers many physical phenomena, such as melt or solution crystallisation, re-crystallisation upon sintering in polycrystalline systems, martensite transformations, spinodal decomposition and formation of magnetic or ferroelectric domains on cooling of the corresponding materials. Conservative self-organisation can also occur during the solid-phase interaction between, *e.g.*, wüstite and corundum in the reaction

$$FeO + Al_2O_3 = FeAl_2O_4,$$

which is accompanied by a large decrease in entropy, $\Delta S = -17$ J (mol K)$^{-1}$. However, this reaction is irreversible, since iron aluminate dissociates at high temperatures by the reaction

$$FeAl_2O_4 \longrightarrow Fe + Al_2O_3 + \frac{1}{2}O_2.$$

Supramolecular chemistry has two terms, static self-assembly [28] and strict self-assembly,[29] for the ordering processes in isolated systems, which proceed towards minimisation of the Gibbs free energy. Such processes undoubtedly include ion hydration, complexation, clustering and formation of molecular crystals through the van der Waals forces.[28 – 32]

A classical example of static self-assembly in biology is provided by the self-assembly of a DNA double helix. The change in the Gibbs free energy for this process is illustrated in Fig. 3. Other examples of static self-assembly of supramolecular structures can be found in the literature.[33 – 42]

The open systems can exchange matter and energy with the environment. In essence, they provide a case for persistently nonequilibrium systems. The evolution of open systems can be characterised in terms of entropy production (dS_i/dt) and entropy

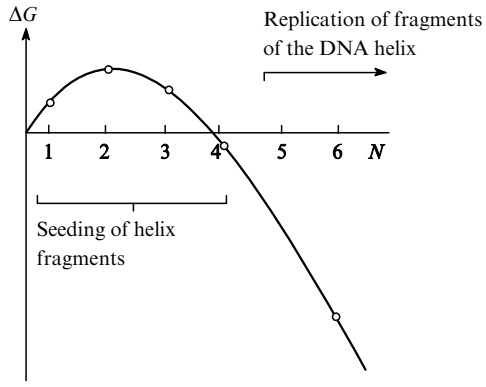


Figure 3. Change in the Gibbs free energy during self-assembly of a DNA double helix.

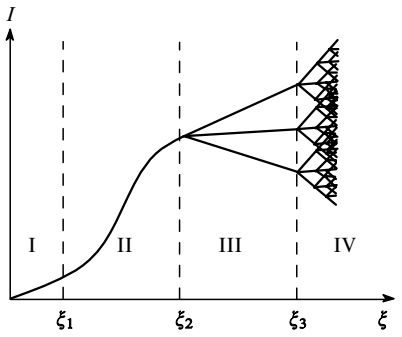


Figure 4. Generalised flux, I, as function of the driving force, ξ, of a process (for details, see text).

flow (dS_e/dt). If the negative entropy flow (entropy release) towards the environment exceeds the entropy production in the system, the total change in the entropy of the open system is negative

$$\frac{dS}{dt} = \frac{dS_e}{dt} + \frac{dS_i}{dt} < 0$$

or, which is the same, the negative entropy (negentropy) of the system increases. As the negentropy exceeds a certain critical value, the formation of new structures (dissipative structures after Nikolis and Prigogine [43]) in the system becomes possible. Dissipative structures are formed due to co-operative interactions between microscopic building blocks in a strongly nonequilibrium macrosystem. The ability of the macrosystem to form various structures is sometimes characterised by exergy (the maximum work, which can be produced by the system on the pathway towards the equilibrium state).[44]

Spontaneous formation and evolution of complex ordered structures in the open systems is called self-organisation while the theory of self-organisation is called synergetics. Having its origin in cybernetics, nonlinear optics and nonequilibrium thermodynamics, synergetics has a strong impact upon the development of modern physics, chemistry, biology, earth sciences, economics, as well as social and political sciences. Synergetics has it own specific lexicon, which includes such concepts as bifurcation, critical state, dissipative structures, feedback, autocatalysis, hysteresis, attractors, scaling, topochemical memory and stochastic and deterministic chaos. Of course, our interest in both synergetics and self-organisation phenomena is limited to their utility in designing advanced materials and technologies.†

Currently, several thousands of communications concerning the use of self-organisation models in solving materials science and technological problems are available. Most of them have been reported during the last five or six years. But admittedly, the equilibrium thermodynamics methodology is still at the frontiers of materials science, especially when one deals with problems concerning high-temperature processes, though most of them occur in strongly nonequilibrium open systems rather than isolated ones. Of course, linear, or additive, thinking is more customary; however, the future may undoubtedly lie with nonlinear models and systems including those used in the field of materials science.[45]

The evolution of an open system can be illustrated by the dependence of the generalised flux I (mass, heat, *etc*.) on the driving force of the process ξ (Fig. 4). The excess Gibbs free energy can act as the driving force in a chemical system. At $\xi = 0$, the system is in the equilibrium state. At small deviations from the equilibrium state (region I), the flux is a linear function of the driving force and the system behaves deterministically, which can be described by the Onsager reciprocal relation. In region II, the $I = f(\xi)$ dependence becomes nonlinear, while transition to region III at a certain critical value $\xi = \xi_2$ is associated with a bifurcation (appearance of several possible pathways of the system's evolution instead of one stable evolution pattern of the process). Here, the system chooses the evolution route by itself but the choice is fluctuation driven.[46] Going to region IV means the appearance of the so-called deterministic or turbulent chaos, which is characterised by an extremely complex structure and is fundamentally different from the stochastic chaos characterising the system in the equilibrium state.

It is possible to formulate at least three necessary (but not always sufficient) conditions for self-organisation in the open systems, resulting in dissipative structures:

— a deviation from the equilibrium state must exceed a certain critical value (*i.e*., the system must be in the bifurcation region);

— the system's volume must be large enough and, in particular, be larger than a certain critical volume in which a necessary number of undamped fluctuations occur; the interaction between these fluctuations creates ordering in the system; and

— the presence of a positive feedback.

At small deviations from the equilibrium state, the system is on the so-called thermodynamic branch of its evolution pathway and its behaviour is a combination of many independent random events. Assuming that such behaviour can be characterised by a certain 'statistically averaged' parameter $\bar{X}_0$ (Fig. 5*a*), one gets that, in accord with the law of large numbers, for a sufficiently large system the deviations from the average value $\bar{X}_0$ are small and normally distributed with the probability distribution $P(X)$. In this sense the behaviour of the system can be treated as deterministic.

As the driving force increases due to the nonlinear behaviour of the system, any possible fluctuations are not damped and, hence, become equiprobable. Therefore, the $P(X)$ distribution near the bifurcation point becomes flattened (Fig. 5*b*). A feature of this state of the system is that any fluctuation can manifest itself on the macroscopic scale, *i.e*., extend to a rather large volume and be undamped for an infinitely long time. At a critical point corresponding to sudden predominance of a certain fluctuation, a minor increase in the driving force of the process is sufficient for the system to make the ultimate choice of a new thermodynamic branch between several alternative branches. Thus, after passing the bifurcation point the distribution $P(X)$ becomes multimodal (Fig. 5*c*), while the choice of the new average value X (new

† To this end, the author of this review initiated the foundation of the Laboratory of Chemical Synergetics at the N S Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, in 1994.

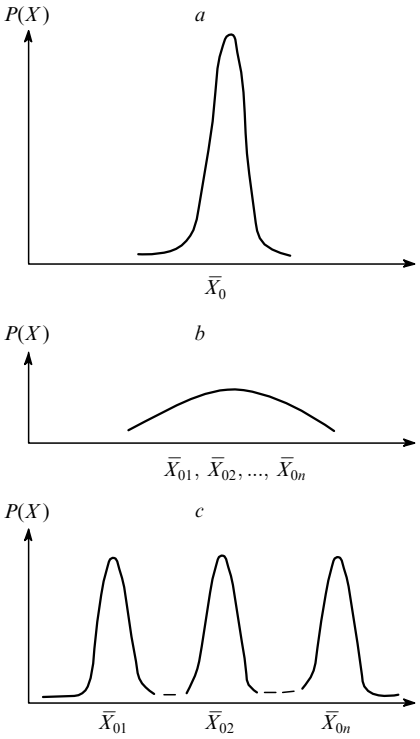


Figure 5. Probability distribution, $P(X)$, at different deviations of the system from the equilibrium state (for details, see text).

thermodynamic branch) from several possible values ($\bar{X}_{01}$, $\bar{X}_{02}$, ..., $\bar{X}_{0n}$) occurs stochastically.

In real systems, such a behaviour can be due to the fact that local nonlinear processes (*e.g.*, an autocatalytic reaction in a small volume or formation of a new solid phase with an ordered crystal lattice) in these systems coexist with the transport (diffusion) processes responsible for different types of exchange between adjacent local volume elements. Were chemical processes to occur in the adjacent local volume elements, they will tend to make the system less spatially homogeneous, while the diffusion processes act in the opposite direction, towards a maximum spatial homogeneity of the system. Clearly, uncorrelated behaviour of the local volume elements (hindered diffusion or no diffusion) results in a random set of combinations of local states. In the case of infinitely fast diffusion (zero response time of the cells) fluctuations are instantaneously damped and disappear. Both limiting cases do not give rise to spatial ordering.

At the same time, both diffusion and local chemical interactions are those essentially nonlinear processes, which are responsible for nonlinear behaviour of the entire system. At a large deviation from the equilibrium state, it can happen that these processes (different in their nature) will have similar characteristic times τ_d and τ_r. In this case both the frequency of chemical fluctuations, $\sim 1/\tau_r$, and the probability of their extension to the adjacent volume elements (relaxation within a given volume element), $\sim 1/\tau_d$, are high.

Thus, under particular conditions the complex systems can go to a certain 'critical state' in which the entire system behaves in a concerted way and chooses a new evolution pathway stochastically.

There is a variety of dissipative structures, *e.g.*,

— spatially nonuniform structures;

— temporal periodic structures (self-sustained oscillations);

— spatio-temporal periodic structures (waves);

— coexistence of several stationary states (bi- and tristability);

— structures with scaling properties (spatial self-similarity — fractals); and

— chaotic dynamic structures.

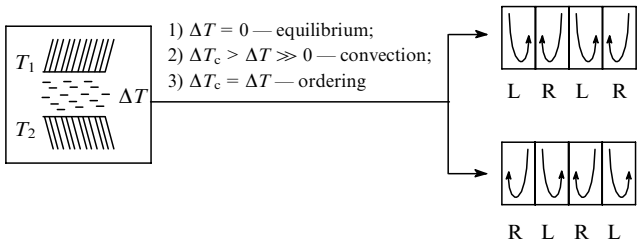


Figure 6. Formation of Benard cells on increasing the temperature gradient.

Dissipative self-organisation can be exmplified by the formation of Benard cells (Fig. 6). As the temperature gradient ($\Delta T = T_2 - T_1$) between horizontal walls of a vessel containing a liquid increases and reaches a critical value corresponding to the bifurcation point, ΔT_c, the type of heat transfer process is changed from convection (chaotic molecular motion similar to Brownian motion) to correlated molecular motion in microscopic fluid cells. The molecular motion occurs in a concerted way by clockwise (R) or couterclockwise (L) rotation. Formation of one of the two dissipative structures shown in the right part of Fig. 6 occurs as a random event as a result of the system's choice. A further increase in ΔT causes destruction of the cell structure and the appearance of turbulent chaos.

This example shows that diffusion, viscous flow and heat transfer, which disorder simple linear systems, can be 'architects of ordering' in nonlinear systems. Numerous examples of dissipative self-organisation in various open systems have been considered in monographs.[47–49] Pioneering observations of self-organisation in physicochemical systems date back to 1828. At that time, Fechner discovered spontaneous oscillations of the electrochemical potential of iron in nitric acid as a result of alternating passivation and depassivation processes (Lillie wires).[50] The best example of self-organisation in homogeneous chemical systems is undoubtedly provided by the Belousov–Zhabotinsky redox reaction, *i.e.*, oxidation of citric (or malonic) acid by potassium bromate in the presence of cerium(III) sulfate.[51,52] This is a very complicated reaction, though visually it appears as a simple oscillating process involving a change in the colour of a solution. According to calculations, changes in the rate constants for the reaction stages by infinitesimal fractions of per cent can cause radical changes in the character of the process at the microlevel. However, under any conditions the most important is the self-oscillation stage, which can be tentatively described by the following equation:

$$HBrO_2 + BrO_3^- + 3H^+ + 2Ce^{3+} \longrightarrow 2HBrO_2 + 2Ce^{4+} + H_2O.$$

Interestingly, pure temporal structures (self-sustained oscillations) can undergo transformation into spatio-temporal ones after some time.

It was Ostvald who contributed largely to the understanding of the energetics of oscillating chemical reactions.[53–55] He generalised extensive experimental information accumulated by the early 20th century, including the data on famous Liesegang rings, dissolution of chromium in acids with oscillating character of H_2 liberation and on periodic decomposition of H_2O_2 on a mercury surface. Some monographs[56–58] provide a rich source of information on recent studies of oscillating reactions. Returning to the problems of materials science, it should be noted that such important properties as the plasticity and yield of materials cannot be adequately described in the framework of the equilibrium methodology. Fracture of a mechanically loaded material is always preceded by ordering of planar defects and formation of dislocations in the region to be fractured. For instance, applying a periodic load to a metal rod causes formation of dislocation packets, which are ordered in some way.[59]

Mechanical fracture of a material can be treated as a consequence of a critical transition (bifurcation) from the elastic

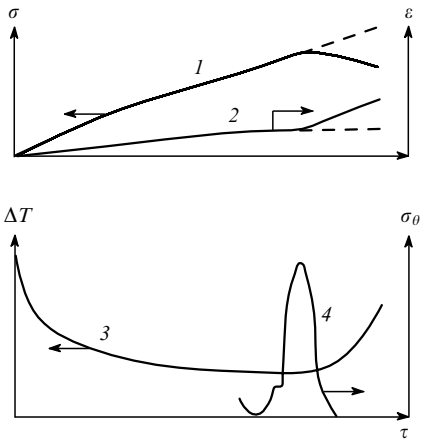


Figure 7. Strain (*1*), stress (*2*), temperature (*3*) and acoustic radiating capacity (*4*) of a mechanically loaded sample as functions of time.

deformation to the plastic deformation regime under the action of a rather heavy external load acting as the driving force of the process. Figure 7 presents the plots of the strain, stress, temperature and acoustic radiating capacity of a mechanically loaded sample constructed *vs*. time. Extrema or singularities in all the plots correspond to the critical point σ_θ. It should be noted that the maximum value of the acoustic radiating capacity at the critical point corresponds to ordering of defects in the sample. Moving the bifurcation point towards the heavy load region favours improvement of a material's strength. For instance, it was found that the doping of metals with zirconia causes a shift of the point corresponding to transition from elastic to plastic deformation due to the fact that ZrO_2 experiences a structural phase transition accompanied by heat release under load.[60]

Of considerable interest are chemical vapour deposition (CVD) processes under strongly nonequilibrium conditions. Figure 8 presents micrographs of ordered structures formed using the CVD technique at high gas flow rates.[61]

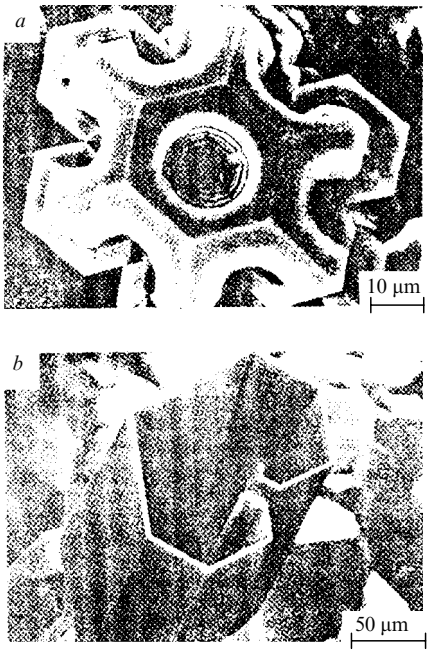


Figure 8. Micrographs of ordered structures formed using the CVD technique at high gas flow rates.
Crystals: Cr_3Si (*a*) and CrB_2 (*b*).

Self-organisation processes also include a class of phenomena accompanying shock-compression induced crystallisation of metastable solid phases. Researchers at the I M Frantsevich Institute of Materials Science (National Academy of Sciences of Ukraine, Kiev) elaborated some methods for creation of strongly nonequilibrium conditions during the formation and quenching of metastable phases.[62] Crystallisation in the presence of strong temperature and pressure gradients allowed the obtention of crystalline modifcations with lower entropy compared to the samples synthesised under nearly equilibrium conditions.

Solid-phase crystallisation of graphite-like boron nitride $(BN)_g$ under supercritical regime of energy supply causes formation of a new modification, würtzite-like boron nitride $(BN)_w$-II.[63,64] The entropy of the newly prepared compound is lower than that of $(BN)_w$-I,[65] which is formed at lower energy supply rates.

Nonequilibrium crystallisation of diamond from the concentrated vapour phase and plasma is accompanied by unusual phenomena. Synthesis at 4500 °C gives a fine-crystalline cubic modification of diamond (X-ray phase analysis data), which is nearly free from microscopic distortions. Carrying out crystallisation at 4300 °C (this temperature corresponds to the triple point in the phase diagram) leads to a crystalline diamond-like phase containing a large number of microdistortions.[66] Hence, synthesis under strongly nonequilibrium conditions permits a structure with less defects to be obtained.

Most likely, formation of 'whiskers' (needle-shaped single-crystals of superconducting bismuth-containing cuprates with T_c = 100 K), which grow on slow cooling of the starting amorphous phase $Bi_2Sr_2CaCu_2O_x$ in an air stream (Fig. 9)[67] is also governed by self-organisation.

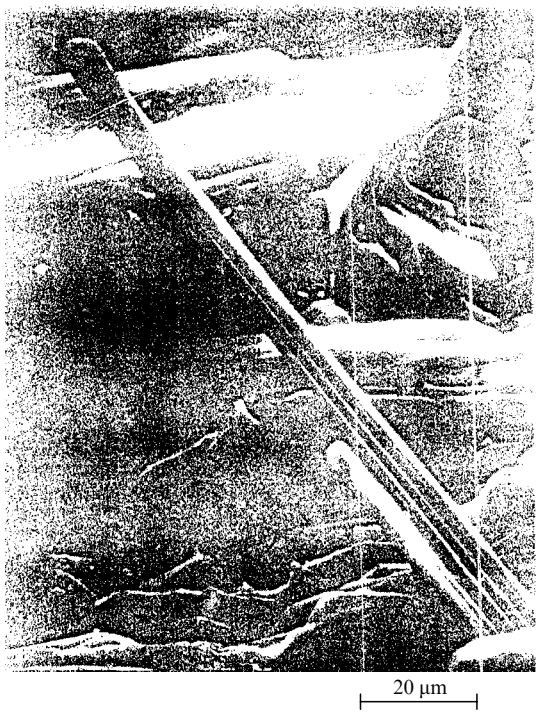


Figure 9. Whiskers of bismuth-containing superconducting cuprates formed on slow cooling of the starting amorphous phase $Bi_2Sr_2CaCu_2O_x$.

IV. Optimum organisation of reaction zone during synthesis of materials

In all stages of its evolution from precursor to the end product, any system exists under thermodynamically nonequilibrium conditions and can be described by some bifurcation pattern with one

or several bifurcation points corresponding to the intermediate phase transformations. It is convenient to consider the evolution of such a system using a model of deterministic chaos.[68,69] This model implies that

— the evolution of a system makes its behaviour increasingly less predictable (*i.e.*, irreproducible);

— the higher the chemical or structural complexity of the system, the shorter the time necessary for transition to the region of indeterministic behaviour; and

— the longer the duration of the process, the more severe the requirements on the initial state of the system (*i.e.*, precursor).

To organise the reaction zone in an optimum manner, one should take into account the following.

1. The higher the complexity of the system, the more indeterministic its behaviour and less reproducible the initial state of the precursor. In this case 'complexity' means not only the chemical and phase compositions but also precursor's reactivity, which is determined by the chemical and heat treatment aspects of its prehistory ('topochemical memory' effect[70]). In this connection the best precursors are provided by compounds with a molecular type of bonding,[71] coordination compounds,[72] solid solutions of double salts (shoenites or alms which are used in, *e.g.*, the synthesis of ferrites[73]) and salt-like products of cryochemical synthesis.[74]

2. The extent to which transformations from precursors to target products deviate from the equilibrium state is in essence the driving force of solid-phase interactions. It affects not only the reaction rates but also their mechanisms and can have both positive and negative effects on the formation of the target product. In particular, the highest homologue in the Bi–Pb–Sr–Ca–Cu–O system, $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$, is usually prepared from Bi_2O_3, CuO, $PbCO_3$, $SrCO_3$ and $CaCO_3$ (a mechanical mixture of these precursors is used). If such a mixture is heated in a gaseous atmosphere at a reduced total pressure, the lead, strontium and calcium oxides are formed under strongly non-equilibrium conditions. Being highly reactive, these oxides readily react with bismuth and copper oxides, thus forming a number of intermediate products simultaneously. Transformation of the products into the highest homologue, $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ ('2223' phase) is a very complicated task and is usually completed only after heating over a period of several days.[75] Decomposition of carbonates at a standard pressure (1 atm) occurs much more slowly, and it is possible to inhibit formation of some intermediates, though in this case low diffusion mobility of cations hampers the formation of the end product ('2223' phase) during reasonably short time intervals. A possible way out is to use efficient methods of activation of the reaction mixture including ultrafine grinding,[76] sonication[77,78] or microwave irradiation.[79–81]

3. Duration of the evolution from precursors to end product. The shorter the evolution, the more easily the deterministic behaviour of the system can be provided and a product with reproducible properties can be obtained. The question arises as to how to shorten the duration of the process taking into account that operation at elevated temperatures leads to bifurcation and to formation of such intermediate products whose crystallisation precludes shortening of the duration of the synthesis. In this case, the use of other methods for activation of the reaction mixture (and, especially, their combination) seems to be more efficient than heating. However, only an empirical approach, *e.g.*, combinatorial chemistry,[82] provides the best way to optimise conditions for treatment of the system.

The efficiency of ultrafast synergistic effects can be clearly exemplified by sintering of ultradispersed ceramic powders of oxide–oxide composites $Al_2O_3-Y_3Al_5O_{12}$ using a press that furnished an increase in pressure on passing pulsed electric current (up to 2000 A) with millisecond-range pulse durations. Sintering was completed after several minutes, resulting in ceramics with rather high density and very narrow crystallite size distribution centred at the size typical of the precursor powder.[83]

4. Bifurcation transformations, which occur during the evolution of a system and manifest themselves as formation of intermediate decomposition products in the reaction zone, should be eliminated, whenever possible. This is all the more important in those cases where such products are formed as readily crystallisable phases characterised by low diffusion mobility of components. This is possible if the phase diagram allows decomposition of the system into some components, which then interact to give the target product. 'Linear' synthesis of superconducting cuprates from copper-free precursors and copper oxide provides a good example of the efficiency of this technique. It was found that the phases $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $Bi_{1.7}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+x}$ can be efficiently prepared using mechanical mixtures of CuO with $Bi_2Sr_2CaO_6$ (Fig. 10) and $Bi_{1.7}Pb_{0,4}Sr_2Ca_2O_{7.35}$, respectively.[75,84]

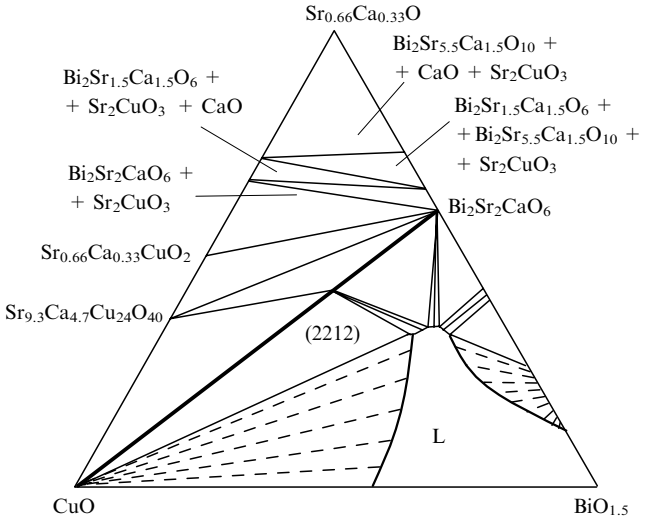


Figure 10. Decomposition of quasi-ternary system $CuO-BiO_{1.5}-Sr_{0.66}Ca_{0.33}O$ along the $CuO-Sr_2CaBi_2O_6$ direction.[75]

In principle, the reaction zone can be organised in such a way that both the precursor and intermediate reaction products lying on the pathway of the figurative point of the system during its evolution are X-ray amorphous and, hence, the formation of a crystalline end product is the first bifurcation. Particular methods for practical implementation of such a process depend on the target oxide products or materials (both of them are chemically complex systems) and, in particular, on the differences between the thermodynamic parameters of the constituent oxides. If these differences are rather large (the most often case), amorphisaton of the precursor and intermediate decomposition products is achieved by quenching oxide melts (*e.g.*, preparation of whiskers[85]) or by freezing of aqueous salt solutions of the material-forming elements (sulfates, nitrates, acetates) followed by thermal decomposition under optimum conditions.[74]

5. Deterministic evolution of a system can be organised using templates (including seeds) in the form of perfect crystals of the oxide product (bulk ceramics) or under conditions that provide epitaxial film growth (substrate with optimally matched structural parameters). An example of a perfect substrate for the growth of perfect high-temperature superconducting films is provided by $NdGdO_3$ single crystals whose parameters are close to those of films, including the thermal expansion coefficients.

An original method for preparation of homogeneous microporous SiO_2, TiO_2 and ZrO_2 ceramics has been reported.[86] The technique involves an oil-in-water emulsion and is based on the use of the interface between monodispersed oil droplets and the water phase as a template (Fig. 11).

6. Intense suppression of chaos by interaction based on a feedback requires thorough knowledge of chaotic behaviour of

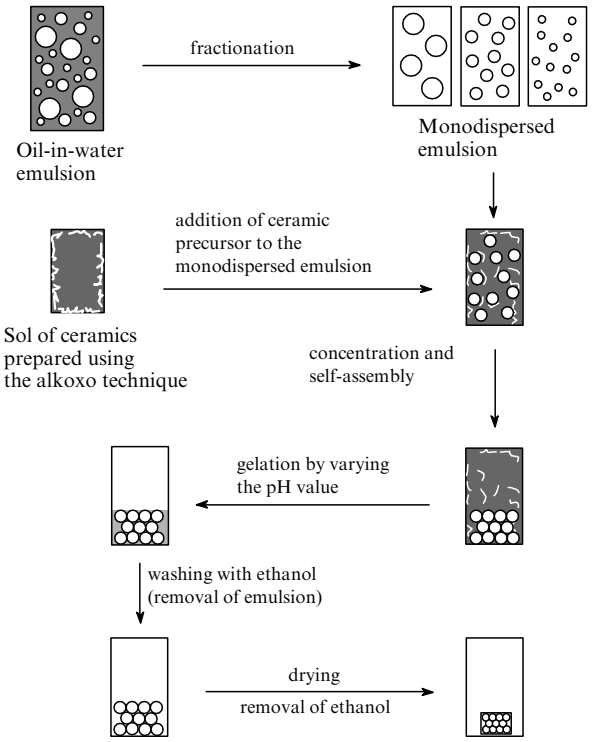


Figure 11. Scheme of formation of homogeneous microporous SiO_2, TiO_2 or ZrO_2 ceramics involving an oil-in-water emulsion and based on the use of the interface between monodispersed oil droplets and the water phase as a template.

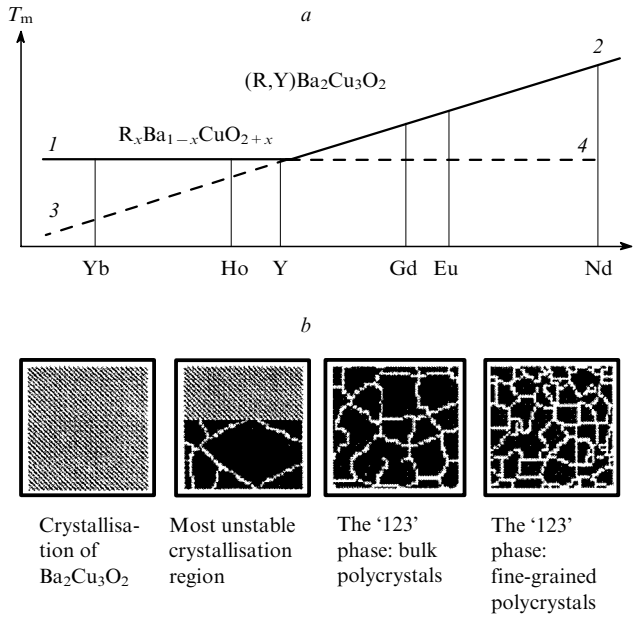


Figure 12. Crystallisation model of REE-doped yttrium-containing cuprates.
(*a*) Crystallisation temperatures of the '$R_xBa_{1-x}CuO_{2+x}$' and (R,Y)$Ba_2Cu_3O_2$ phases doped with different REE at constant dopant concentrations ($V_{REE}/V_Y = 0.1$): stable crystallisation branch of barium cuprate [$T_{cr(011)} \approx$ const] (*1*), stable crystallisation branch of yttrium–barium cuprate [$T_{cr(123)} \neq$ const] (*2*), unstable crystallisation branch of yttrium–barium cuprate [$T_{cr(011)} > T_{cr(123)}$] (*3*) and unstable crystallisation branch of barium cuprate [$T_{cr(011)} < T_{cr(123)}$] (*4*); (*b*) results of computer simulation of crystal morphology corresponding to real experiments.

the system. This method for control of chaos involves both computer simulation and experimental studies of topochemical reactions proceeding in the kinetic, diffusion or mixed regimes.

Controlled suppression of chaos can be achieved using different methods including directed chemical complication of the system. This can be exemplified by the effect of rare-earth element (REE) ions, which partially replace yttrium in the superconducting cuprate $YBa_2Cu_3O_{7-x}$, upon melt crystallisation of this compound.[87] For instance, doping with Yb^{3+} ions results in the formation of giant ribbed crystals of the $BaCuO_2$ phase, which cover nearly the whole surface of the sample. Doping with Eu^{3+} ions causes the formation of rather large square-shaped surface crystallites, while Nd^{3+}-doped samples are comprised of small plate-like crystallites of the (R,Y)$Ba_2Cu_3O_{7-x}$ phase, which form a fine-grained ceramic structure. Finally, studies of both blank samples and samples doped with Ho^{3+} ions revealed the presence of two types of crystallite, *viz*., 'cubic' crystallites of the superconducting phase and 'pyramidal' barium cuprate crystallites.

As can be seen in Fig. 12, doping with Nd^{3+}, Eu^{3+} and Gd^{3+} should favour retention of homogeneity of the system and formation of high-temperature superconducting material with strongly coupled grains. This is due to the fact that the crystallisation centres of the superconducting phase are formed in the 'stable' crystallisation branch of (R,Y)$Ba_2Cu_3O_{7-x}$ solid solutions (line *2*), which is characterised by higher temperatures than the crystallisation temperature of $R_xBa_{1-x}CuO_{2+x}$ (line *4*).

No crystallisation centres of the '123' phase occur upon doping of the system with Yb^{3+} ions. As a result, barium cuprate is formed in the 'unstable' crystallisation branch of solid solutions (line *3*) in the melt region of the system, which precedes crystallisation of the superconducting phase.

In the case of intermediate 'unstable' crystallisation of (Y,Ho)$Ba_2Cu_3O_{7-x}$ the process becomes very sensitive to particular experimental conditions.

This model was substantiated by the results of computer simulation of crystallisation. It was established that

— under certain critical conditions, local interactions in the complex system are responsible for the appearance of new interrelations determining transformation of the evolution pattern of the entire system into a self-organisation regime;

— depending on the initial state of a peritectic melt, its solidification can occur in different manners, thus causing the appearance of different crystallisation regions. Each of them corresponds to a specific morphology of polycrystalline finished material (target product). The most important condition for preparation of high-temperature superconducting materials with high current densities is to provide stable crystallisation of the superconducting phase by stabilising the nucleation process;

— preparation of high-temperature superconducting materials in the region of stable crystallisation of the superconducting phase requires the formation of a rather large number of seeds; if the seed lifetimes are longer than the mutual seed 'adjustment' time, the one and only process in the system is 'front-side' crystallisation followed by the formation of a material comprised of strongly coupled crystallites.

Based on the aforesaid, we can state that the nonlinear character of the evolution of processes in the open physicochemical systems complicates preparation of many chemically complex products and materials with reproducible compositions, structure and properties. This problem can be to some extent solved [88] by organising the reaction zone in an optimum manner. This includes:

— the use of highly homogeneous (better, molecularly bonded) precursors (alkoxides) or complex compounds in the form of solutions, melts, or vapours;

— treatment of precursors to provide preparation of X-ray amorphous intermediate states and formation of target crystalline products at lowest possible temperatures due to synergistic effects

of different forces (low pressure, intense grinding, sonication and microwave irradiation); and

— template synthesis or directed chemical complication of the system to ensure the preferred formation of the product with a prescribed structure.

V. Onset and suppression of chaos in metal corrosion processes

A number of communications concerning the conditions for onset and suppression of chaos in metal corrosion processes have been reported.[89–91] Figure 13 presents a scheme of corrosion of metal M in an aqueous solution. The process is accompanied by the formation of two products, a metal hydroxide and a metal oxide. Let S_{OH} and S_O be the fractions of the metal surface covered by the hydroxide film and oxide film, respectively, and c_M be the concentration of metal ions in the solution. Then, the state of the system at any instant of time can be characterised by the position of the point in a three-dimensional phase space, *i.e.*, in the $S_{OH}-S_O-c_M$ coordinate system.

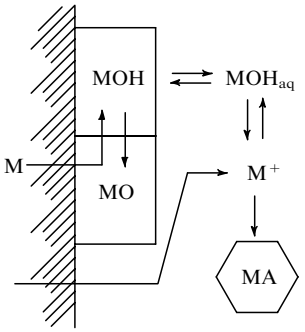


Figure 13. Corrosion scheme of metal M in aqueous solutions. Oxide film (MO), hydroxide film (MOH), dissolved hydroxide (MOH_{aq}), metal ions (M^+) and salt (MA).

The rate of change in each parameter can be calculated by solving the corresponding kinetic equations and plotting the trajectory of the motion of the figurative point based on the results obtained. Figure 14 presents a projection of this trajectory on the S_O-S_{OH} plane. As can be seen, after some time the trajectory represents an attractor of a rather complex shape. The question arises as to how to distinguish between the deterministic chaos and the pure stochastic process (the so-called stochastic chaos) based on experimental results. For instance, corrosion studies allow one to measure the corrosion current I at different time instants. The $I(t)$ plot (Fig. 15) is typical of random processes. Construction of the phase trajectory using these data requires the use of the return map method. The essence of the method is as follows: an appropriate time interval, τ, is chosen, corresponding to repetition of the height of corrosion current peaks, and then the phase trajectory is constructed in the $I(t)-I(t+\tau)$ coordinates. The shape of this trajectory (Fig. 16) indicates that the corrosion process is in some way deterministic. Though at first glance the corrosion current changes randomly during the process, the trajectory of the system in the correctly chosen phase space is a strange attractor. To inhibit corrosion, one should find certain conditions corresponding to degeneration of the system's attractor into a point. The results of suppression of the corrosion process using the return map technique are demonstrated in Fig. 17. The initial $S_O(t)$ dependence is shown in the left part, while the $S_O(t)$ plot after applying the suppressing signal

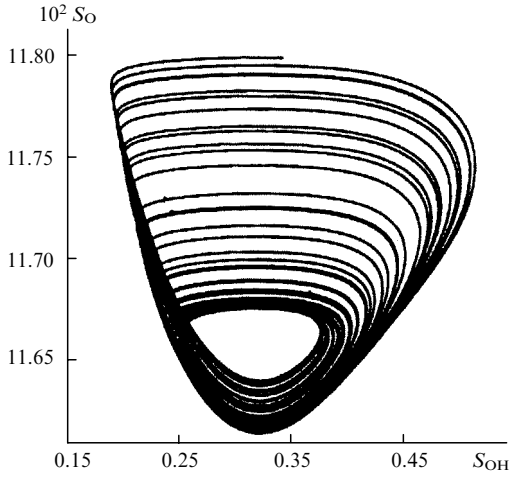


Figure 14. Phase trajectory of corrosion process (projection of the trajectory on the S_O-S_{OH} plane).

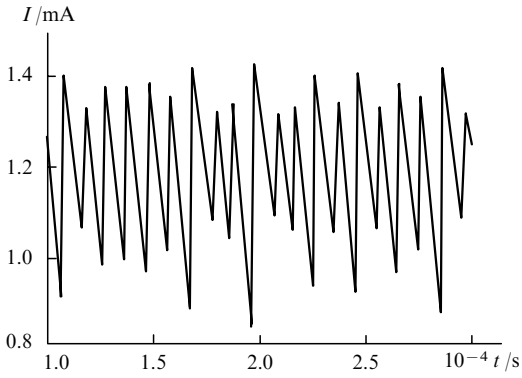


Figure 15. Experimental dependence of corrosion current, I, on time t.

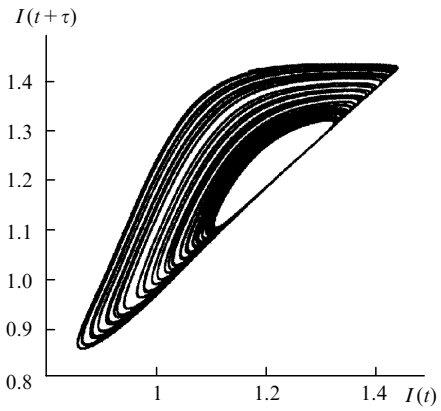


Figure 16. Attractor reconstructed from the experimental dependence $I(t)$ using the return map method (for details, see text).

(specially chosen voltage pulse) is presented in the central part; switching off the suppressing signal causes re-appearance of chaotic oscillations in the system (right part of Fig. 17), indicating that corrosion continues. By regularly applying such voltage pulses it is possible to achieve complete inhibition of corrosion.

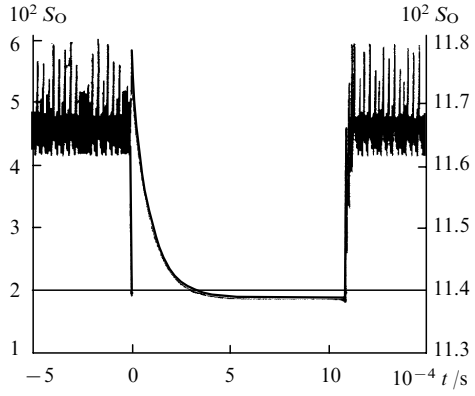


Figure 17. Suppression of chaotic oscillations during metal corrosion using special voltage pulses (for details, see text).

VI. Application of deterministic chaos models to poorly reproducible physicochemical processes

Chemistry of materials often deals with poorly reproducible solid-phase or heterophase processes. For instance, a yield of 25% is considered good in large-scale production of single crystals of many functional materials (ferrites, piezoelectrics). In the case of single crystals the (potentially) changeable (variable) parameters are the size, shape, composition, dislocation structure and some other, despite a high accuracy of control of the synthesis conditions. Some other examples of poorly reproducible processes can be found in the literature.[91–93]

Traditionally, the dynamics of chaotic systems have been studied using time-series analysis, which involves observation of changes in a certain experimentally measured parameter. This approach allows determination of the type of system's behaviour (*e.g.*, chaotic one) and obtaining valuable information on the system's dynamics. However, specific features of solid-phase systems sometimes preclude measurements of characteristic dependences of their parameters on time (*e.g.*, for growth of single crystals). At the same time, it's quite an easy matter to obtain statistical data on the results of repeated experiments carried out under identical (within the limits of experimental error) conditions.

A procedure for determining fundamental characteristics of a chaotic system from statistical data obtained by repeated reproduction of experiments has been elaborated.[94] It was assumed that poor reproducibility of experimental results obtained under identical conditions is due to high sensitivity of the system's dynamics to minor changes in the starting parameters. The initial conditions for different experiments can be set to some finite accuracy, which is determined by the accuracy of the equipment used in the experiments. However, if the system under study behaves chaotically, small, experimentally undetectable, differences can have a strong effect on the overall result.

The model chaotic system was described by a differential equation of Duffing's oscillator[95]

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + 0.05\frac{\mathrm{d}x}{\mathrm{d}t} + x^3 = 7.5\cos t,$$

which has a set of three phase variables, namely, the coordinate x, velocity $\mathrm{d}x/\mathrm{d}t$ and time t.

Numerical integration of this equation was carried out by the fourth-order Runge–Kutta method. Randomly chosen initial conditions $x_0 = x$ ($t = 0$) were normally or uniformly distributed with different dispersions. All numerical experiments were carried out with the same initial velocities, namely, $\mathrm{d}x/\mathrm{d}t = 0$ at $t = 0$. Calculations were terminated after a rather long time ($t \geqslant 470$ arbitrary units) to ensure that the system's trajectory is the strange attractor.

Numerical experiments showed that the distribution of the end points obtained by integration at different initial conditions reflects only the attractor's structure and is independent of the distribution of initial conditions.

More detailed information was obtained by analysing the distributions of two (or more) independent parameters of the system. Fig. 18 *a* presents a correlation between the final values of the variables $\{x, \mathrm{d}x/\mathrm{d}t\}$ obtained after completion of calculations. In real experiments, the measured parameters can be functions of one or several phase variables. As can be seen, the final values obtained at $t = 470$ are distributed over the Poincarè cross-section of the strange attractor. The visual appearance of this cross-section is independent of the type and dispersion of initial conditions. It should be noted that exactly the same Poincarè cross-section can be obtained by applying a conventional time-series analysis procedure to the $\{x, \mathrm{d}x/\mathrm{d}t\}$ pair at times $470 + 2\pi n$, where $n = 1, 2, 3$ (Fig. 18 *b*).

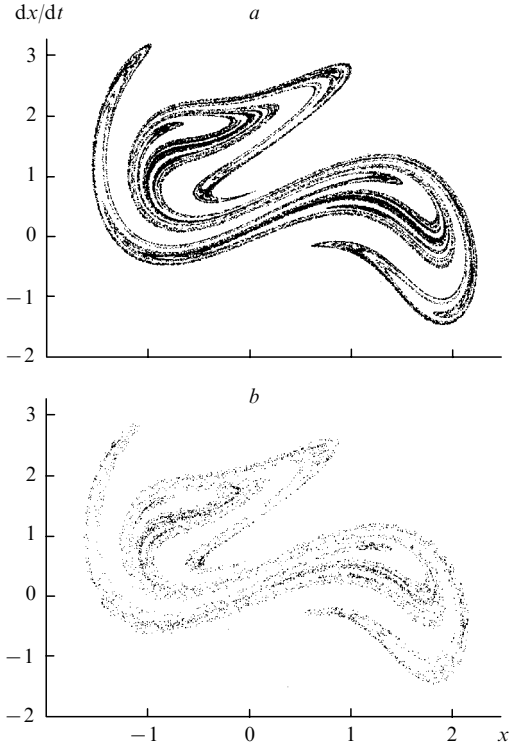


Figure 18. Poincaré cross-sections of Duffing's attractor, obtained from reproducibility experiments ($t = 470$, 30 000 points) (*a*) and using conventional time-series analysis ($t_n = 470 + 2\pi n$, 15 000 points) (*b*).

This approach can also be employed in reconstructing the attractor of the system under study. This requires knowledge of the number of dynamic variables. In the case of the Duffing oscillator, the third phase variable is the time t (see above). To reconstruct the attractor, a total of thirty-one Poincarè cross-sections were obtained at different times $t = 470 + 2\pi n/30$; the cross-section at $n = 0$ was equivalent to that obtained at $n = 30$. Each Poincaré cross-section contained a set of 2000 points obtained by numerical integration of Duffing's equation at normally distributed initial conditions. The three-dimensional image of the strange attractor is shown in Fig. 19. In the general case, reconstruction of the attractor of a poorly reproducible system requires that (i) as many parameters of the process under study as possible be measured to be deliberately larger than the number of phase variables; (ii) independent variables be chosen and (iii) a correlation between the independent variables be

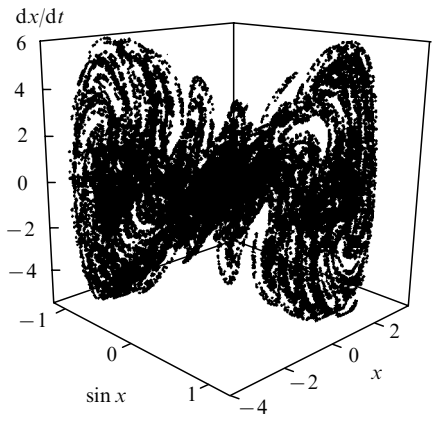


Figure 19. Three-dimensional image of the strange attractor of Duffing's oscillator in the $x-\sin x-\mathrm{d}x/\mathrm{d}t$ coordinates.

plotted. By virtue of the fact that the fundamental phase variables for the system are usually unknown, the shape of the reconstructed attractor can be distorted. This is also a standard situation for conventional reconstruction of an attractor using time-series analysis.

Thus, even by measuring a single parameter of the system one can say whether or not the poor reproducibility is due to chaos in the system. In this case, it is possible to determine fundamental characteristics of the chaotic system, such as the fractal dimension of the Poincaré cross-section, D_P, and then calculate the fractal dimension of the strange attractor (usually, this parameter equals $D_P + 1$). The possibility of using the reproducibility data for determining other dynamic properties of chaotic systems (*e.g.*, Lyapunov indices,[96] K-entropy,[97] *etc.*) is still to be clarified.

Yet another important problem concerns the number of experimental points necessary to obtain correct results. From the aforesaid it follows that even a thousand experimental points can appear to be insufficient. This is a serious impediment, since carrying out, *e.g.*, a thousand of syntheses of single crystals is usually impracticable. However, a way to obtain more than a single point in one experiment should be pointed out. In particular, each experiment on melt growth of superconducting cuprates gives nearly a hundred single crystals with (usually) different parameters (size, composition, *etc.*). Another method for solving this problem involves analysis of statistical data on quality control in large-scale productions. This is of considerable value for these productions, since an intimate relationship between poor reproducibility and chaos makes possible significant improvements in reproducibility of the characteristics of end products by suppression of chaos using known methods.[98, 99]

The examples considered above do not exhaust the list of materials science problems that can be solved using nonlinear dynamics approaches. In particular, such problems include studies of phase boundaries as self-organising systems. The phase boundary was treated [100] as an open nonequilibrium system comprising a number of interacting subsystems. A feature of the system is nonlinear interactions between subsystems and the presence of feedbacks. An example of a self-organisation related phase boundary is provided by the semiconductor/electrolyte interface. This interface comprises the ionic electrolyte layer adjacent to the semiconductor surface, the region of 'alien' surface phases, the region with the changed or broken crystal structure of the semiconductor and the space charge region, which retains the crystal structure of the bulk semiconductor but has different electronic characteristics. Specific properties of such a surface are determined by the processes occurring within all the above-mentioned regions and by their interactions. A salient feature, which serves as a prerequisite for self-organisation, is that the interface is formed as a result of nonlinear interaction between the electronic subsystem of the semiconductor and the ionic subsystem of the electrolyte. Most often, the polarisation of semiconductors and adsorption of molecules on their surfaces are accompanied by phase transitions, which cause a jumpwise change in the charge of the interface. Sometimes these processes are accompanied by irreversible change in the charge, which is characteristic of the surface of the semiconductors with low density of surface states. This makes possible, *e.g.*, exclusion of pinning of the Fermi level on the GaAs and GaP surfaces and extension of the range of the surface potential values, which can be practically implemented in designing and fabricating metal–insulator–semiconductor transistors.

Of considerable interest are systematic studies on the nonlinear processes accompanying the first-order phase transitions on the surface of solids and on the growth of thin films from multicomponent vapour carried out by Kukushkin and Osipov.[101, 102] These researchers analysed various models for the vapour-phase and melt-solution growth of multicomponent films and proposed efficient methods of control of these processes.

VII. Self-assembly of supramolecular compounds

The evolution of a physicochemical system from atomic vapour to a solid depends on the system's composition. If the system comprises atoms of the same element, the evolution begins with formation of covalently bonded diatomic molecules followed by larger associates, clusters and nanoparticles that are often stabilised in inert matrices in the form of nanocomposites. The assembly is completed with the formation of a covalent (diamond), molecular (iodine) or metal (alkali and alkali-earth metals) crystals as the end product. At any non-zero temperature (in K), the crystal has to some extent a disordered structure, which contains, in the simplest case, point defects (vacancies or atoms occupying the interstitial sites). Thus, the evolution resulting in an elementary crystal as the end product can be represented by the following scheme:

atomic vapour ⟶ molecules ⟶ associates ⟶
⟶ clusters ⟶ nanoparticles and nanocomposites ⟶
⟶ real crystal (point defects) ⟶
⟶ perfect crystal.

In a more chemically complex system the interactions of different-type atoms cause the formation of molecules bonded through covalent or mixed ionic–covalent interactions. In the latter case the bond ionicity increases as the difference in electronegativity between the constituent elements increases. The next stage of the interaction involves formation of the so-called noncovalently bonded supramolecular ensembles and supramolecular materials. Usually, the formation of supermolecules is assumed to be driven by the system's tendency towards a minimum of the Gibbs free energy (the enthalpy of formation of supermolecules from individual molecules or molecules and ions contributes predominantly in this case). In spite of extensive literature on supramolecular chemistry, from academic monographs (see, *e.g.*, Refs 103–105) to recent publications in scientific journals (see, *e.g.*, Refs 106–110), the nature of the self-organisation of supermolecules and supramolecular crystals has been poorly studied. This uncertainty also covers the terminology of supramolecular chemistry.[111] First of all, the case in point is the so-called self-assembly and self-organisation processes, which are sometimes (but not always) treated as different. The term self-assembly can be used in a broader sense. It relates to all types of spontaneous binding of components through both covalent and noncovalent forces. According to Lehn,[103] self-organisation

(1) involves the interactions between systems, which can experience spontaneous ordering in space and/or time;

(2) involves spatial (structural) and temporal (dynamic) order in both the equilibrium and nonequilibrium dissipative structures;

(3) concerns only the noncovalent, supramolecular level of structural organisation; and

(4) results in the formation of polymolecular ensembles due to specific acts of molecular recognition of components.

The higher the extent of spatial organisation of fragments, the more substantiated the reasons for their treatment as self-organised (molecular layers, membranes, micelles, colloids, liquid crystals, molecular crystals). Thus, self-organisation extends to the interactions between fragments and the integration of these interactions, which are responsible for the collective behaviour of the system, as is observed during, *e.g.*, phase transitions or creation of spatial and temporal waves).

The interrelation between conservative and dissipative self-organisation during the evolution of physicochemical systems involving formation of supermolecules has not been studied as yet. We believe that such an evolution is possible due to a complex combination of these factors based on chance and necessity, respectively. According to Müller *et al.*,[28] conservative self-organisation processes play a crucial role in the formation of supermolecules. On the other hand, Lehn pointed out that 'the inclusion of dissipative nonequilibrium processes, like those present in the living world, constitutes a major goal and challenge for supramolecular chemistry'.[31] An important role in the formation of supermolecules is played by prehistory, or the topochemical memory, as well as the template effect of the central ion or molecule towards other fragments of supermolecules formed. Self-assembly of supermolecules can be employed to prepare advanced functional materials.[112]

Let us consider the self-assembly of comb-like supermolecules *via* formation of primary and secondary structures as an example.[113] The simplest case is a flexible polymer having free binding sites along its main chain (component A in Fig. 20). Usually, the main chain is polar, while non-polar side groups can be connected by complementary bonds, thus leading to comb-like supermolecules, which then self-organise. The side chains are bonded to the main polymer chain by hydrogen or coordination bonds.[114] Ionic

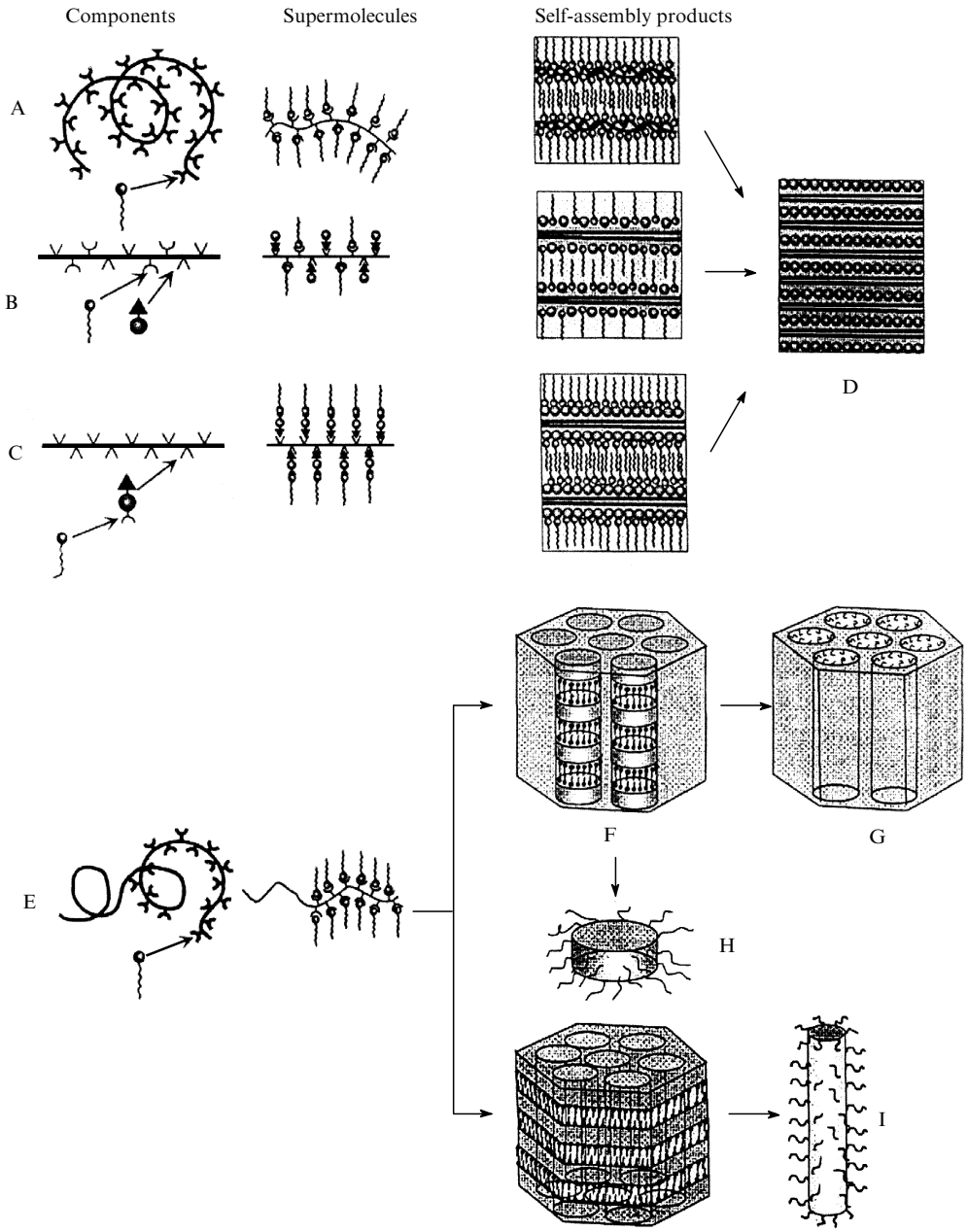


Figure 20. Self-assembly of comb-like supermolecules involving primary and secondary polymer structures (for details, see text).[113]

interactions in polyelectrolyte – surfactant complexes were also used to form comb-like supermolecules.[115] The resulting self-organised multidomain structures can be transformed into single-domain ones.[116] The properties of the latter group of structures can be tuned by varying the nature of the side chains. For instance, partial fluorination of the side chains reduces the surface energy and the friction coefficient of the material.[117]

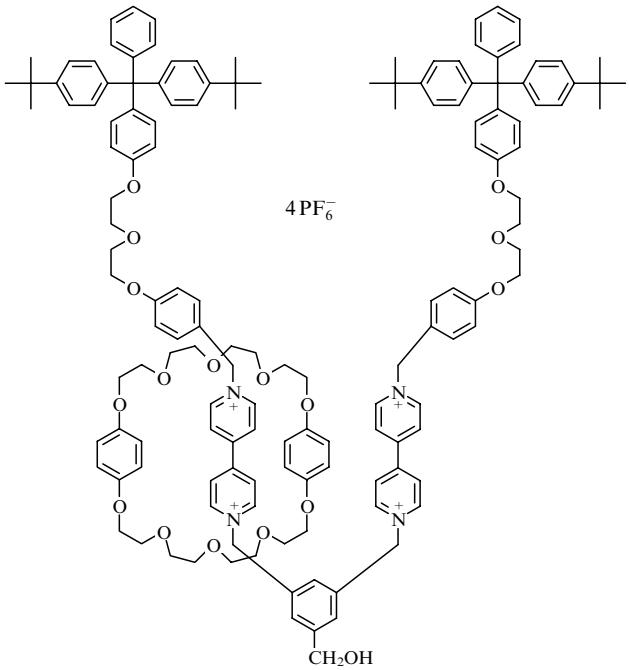
If the main chain consists of the double helix of DNA, self-organisation can be achieved by ionically bonding liposomes or cationic surfactants to the anionic phosphate sites.[118, 119] This allows for materials design possessing unusual biochemical properties. For instance, colour centres can be intercalated into the DNA helices, thus suppressing their aggregation. Such structures can be used as templates for photonic applications.[119] The main polymer chain can have two sorts of binding sites to which fragments of different nature can be bonded (component B in Fig. 20).

The side chains can also have different functional groups. For example, in addition to the side chains required for self-organisation, the system can contain acid groups that act as dopants for the conjugated polymer (*e.g.*, polyaniline), which leads to electronic conductivity.[120] An additional degree of freedom is introduced when polyaniline is first doped with, *e.g.*, camphorsulfonic acid and subsequently connected to hexylresorcinol molecules (component C in Fig. 20) through two H-bonds.[121] The alkyl chains of the hexylresorcinol molecules act as plasticisers, thus making the infusible polymer thermoplastic. Camphorsulfonic acid doped polyaniline chains confined within nanoscale cylinders improve the material's conductivity. This technique also allows modification of rigid-rod polymers similar to polypyridine, which consists of *para*-linked heteroatomic rings. The optical properties of such polymers can be controlled by doping them with camphorsulfonic acid. Subsequent bonding to alkylresorcinol leads to comb-like supermolecules, which self-organise into lamellae in such a way that the material becomes fluid even without solvents.[122] Such an unusual fluid contains rigid polymer 'rods' and allows processing towards monodomains with aligned 'rods.'

Finally, the plasticising alkylresorcinol molecules can be removed by evaporation *in vacuo*, thus interlocking the chains in solid stable polymer films (product D in Fig. 20). As a result, polarisation-induced luminescence is achieved.[122] It is also possible to combine different self-organisation and recognition mechanisms within the same polymeric material. For instance, block copolymeric self-organisation fragments of lengths 100 to 200 Å can be combined with amphiphilic self-organisation fragments of length 10 to 60 Å (component E in Fig. 20).[114, 123] After selective doping of one block, the material's conductivity can be changed by using a sequence of phase transitions.[114] Three-dimensional conductivity can be achieved by ordering the local structure.[124] There is a vast variety of phases,[123] such as lamellae-within-cylinders (product F in Fig. 20), which, by analogy with the product D, also permit selective cleavage of the constituent fragments that form the supermolecules. For instance, starting from polystyrene-*b*-poly(4-vinylpyridine), in which pentadecylphenol is hydrogen bonded, one can obtain a structure in which the glassy polystyrene matrix contains cylindrical pores with poly(4-vinylpyridine) 'brushes' on the walls (product G in Fig. 20).[125] By choosing different block copolymers and amphiphiles it is possible to tune the thickness of the pore walls. In principle, the shape of 'nanobrushes' can be controlled by selecting appropriate polymer and solvent. For instance, Saito [126] cross-linked the poly(4-vinylpyridine) slices using an original method for preparation of nanoscale colloidal disks (product H in Fig. 20). Other shapes of nanoparticles can also be obtained, *e.g.*, polymer 'rods' (product I in Fig. 20).[127]

Complex self-organised supermolecules open up prospects for targeted variation (tuning) of many physical parameters. The possibility of using such molecules in design of advanced biomaterials is particularly attractive, which was successfully demonstrated taking DNA and self-organising fungal proteins as examples.[128]

Rotaxane molecules that are active in redox processes were used to create 'molecular switches', which can act as logical gates.[129] The rotaxane molecule consists of a dumb-bell chain and a macrocycle mechanically strung on the dumb-bell.



The dumb-bell fragments of the molecule comprise charged bipyridine moieties while the macrocycle consists of crown-ether chains. The molecules of rotaxane are formed as a monolayer and located between the metal and metal oxide electrodes. Passage of electric current causes oxidation of the rotaxane molecules and induces conformational changes, which lead to an increase in the resistance. In fact, the rotaxane molecules behave as a molecular switch. Switching on (oxidation of rotaxane) is a reversible process, while the resistance difference between the on and off states is readily detectable (resistance changes by a factor of 15 to 30).

VIII. Self-organisation in nanosystems

A decrease in the particle size in a dispersed system down to the nanometre scale is accompanied by changes in the bulk properties of the system, including the crystal lattice parameters (sometimes, also the lattice type), melting temperature, electric and heat conductivity, *etc.* This changes the character of interparticle interaction, thus providing a way to various nanostructures possessing unique optical, magnetic, catalytic properties and reactivity.[130, 131] The closer the particle size to the atomic scale, the more pronounced these changes and effects.[132]

Nanoparticles are divided into two types. The first group comprises nanoclusters or nanocrystals, which consist of at most a thousand atoms, have ordered structure and are of size 1 to 5 nm. The second group comprises nanoparticles consisting of 10^3 to 10^6 atoms having diameters from 5 to 100 nm.[133] However, this classification is correct only for isotropic (spherical) particles. Whiskers and plate-like particles can comprise a much larger number of atoms and their linear dimensions (one or even two) can much exceed the threshold value, but the properties of these objects remain typical of matter in the nanocrystalline state. Based on the ratios of linear dimensions, nanoparticles can be treated as one-, two- or three-dimensional (1D-, 2D- and 3D-nanoparticles, respectively).[134] If a nanoparticle has a complex shape and structure, the linear dimension of the structural element rather than the entire particle is taken as the characteristic size. Such

particles are usually called nanostructures; their linear dimensions can be much larger than 100 nm. Depending on the predominant type of the anisotropy of structural elements, nanostructures are also divided into one-, two- or three-dimensional ones.

The most important feature of nanosystems is manifestation of quantum size effects. From the classical standpoint, as the particle size in the system decreases, the specific surface area of the particles increases. The effect of the particle size on the thermodynamic properties of the system is included by introducing an additional term, γds (γ is the size-independent surface tension coefficient and s is the surface area), into the expression for the free energy. According to Thompson's equation, a decrease in the particle size is accompanied by an increase in the equilibrium vapour pressure and solubility and by changes in the temperatures of melting and other phase transitions. At the same time, a number of extensive parameters of the system, related to surface processes (*e.g.*, adsorption and catalysis), are proportional to the specific surface area. The role of the specific surface area of nanoparticles becomes much more important as their sizes approach the atomic scale. This is due to a considerable increase in the number of surface atoms.

On the other hand, many properties of materials (including magnetic, optical and electrical properties) are due to co-operative interactions in solids that are not retained on going from the bulk material to nanoparticles. In this case the properties of materials cannot be rationalised solely by an increase in the specific surface area and the number of surface atoms without considering quantum size effects. This can be exemplified by the formation of quantum dots in those cases where the sizes of the semiconductor particles are comparable with the de Broglie wavelength of the electron, by a change in the width of the band gap due to localisation of excitons and by transition of ferromagnetic materials to the superparamagnetic state. Sometimes the size effect manifests itself as a dramatic enhancement or reduction of catalytic activity (or reactivity) per metal atom with a decrease in the particle size. This effect is usually most pronounced for nanoclusters.

The magnetic, electrical and optical properties of matter also significantly change as the particle size decreases from 5–10 nm downward.[135, 136] The properties of nanoclusters depend non-monotonically on the cluster size (*i.e.*, the number of atoms).[136]

Unique properties of nanoclusters are likely due to the limited number of constituent atoms. In most cases the cluster core is formed following the close packing principle. The number of atoms in a regular dodecahedral core is given by the expression

$$N = \frac{10n^3 + 15n^2 + 11n + 3}{3},$$

where n is the number of shells surrounding the central atom. Thus, the smallest close-packed cluster core comprises a total of thirteen atoms (a central atom and twelve atoms of the first outer shell). As a result, one gets a set of 'magic' numbers N = 13, 55, 147, 309, 561, 923, 1415, 2057, 2869, *etc.*, which correspond to the most stable cluster cores.[136, 137] A tendency towards formation of cores containing 'magic' numbers of atoms can be followed taking metal clusters as examples. A number of gold, rhodium, platinum and palladium compounds were synthesised, containing from thirteen {*e.g.*, $[Au_{13}(diphos)_6](NO_3)_4$; diphos is $PPh_2CH_2PPh_2$} to a total of 2057 metal atoms [*e.g.*, $Pd_{2057}(phen)_{840-1600}$].[138] It should be noted that clusters comprising non-'magic' numbers of atoms are also formed. The existence of more energetically favourable 'magic' clusters provides an explanation for non-monotonic dependence of the properties of nanoclusters on their sizes.[139] On going from nanoclusters to nanoparticles this effect becomes less pronounced. Detailed studies of gold and palladium clusters revealed that their conductivities, heat capacities and magnetic susceptibilities are significantly different from the corresponding properties of bulk metals.[140] It was established that, unlike the orbitals of metal atoms in bulk samples, those of the metal atoms of the cluster core are not delocalised and form discrete energy levels that differ from molecular orbitals. On going from a bulk metal to nanoclusters and then to molecules and single atoms the metallic band structure (conduction band formed by delocalised s- and d-electrons) turns into discrete energy levels formed by localised electrons in cluster and then into molecular and atomic orbitals. The appearance of discrete electronic energy levels in clusters causes single-electron transitions that are characteristic of single atoms.

Very interesting quantum size effects were observed in studies of the magnetic susceptibility and heat capacity of nanoclusters.[141] It was shown that the magnetic susceptibilities of both the Pd_{2057} cluster and a bulk palladium sample are temperature independent (the absolute value of a cluster's susceptibility is much lower than that of the bulk sample). With inclusion of magnetic effects this means that the Pd_{2057} cluster is a Pauli paramagnetic and similar to the bulk metal. A decrease in the cluster size down to Pd_{1415} causes an increase in the low-temperature magnetic susceptibility, which is in good agreement with the results of quantum-mechanical calculations and is associated with a decrease in the density of states near the Fermi level. At the same time, increasing the cluster size leads to an increase in the specific magnetic susceptibility, which reaches a value typical of bulk metal at a particle size of nearly 30 nm. Nanoclusters exhibit a quadratic (or more complex) temperature dependence of the heat conductivity (*cf.* a linear dependence for bulk material and larger nanoparticles). The quadratic temperature dependence of the heat conductivity is typical of amorphous solids; in the case of nanosystems it is associated with tunnelling effects.

We have considered only a few examples of specific properties of small nanoparticles. Due to the small number of atoms these properties can be reasonably described using quantum-mechanical approaches. However, many fundamental properties of matter in the nanocrystalline state are different from the properties of bulk materials over a rather wide range of particle sizes (up to hundreds of nanometres).[142] In this case one can use both statistical and thermodynamic methods that allow for the excess surface energy.[143]

Unique physicochemical properties of nanoparticles and nanostructures make the design of functional nanomaterials based on them a quite interesting research avenue. Recently, particular emphasis has been placed on the magnetic and semiconductor nanomaterials. This is due to great practical value of these classes of materials for the development of information technologies. For instance, superparamagnetic materials based on transition-metal (*e.g.*, Fe, Co, Ni) nanocrystals are used in memory devices with ultrahigh recording density.[144] Nanomaterials based on, *e.g.*, $A^{II}B^{VI}$ and $A^{IV}B^{VI}$ semiconductors possess unique optical properties and are thought to be promising for active elements of tunable lasers, nonlinear optical elements and devices for nanoelectronics.[145]

Advances in studies of nanosystems are closely related to the improvement of field-ion, tunnelling, atomic force and high-resolution electron microscopies that allow visualisation and determination of the properties of individual nanoparticles and to the development of computational methods that would permit computer simulation of molecular motions in large molecular ensembles.

Summarising the investigations of nanosystems,[146] the following conclusions were drawn.

1. Modern theoretical concepts of nanosystems are too rough to underlie the practical use of nanosystems. Essential development of the theory of nanosystems is required. Most nanosystems are far from the equilibrium state; their state is continuously changed with time. That is why the establishment of laws of the physicochemical evolution of nanosystems is of crucial importance. The available data on this evolution are scarce as yet.

2. Methodologically, the properties of nanosystems should be studied by combining expeimental studies and mathematical modelling. It is a combination of 'full-scale experiments and

computer simulation' that was used to obtain essential, unambiguously interpretable information on nanosystems.

3. Characterisation of nanosystems is still a challenge. Quantitative data on the properties of individual nanoparticles are hard to obtain. Information on the behaviour of nanoparticles in the measuring devices is of great importance. The most informative studies have been carried out by those research groups, which not only use but can also modify their measuring devices and adjust them in the course of measurements.

4. Currently, the emphasis has been placed on the following avenues of research on nanosystems:

— elaboration of theoretical foundations of preparation and operation of nanomaterials including superstrong metals and alloys, ceramics, film compositions and materials possessing specific optical, magnetic and electrical properties;

— elaboration of physicochemical foundations of nanotechnologies, including development of methods for preparation and characterisation of technological nanosystems and investigation of their behaviour under the operating conditions;

— development of nanopharmacology and nanomedicine, including elaboration of methods for the synthesis and characterisation of ultradispersed forms of pharmaceuticals and investigations of the mechanisms of their interaction with living organisms;

— creation of ecological nanophysicochemistry, which would study the mechanisms of formation and transformations of natural and technogenic air and water pollutants (aerosols and hydrosols, respectively); development of methods for cleaning the environment of nanoparticles.

Experiments with hydroxyapatite, acetylsalicylic acid and phthalocyanines showed that going to ultradispersed forms of these compounds causes dramatic changes in their therapeutic effects and opens up prospects for the formation of pharmaceuticals immediately inside invaded tissues. Therefore, the development of concepts of physicochemical evolution of ultradispersed pharmaceuticals from their formation in chemical reactors or in tissues to complete excretion is of paramount importance. Melikhov [146] posed a problem of development of physicochemical evolution of nanopharmaceuticals, which should provide methods for solving the following applied tasks.

1. Creation of materials possessing osteoinductive properties (inductors of osteogenesis), osteoporosis remedies and carriers for pharmaceuticals based on ultradispersed hydroxyapatite. For instance, the 'Ostim-100' osteoplastic material (ultradispersed form of hydroxyapatite) was proved to be highly efficient in acceleration of bone tissue regeneration. This opens up prospects for preparation of compositions containing this material and hormones or broad-spectrum antibiotics. However, this requires that hydroxyapatite nanoparticles be capable of forming 'complexes' with macromolecules of different nature.

2. Creation of 'nanofluids' based on hydroxyapatite and hydrotalcite doped with iron oxides for magnetic-field driven, directed transportation and delivery of pharmaceuticals in organisms. Preliminary experiments showed that both the interplanar space of hydrotalcite microcrystals and the aggregates of two-dimensional hydroxyapatite crystals can be intercalated with large amounts of various pharmaceuticals and with magnetic nanoparticles of iron oxides, thus making such materials magnetically sensitive. Therefore, studies on the possibility of creating pharmaceuticals based on these composites would be appropriate.

3. Development of methods for the preparation of nanostructured alloys based on nitinols to create materials for implants and medical instruments. Experiments revealed significant improvement of the consumer properties of the products made of nanostructured alloys. However, to meet all medical requirements, one should study the physicochemical evolution of the alloy.

4. Elaboration of methods for tumour therapy by sonostimulated inhibition and destruction of malignant cells using ultradispersed substances; search for compounds which can selectively crystallise and accmulate within malignant cells. There are experimental grounds to believe that tumour cells containing a rather large amount of phthalocyanine nanoparticles can be killed by exposing to a weak acoustic field. Studies on crystal sensorics revealed that the frequency of formation of solid nanoparticles in cells can increase upon minor variations of the compositions and molecular structures of the substances present in the cells. Therefore, a promising avenue of pharmacological research consists in search for compounds, which can selectively form nanoparticles in tumour cells and thus provide a route to cell destruction using acoustic fields that is innocuous for normal tissues.

Returning to the role of nonlinear processes and self-organisation in the chemistry of nanomaterials, it should be emphasised that self-organisation is possible in different stages of their synthesis and exploitation, from the formation of nanocrystallites or nanoclusters to long-term operation of nanostructures in various technical, technological and biomedical systems.[147, 148]

Indeed, in most cases nanoparticles (nanoclusters) are formed under strongly nonequilibrium conditions, which provides the necessary ratio of the rate of spontaneous nucleation to the seed growth to particular sizes. Historically, nanoparticles were first prepared using methods of colloid chemistry, which allowed the synthesis of particles of size 1 nm to 100 μm. In Fig. 21 we compared the linear dimensions of various colloidal systems, which are most often used in practice.

In 1968, Stöber, Fink and Bohn [149] first demonstrated that polycondensation methods are also efficient in the preparation of monodispersed silica particles. They hydrolysed a solution of tetraethylorthosilicate in alcohol at high pH values and obtained homogeneous spherical particles of amorphous SiO_2. The particle size could be varied from 50 nm to 2 μm by varying only one parameter (reagent concentration). Matijevic *et al.*[150–154] and the authors of Refs 155–157 also have made large contributions to the development of polycondensation methods. Methods of preparation of colloidal particles using polycondensation in solutions both in the presence and in the absence of surfactants (inhibitors of aggregation) have also been analysed.[158]

The next group of methods for the preparation of nanoparticles comprises high-energy methods based on rapid condensation of vapours under such conditions that exclude aggregation and growth of the particles thus formed. These methods mainly differ in the procedures employed for evaporation of the starting compound and stabilisation of nanoparticles. Evaporation can be achieved by plasma excitation, laser methods, arc melting, heat treatment, *etc.*[159–161] Condensation can occur either in the presence of a surfactant (adsorption of surfactant on the surfaces of particles hampers their growth) or on a cold substrate (here, the growth of particles is limited by diffusion rate).[162]

Yet another group of methods involves the use of spatially confined systems, or the so-called synthesis in nanoreactors (micelles, droplets, films, *etc.*).[163] Here, one deals with the synthesis in reversed micelles, Langmuir–Blodgett films, adsorption layers, *etc.*[164–167] Clearly, the particles thus obtained cannot be larger than the size of the corresponding nanoreactor; therefore, these methods allow preparation of monodispersed systems.[168] Biomimetic and biological approaches, which involve the use of biomolecules (proteins, DNA, *etc.*) as nanoreactors,[169–171] can also be placed into this group.

Synthesis in colloidal nanoreactors permits not only the preparation of nanoparticles with very narrow and controllable size distribution but also particles of different shape and anisotropy (including small particles) as well as coated particles. This technique can be employed to prepare virtually all classes of nanostructures, from single-component metal to multicomponent oxide nanostructures.[172–174]

It should be noted that the use of free nanoparticles as materials is strongly complicated by the fact that matter in the nanocrystalline state exhibits metastable properties. As mentioned above, this is due to an increase in the specific surface area of particles with decreasing linear size down to the nanometre scale, which leads to an increase in the reactivity of a compound and enhanced aggregation of nanoparticles. The method most

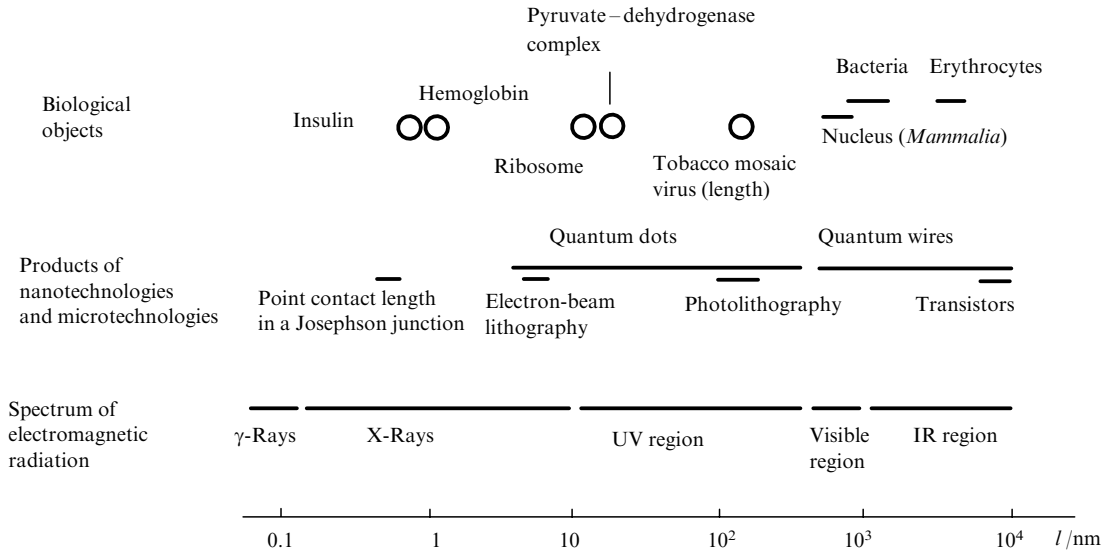


Figure 21. Linear dimensions of various colloidal objects.

widely used to solve this problem involves fabrication of nanocomposites (*i.e.* nanoparticles encapsulated in a chemically inert matrix).[175] This approach provides a way to eliminate aggregation of nanoparticles and protect them from external conditions (*e.g.*, from oxidation by air oxygen), which significantly facilitates the practical use of nanomaterials.

Nearly ten methods of matrix isolation of nanoparticles have been proposed to date. They can be conventionally divided into two groups. The first group comprises methods for the preparation of free nanoparticles followed by their incorporation into an inert matrix. The second group includes methods of formation of nanostructures in the bulk of the matrix during its chemical modification.[176, 177] Methods from the first group are simple but impose strong limitations on the choice of matrix. Usually, organic polymers are employed as matrices, but these substances do not possess high thermal stability and sometimes do not exhibit the necessary physical properties (*e.g.*, high optical transparency).[178] Besides, incorporation of nanoparticles does not exclude their aggregation.[179] The second approach not only allows one to eliminate these problems but also provides a way of controlling the parameters of nanoparticles immediately in the matrix during their formation and even changing these parameters in the course of exploitation of the material. In this case, the matrix must contain some structural voids, which can be filled with appropriate compounds; subsequent modification of these fillers should cause the formation of nanoparticles in the voids.[180] In other words, these voids should confine the zone of the reaction involving the incorporated compounds, *i.e.*, act as a specific kind of nanoreactor. Clearly, by choosing compounds with different shapes of structural voids it is possible to synthesise nanostructures with different morphologies and anisotropies.

The best known example for this approach is the synthesis of nanomaterials using porous oxide matrices (usually, SiO_2 or Al_2O_3).[181, 182] In this case, pores are filled with various compounds, which are then chemically modified. However, disordered porous structure and broad pore size distribution preclude preparation of good nanosystems. As a rule, such materials are used in catalysis, where the requirements imposed on the particle size distribution and particle morphology are not too strong.[183] A possible solution to the problem is provided by using porous materials with ordered pore structure, such as mesoporous silica and zeolites having 1D-channels or 2D-voids.[184–186] In this case, it is possible to obtain whiskers, plate-like or spherical nanoparticles (depending on the type of the porous structure) with narrow particle size distribution.[187, 188] Sometimes, rapid directed formation of nanoparticles in the matrix is achieved by exposing the system to, *e.g.*, sonication, microwave and laser irradiation.[189–191] However, a rigid porous structure precludes variation of the particle size and morphology during synthesis. As a rule, these parameters are strongly dependent on the pore size and morphology.[192]

The use of structures with variable void sizes seems to be a convenient version of this method. A recently proposed technique involving compounds with layered aluminosilicate structures also seems to be promising.[193] In these compounds the layers are linked together through weak van der Waals forces, which allows one to change the volume of the interplanar space with ease. Besides, a layered structure permits considerable acceleration of gas diffusion in the interplanar space, thus facilitating chemical modification of layered compounds.[194, 195]

Several tens of communications on the preparation of nanocomposites *via* layered compounds have been reported so far.[196–200] Most of them are concerned with aluminosilicates, which have negatively charged layers and cations located in the interplanar space. However, these compounds usually have nonstoichiometric compositions and are highly hydrated and crosslinked, which strongly complicates the synthesis of nanomaterials and has a negative effect on the reproducibility of their properties.[201, 202]

A large surface area and, hence, an excess surface energy of nanoclusters make aggregation processes unavoidable. They are directed towards a decrease in the Gibbs free energy, occur spontaneously and can be described in the framework of the model of conservative self-organisation in the absence of kinetic difficulties. Figure 22 presents a micrograph of a nearly spherical colloidal gold particle obtained after spontaneous aggregation of nanocrystals of average size 35 ± 5 nm.[203] It was quite correctly pointed out[204] that formation of nanostructures from nanoclusters is similar to the formation of bulk crystals from atoms, but the fundamental difference between these processes is that, unlike atoms, clusters are characterised by real surfaces and intercluster boundaries. What is more, cluster–cluster innteractions produce strain as well as excess energy and excess pressure at the cluster boundaries. The excess energy per dislocation can be calculated by the formula

$$E_d = \frac{Gb^2}{4\pi(1-\nu)} \ln \frac{r}{r_0}$$

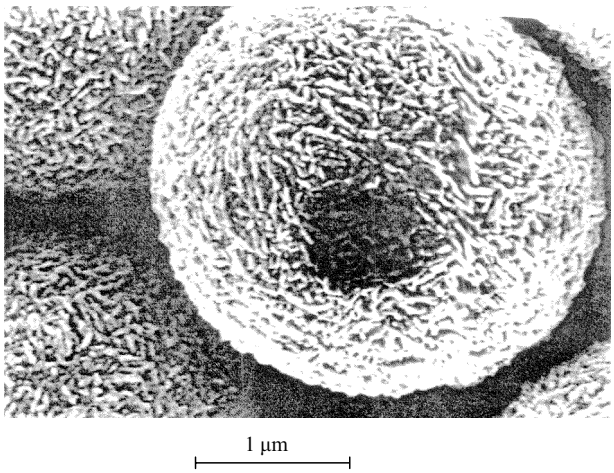


Figure 22. Micrograph of a colloidal gold particle formed upon spontaneous aggregation of nanocrystallites of average size 35 ± 5 nm.

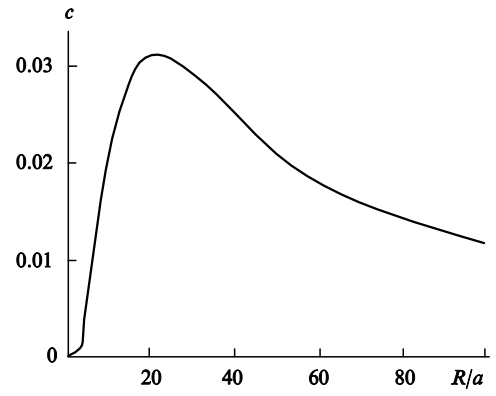


Figure 23. Defect concentration in clusters plotted *vs.* cluster size.

where G is the shear modulus, $\boldsymbol{b}$ is the Burgers vector, which characterises the displacement of the edge dislocation, ν is the Poisson coefficient (usually, $\nu = 0.3$), r is the range of the effect of dislocations and r_0 is the minimum dislocation size. Assuming that the concentration of dislocations in the cluster is determined by the surface-to-volume ratio, the density of the excess energy of a cluster is given by the following expression

$$\varepsilon = \frac{G\boldsymbol{b}^2}{4\pi(1-\nu)}\frac{1}{R}\ln\frac{r}{r_0},$$

where R is the cluster size.

Thus, the density of the excess energy decreases with an increase in the cluster size R and equals zero for the bulk material.

Considering the effect of defects and dislocations on the properties of nanosystems comprised of nanoclusters of arbitrary sizes, one should start from the thermodynamic concentration of defects and dislocations, which includes the chemical potential and excess energy of the cluster surface. The excess energy causes the production of excess pressure, which can be estimated at $\sim 10^9$ Pa for clusters of size 1 nm.[136] Ignoring the difference between the pressure within the cluster and at its surface, the concentration of defects in the cluster (c_0) can be calculated by the formula

$$c_0 = \frac{a(3R^2 - 3aR + a^2)}{R^3},$$

where a is the thickness of the surface layer.

Taking into account the difference between the pressure within the cluster and at its surface, the following expression was derived [136]

$$c = c_0 \exp\left(-\frac{2\alpha V/R}{kT}\right),$$

where α is the surface stress and V is the volume of the defect.

The dependence of c on the cluster size is plotted in Fig. 23. The maximum in the c–$f(R/a)$ curve is observed at $R/a = 25$, which corresponds to $R = 10-50$ nm. This range of cluster sizes provides the maximum concentrations of defects and excess energies, and such clusters are involved in the formation of nanosystems.

Nanostructures comprised of molecular clusters CO_2, N_2 and SF_6 exhibit an increase in strain with increasing cluster size.[205] X-Ray diffraction studies of nanosystems revealed the effect of the cluster size and interfacial strain on the structure of nanosystems.[206] Analysis of nanocrystalline samples of Al, Ru, Cu and AlRu showed [207, 208] that their deformations lie between 1% and 3%, which much exceeds the deformation of coarse-grain metals. Small clusters do not contribute to elastic deformation of the crystal lattice, which is due to interfacial dislocations.[209] The major contribution comes from large nanoclusters. Hence, there is some intermediate range of cluster sizes, corresponding to maximum effect of interfacial strain, which is in agreement with the conclusions drawn based on the thermodynamic model of the influence of structural defects.

Nanosystems possess unusual mechanical properties. At room temperature, their microhardness is 2–7 times higher than that of the corresponding bulk materials. The Vickers microhardness of a cluster is given by the expression [210]

$$H_V \approx H_0 + kR^{-1/2}$$

and increases with a decrease in the cluster size R. Experiments showed that a decrease in the size of Ag, Cu, Pd, Fe and Ni clusters is accompanied by an increase in the hardness of nanosystems.[211] The microhardness of a nanosystem also depends on the treatment conditions, which affect the interface structure, cluster–cluster interactions and the cluster size. For instance, relaxation and annealing of interfacial defects at a constant size of $Al_{98.5}Mg_{1.5}$ clusters ($R \approx 150$ nm) cause a decrease in the microhardness from 1.7 to 1.45 GPa.[212] However, annealing has a much more pronounced effect on R. In particular, heat treatment of a nanosystem comprised of palladium clusters at 475–600 K results in an increase in the cluster sizes and, correspondingly, in a nearly three-fold decrease in the microhardness of the system.

Yet another remarkable feature of nanosystems is their superplasticity, which was observed [213] for nanocrystalline Ni and Ni_3Al at 470 and 450 °C, respectively (this is nearly one third of the melting temperatures of these compounds). Superplasticity of oxide ceramics is of considerable interest for both theoretical studies and practical implementation. This property manifests itself at cluster sizes lying between 1 nm and 1 μm; the cluster size should not change on heat treatment.[214] The presence of amorphous phases can influence the superplasticity effect.[215]

Structural transformations in nanosystems also attract considerable attention. It was established [216] that nanoclusters comprised of thermodynamically unstable γ-Fe phase are stable even at room temperature, whereas bulk samples are stable only at 800 °C. Cadmium sulfide nanoclusters with a rock salt structure are also known;[217] a bulk sample of CdS with the same structure is stable at high pressure only. Stabilisation of nonequilibrium (at a given temperature) structures due to formation of small clusters ($R < 10$ nm) can be explained by the effects of the surface energy and the surface pressure, which can be as high as several GPa for clusters of size 1–2 nm.

Thermodynamic features of the behaviour of nanosystems including surface phenomena, phase transformations and aggregation of free molecules or ions into various supramolecular structures have also been studied.[218, 219]

IX. Fractal, epitaxial, template structures and nanocomposites

The evolution of any physicochemical systems existing under nonequilibrium conditions can involve formation of various structures (including fractal, epitaxial and template ones) and nanocomposites.

Formation of fractal structures in macroscopic and nanosystems is due to manifestation of dissipative self-organisation under such conditions where the driving force of the process (*e.g.*, the temperature or chemical potential gradient) exceeds a critical value corresponding to the bifurcation point. Many materials have fractal structures in different stages of preparation and exploitation.[220, 221] A classical example is provided by the formation of fractal particles during aggregation in solutions and gases.[222–224] The formation of dendritic structures in the course of, *e.g.*, nonequilibrium electrochemical deposition of metals, solidification of alloys under strong supercooling conditions or phase separation processes is also well known.[224–227] The surface structures of many catalysts and adsorbents are also described in terms of fractal geometry.[228] Finally, cracks and surfaces, which develop on fracture of many materials, also have a fractal structure.[229–231] Clearly, periodic geometric patterns characteristic of fractal objects strongly affect their behaviour in various physicochemical processes, among which the most important for materials science are heat treatment processes, catalytic and surface phenomena and solid-phase reactions. The fractal structure also influences the characteristics of diffusion in such objects.

The main laws and peculiarities of diffusion processes and reactions in fractal media, which do not involve changes in the fractal structure, have been studied in considerable detail.[232–235] Much less attention has been paid to the effects of excess surface energy and to significant geometric nonuniformity on the thermodynamic and kinetic properties of fractal objects (in particular, on their behaviour during ageing, sintering, *etc.*). Here, of particular interest for materials science is the evolution of dendritic inclusions on annealing, as well as crack healing in ceramic materials, structural changes in composites at elevated temperatures, *etc.* A common property of these processes is that they occur with a constant amount of matter in the system (*i.e.*, at a conserved order parameter). This differs from dissolution of particles in reactive media or etching.

A computer simulation of the evolution of fractal particles in systems with a conserved order parameter during ageing and sintering has been reported.[236] The fractal cluster was generated by the diffusion limited aggregation (DLA) mechanism with preset joining probabilities assuming that the change in the density at each point of the cluster is described by the Cahn–Hilliard equation

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \nabla^2 c - V(c),$$

where c is the dimensionless density ($0 \ll c \ll 1$); $V(c) = K(c^2 - c)^2$ is the potential whose minima correspond to the bulk ($c = 1$) and free ($c = 0$) phases and K is a constant. At different stages of evolution, the geometry of the structure of the particles thus obtained was characterised using the box-counting method and by analysing the correlation functions. It was found that the observed evolution pattern is strongly dependent on the geometry of the seed particles, which is prescribed by the ratio of the upper and lower fractality boundaries, $R_{\max}/R_{\min}$, and by the fractal dimension D.

It was also found[236] that, depending on the self-similarity range of the 'seed,' the evolution of the fractal cluster can occur in different manners, namely, with and without fragmentation of the initial particles (long-range and short-range cases shown in Figs 24 and 25, respectively).

The principle of orientational and dimensional correspondence, which was first formulated by Konobeevskii and then by Dankov (see Ref. 237), serves as the basis for the growth of epitaxial structures. According to this principle, the shape and orientation of the seeds of new phases crystallising in an anisotropic medium should correspond to the free energy minimum, which is achieved when the patterns of atomic arrangement in adjacent faces of the new and old phases are best matched. The condition for oriented crystallisation has the form of inequality

$$A + E - Z \leqslant A_1,$$

where A and E are respectively the work of formation and the energy of two-dimensional nucleus for oriented crystallisation; Z is the work of adhesion (adhesive forces are responsible for enhanced deformation); and A_1 is the work of formation of a three-dimensional nucleus in the case of spontaneous crystallisation. It was shown[238, 239] that oriented crystallisation is possible if the parameters of the lattices to be matched differ by at most 18%.

It was established[240] that epitaxial stabilisation is often followed by the formation of film structures, which are thermodynamically unstable in the absence of such a stabilisation. This can be exemplified by the formation of thin films of REE-containing nickelates and cobaltites on $LaAlO_3$, $SrTiO_3$ and

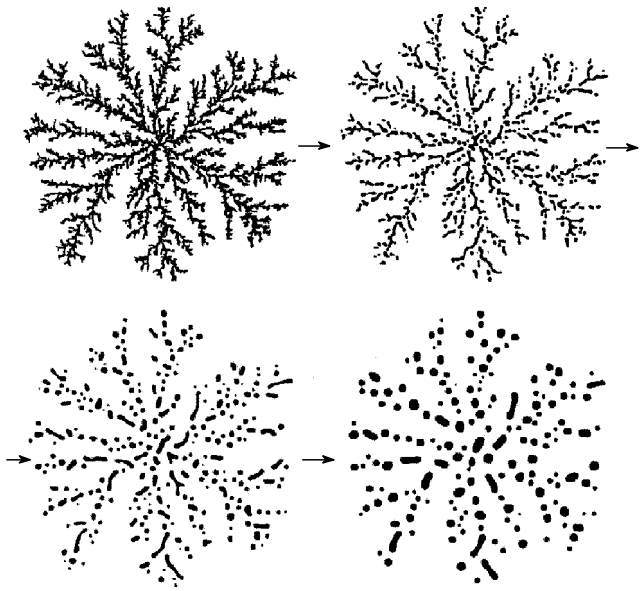


Figure 24. Evolution of a fractal cluster involving fragmentation.

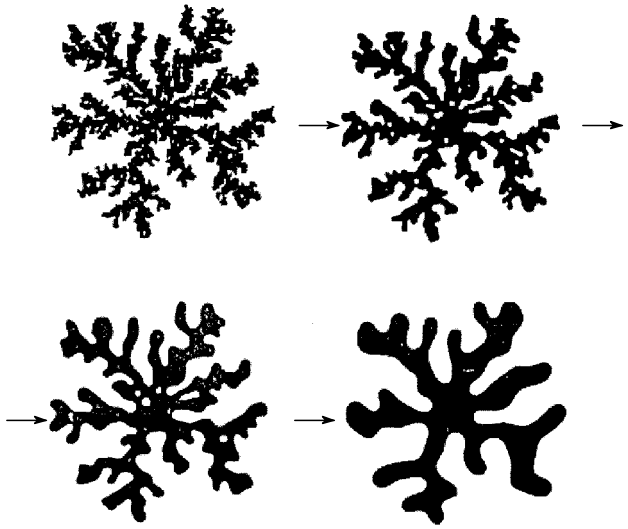


Figure 25. Evolution of a fractal cluster involving no fragmentation.

$NdGaO_3$ substrates, though the changes in the Gibbs free energy of the reactions

$$\frac{1}{2}R_2O_3 + \frac{1}{2}Ni_2O_3 = RNiO_3,$$

$$\frac{1}{2}R_2O_3 + \frac{1}{2}Co_2O_3 = RCoO_3$$

are positive and, hence, the bulk phases of the nickelates and cobaltites are thermodynamically unstable.

Stabilisation of epitaxial structures can also be exemplified by the behaviour of bulk samples of REE-containing manganites $RMnO_3$, which can be divided into two groups, namely, samples with a perovskite structure (*Pnma*) for the early REE (R = La–Dy) and samples with hexagonal structures ($P6_3mc$) for the late REE (R = Ho–Lu). Figure 26 presents the Δ_fG° of the reaction

$$\frac{1}{2}R_2O_3 + \frac{1}{2}Mn_2O_3 = RMnO_3 \quad (1)$$

plotted *vs.* the ionic radius of REE, which confirms the above-mentioned structural evolution.[241]

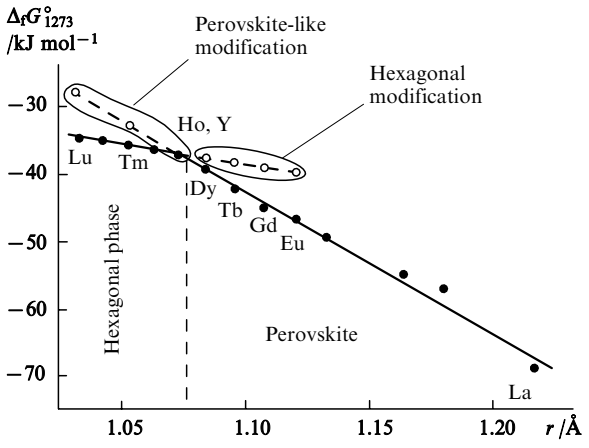


Figure 26. Plot of Δ_fG° for reaction (1) *vs.* ionic radius of REE.[241]

However, it is possible to grow thin films of (i) manganites of the late REE with the perovskite structure on substrates with the perovskite structure and (ii) manganites of the early REE with a hexagonal structure on substrates with the hexagonal structure under conditions of epitaxial growth. In other words, the oxide substrate can 'force' the film of the REE-containing manganite to grow following the epitaxial pattern, which is atypical of the manganite film under the equilibrium synthesis conditions.[241]

It should be noted that heteroepitaxy of the vapour and liquid phases on single crystals or biaxially textured substrates is efficient only when preparing oriented films of thickness at most 1 μm. Epitaxial effects dramatically weaken as the film thickness increases. Usually, thin epitaxial films exhibit record values of specific characteristics (*e.g.*, the maximum critical current densities for superconducting cuprates). However, they cannot be used to achieve high absolute values of operating parameters, as is the case of bulk ceramics, which, unfortunately, possesses poor mechanical properties (first of all, it is highly brittle). A way out was to use a hybrid method elaborated by researchers from the Aachen Centre for solidification in space (Germany) and the Department of Chemistry, M V Lomonosov Moscow State University. To obtain textured thick (50 to 100 μm) superconducting films, the orientational effect of the substrate (formally, it is similar to the epitaxial effect in the case of thin films) was combined with the melt growth of large grains, which is typical of bulk materials.[242] Here, the substrate had an artificial symmetrical relief, which matched the symmetry (grooves or a square grid) and typical sizes (0.1–1 mm) of the crystallising $YBa_2Cu_3O_x$ phase (Fig. 27), instead of short-range orientational effect (molecular epitaxy). By creating such a surface relief using strips made of cheap, untextured commercially available polycrystalline silver as the substrate it is possible to obtain up to 90% of the *ab*-biaxially textured, melt grown crystallites of high-temperature superconductors.

The origin of texture formation is based on various physicochemical phenomena including wetting (some specific aspects), surface tension, meniscus, heterogeneous nucleation, redistribution of melt components, capillary effects, effects of crystallisation pressure and topographic wall effect of relief elements.[242, 243] By analogy with 'graphoepitaxy' (a well-known thin-film process),[243, 244] a 'graphotexturing' technique was developed, which can be employed in studies of various materials and arbitrary substrates. This approach can lead to virtually complete texturing of a polycrystalline layer in accord with the relief symmetry. The process occurs as a 'self-assembly' of the crystallite layer at the mesoscopic level. All tape fragments behave identically, so that the length of the tape crystallising per unit of time can be infinitely long provided that the entire sample is heat treated in the furnace.

Porous structures with pore sizes ranging from 10 nm to 10 μm can be formed using template synthesis,[245–248] which is exemplified by Fig. 28. Structural units of the matrix to be formed self-organise into a continuous framework around the template particles. The structure obtained after post-synthetic removal of the template contains channels, which exactly match the size and shape of the template. Once the framework is formed, the template (most often, polystyrene or silica beads) is removed. Namely, polystyrene beads are burnt out in air or dissolved in toluene, while silica beads are etched with hydrofluoric acid. Typical examples of template porous structures are shown in Fig. 29.[249] Template synthesis is convenient for preparation of mesoporous, metal,[250, 251] metal oxide,[252–254] chalcogenide,[255, 256] polymeric[257] and silica[253, 258] materials. This method is of prime interest for the formation of photonic crystals (periodic structures comprised of fragments with different dielectric constants). The most important feature of photonic crystals is the forbidden photon energy band, which excludes passage of photons with a particular wavelength through the crystal. Photonic crystals are similar to semiconductor crystals but manipulate photons rather than electrons, thus opening new prospects for development of photonic applications.

In contrast to semiconductor crystals that are characterised by spontaneous formation of periodic atomic structure, photonic

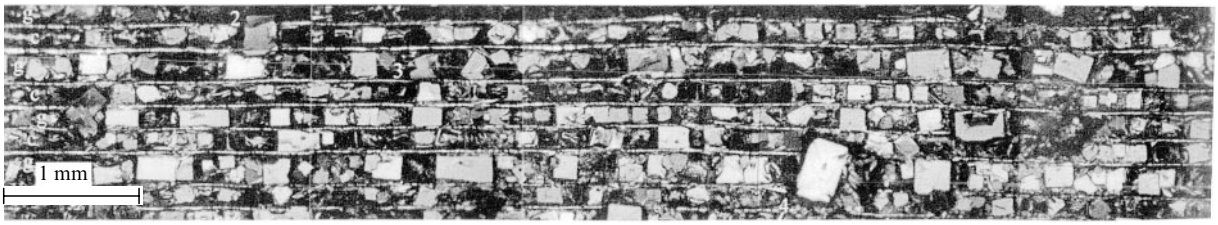


Figure 27. Biaxial texturing of superconducting phase $YBa_2Cu_3O_x$ on a silver substrate with artificial relief.

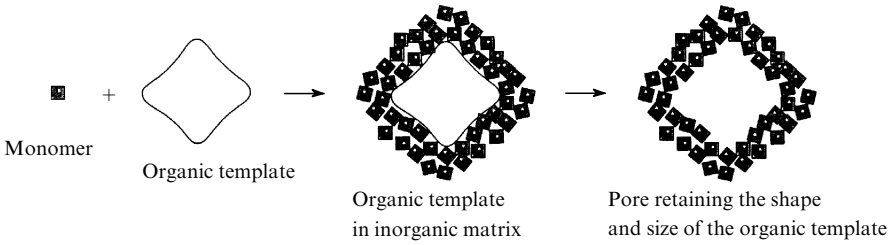


Figure 28. Scheme of the template synthesis of porous structures.

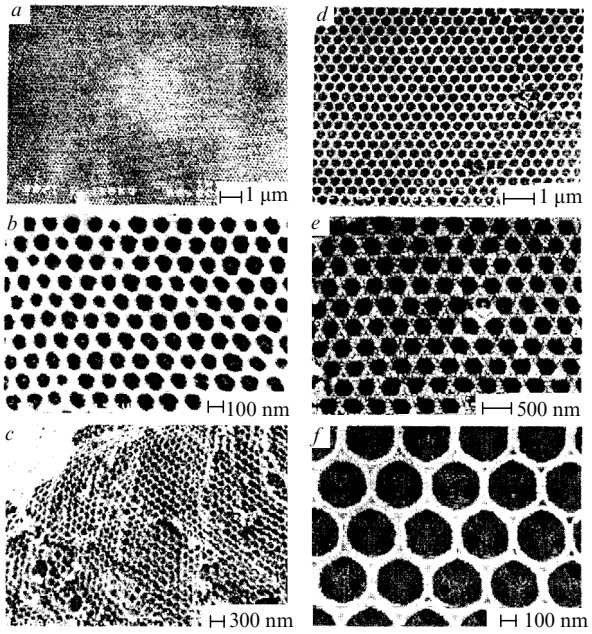


Figure 29. Typical examples of porous template structures in polyurethane-based polymeric materials (*a*–*c*) and in ceramics based on SiO_2 (*d*), SnO_2 (*e*) and TiO_2 (*f*).

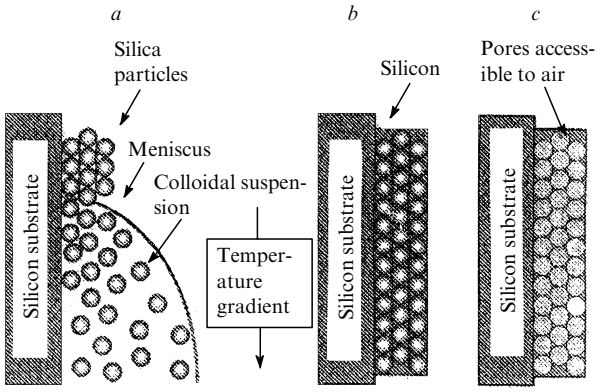


Figure 30. Scheme of the template synthesis of photonic silicon crystals (for details, see text).

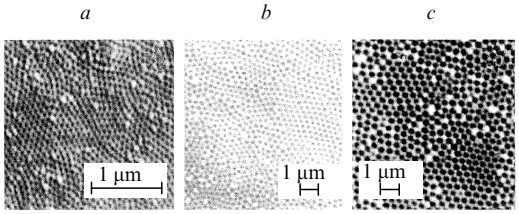


Figure 31. Micrographs of porous alumina film prepared by anodic oxidation of aluminium foil under different conditions.
$H_2C_2O_4$, 40 V (*a*); H_3PO_4, 140 V (*b*); and H_3PO_3, 195 V (*c*).

crystals are produced artificially using specific methods of template synthesis. The 'lattice' constant of a photonic crystal is comparable with the wavelength of light (of the order of 1 μm), which is more than three orders of magnitude larger than typical lattice constants of 'normal' crystals. At the same time, this value is nearly two orders of magnitude smaller than the diameter of a human hair. A version of template synthesis of photonic silicon crystals elaborated by Vlasov *et al.*[259] is illustrated in Fig. 30. The technique is based on self-organisation of colloidal spherical silica particles that act as an ordered template. The starting point is ordered, temperature gradient driven self-organisation of silica particles on the surface of a vertical silicon plate due to surface tension by evaporation of solvent (Fig. 30 *a*). The temperature gradient permits minimisation of undesired sedimentation processes. The space between spherical silica particles is uniformly filled with silicon using a CVD technique (Fig. 30 *b*). Then, silica is etched with hydrofluoric acid to leave a photonic crystal, *i.e.*, a periodic three-dimensional structure comprised of a porous silicon framework adjacent to the silicon chip (Fig. 30 *c*). Thus, self-organisation processes play a key role in the formation of template structures including photonic crystals.[260] Two-dimensional photonic structures, *e.g.*, alumina films (Fig. 31), are also of interest. Here, the ordered pore system is formed as a result of self-organisation of alumina films during the oxidation of aluminium.[261]

As mentioned in the preceding Section, nanocomposites (*i.e.*, composites comprised of nanoparticles encapsulated in a chemically inert matrix) belong to those promising materials whose formation is strongly affected by self-organisation processes. In this case, the matrix allows one to avoid uncontrollable aggregation of nanoparticles and protect them from external factors (*e.g.*, oxidation by air oxygen), thus facilitating practical use of such materials. Considerable attention has been paid to the method for preparation of nanocomposites,[196,262–264] which is based on chemical modification of layered double hydroxides (LDH). The LDH are compounds of the compositions $[M^{z+}_{1-x}M^{3+}_x(OH)_2]^{A+}\cdot[(A^{n-})_{A/n}\cdot m\,H_2O]$, where $A = x$ at $z = 2$ and $A = 2x-1$ at $z = 1$, M^{z+} is the metal in the oxidation state $+2$ or Li^+, M^{3+} is the metal in the oxidation state $+3$ and A^{n-} is any anion incapable of forming stable complexes with these cations.[265] The structure of LDH comprises positively charged hydroxide layers $[M^{z+}_{1-x}M^{3+}_x(OH)_2]^{A+}$ and anions present in the interplanar space (Fig. 32), which is usually filled with labile water molecules too. This structure was named hydrotalcite after a natural mineral of the composition $Mg_{1-x}Al_x(OH)_2[(CO_3)_{x/2}\cdot m\,H_2O]$ ($x \sim 0.25$, $m \sim 0.5$). The method for the synthesis of nanocomposites is based on chemical modification of the anions present in the interplanar space of LDH. The reaction zone is confined by the hydroxide layers, which makes the conditions for the synthesis of

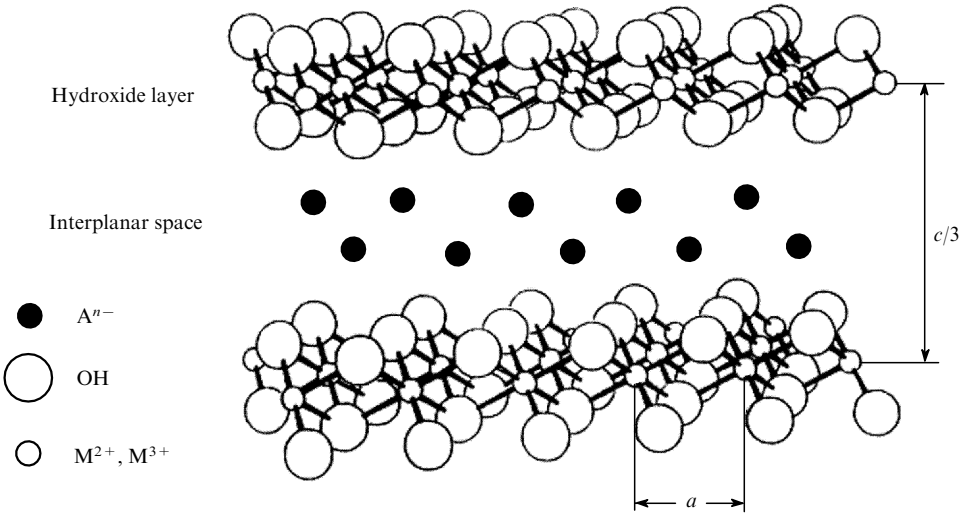


Figure 32. LDH structure.

nanophase similar to the conditions for the synthesis in two-dimensional nanoreactors.

Compounds like clays, zeolites and Chevreul's phases also have layered structures; however, only the LDH possess some unique properties that are of great importance for directed synthesis of nanomaterials.[266] On the one hand, the LDH containing a very broad range of cations and anions (compounds with $M^{2+} = Mg^{2+}$, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+} and $M^{3+} = Al^{3+}$, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Sc^{3+}, Ga^{3+}, Ln^{3+} have been characterised to date) retain stable layered structures and the interplanar space of the Mg-Al LDH can be intercalated with various anions of sizes 3 to 50 Å. On the other hand, the number of anions present in the interplanar space of the LDH is determined by the M^{2+}/M^{3+} ratio, which can be controlled with ease during the synthesis. This allows preparation of LDH with a prescribed stoichiometric composition and, hence, variation of the concentration of the reactive sites in the matrix. Besides, these compounds can retain the layered structure on thermal decomposition due to high rate of gas diffusion in the interplanar space. This permits chemical reactions involving the anions present in the interplanar space to be carried out at elevated temperatures (*e.g.*, hydrogen reduction, which is necessary for preparation of magnetic nanocomposites) without breaking the matrix that confines the reaction zone.

This synthetic approach was employed for the preparation of various LDH-based functional nanocomposites (*e.g.*, magnetic Fe- and Ni-containing nanocomposites).[263, 267] To this end, the Mg-Al LDH of various cationic compositions were intercalated with anionic complexes of these metals [$Fe(EDTA)^-$ and $Ni(EDTA)^{2-}$]. The anion-substituted LDH thus obtained were reduced in a hydrogen flow at different temperatures (Fig. 33). It was shown that, depending on the LDH compositions and reduction conditions, the reaction results in one-, two- and three-dimensional metal nanostructures (Fig. 34). An increase in the content of the complex in the LDH matrix causes a decrease in the dimension of the newly formed nanostructures and an increase in the anisotropy factor. It should be noted that lowering the temperature has virtually no effect on the morphology of the nanoparticles thus formed. Namely, an increase in the reduction temperature leads to an increase in the average size of nanoparticles, while the ratio of their linear dimensions (anisotropy factor) varies only slightly. By varying the reduction temperature it is possible to vary the sizes of the newly forming nanoparticles over a rather wide range from several to several tens of nanometres. The results obtained show that magnetic nanocomposites thus obtained can be promising materials for memory devices with ultrahigh recording density.[268]

The possibility of using the LDH for preparation of semiconductor PbS nanoparticles coated with an amorphous sulfur shell is of considerable interest.[269, 270] The sulfur shell allows a substantial increase in the luminescence intensity and quantum yield. Usually, the preparation of such nanostructures requires multistage synthesis. The use of LDH allowed a single-stage synthesis of matrix isolated PbS/S nanostructures by photochemical modification of Mg-Al LDH intercalated with $[Pb(S_2O_3)_2]^{2-}$ anions (Fig. 35). Nanocomposites thus obtained possess unusual

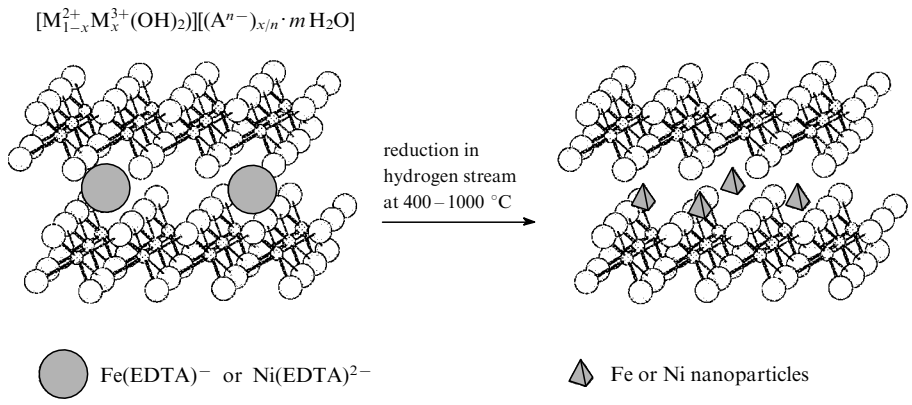


Figure 33. Scheme of preparation of nanocomposites based on iron or nickel.

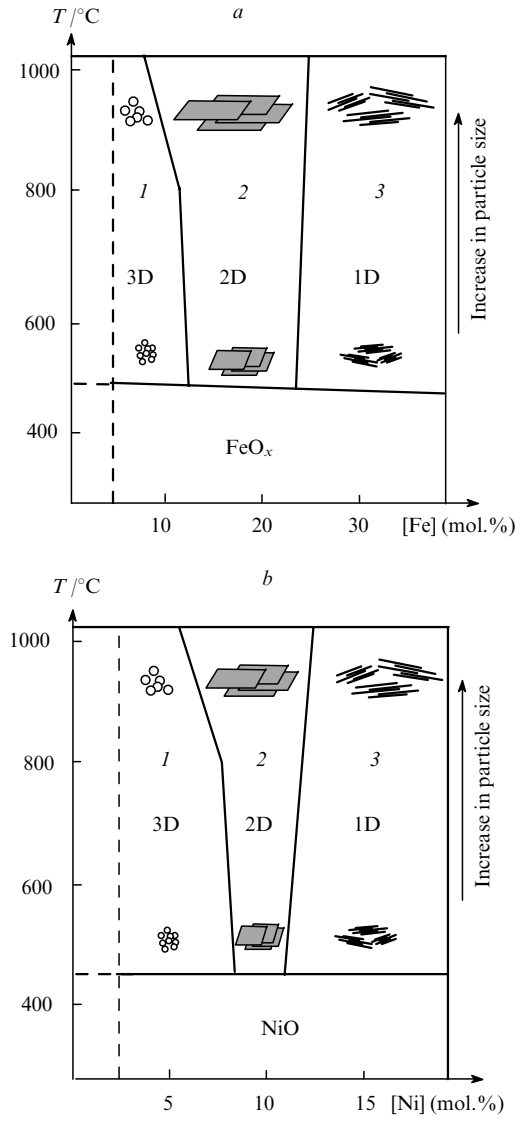


Figure 34. Diagrams showing the formation regions of different types of particles in Mg–Al–Fe(EDTA)$^-$ (*a*) and Mg–Al–Ni(EDTA)$^{2-}$(*b*) systems.
(*a*): Iron spheres of size 1–10 nm (*1*), iron plates 10–100 nm long and 1–3 nm thick (*2*) and iron wires 10–100 nm long and 1–5 nm thick (*3*); (*b*): nickel spheres of size 1–10 nm (*1*), nickel plates 10–70 nm long and 1–3 nm thick (*2*) and nickel wires 10–150 nm long and 1–5 nm thick (*3*).

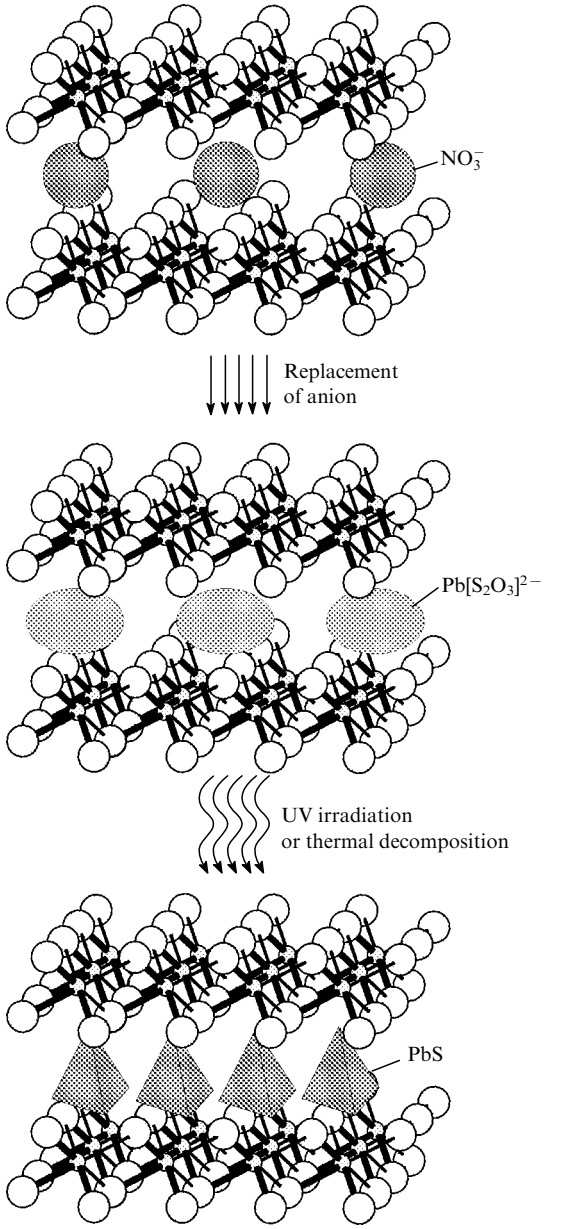


Figure 35. Scheme of the synthesis of PbS nanoparticles in a LDH matrix.

optical properties (increased luminescence intensity, additional exciton bands in absorption spectra) due to modification of the surface of PbS nanoparticles with amorphous sulfur (Fig. 36). The use of Mg-Al LDH as precursors allows exact control of the amount of nanoparticles in the matrix by varying the Mg/Al ratio in the initial stage of the synthesis of LDH. This is of crucial importance for fabrication of optical devices based on quantum dots.

Platinum nanoparticles can be obtained in the LDH matrix in one stage.[271] Reduction of LDH intercalated with hexahydroxoplatinate(IV) anions is accompanied by the formation of platinum nanoparticles of a size of at most 10 nm. The specific catalytic activity of such nanocomposites in the oxidation of CO, hydrocarbons and alcohols is ten to fifty times higher than the activity of bulk platinum metal. As a consequence, these nanocomposites seem to be promising catalysts for the afterburning of exhaust gases. It should be noted that the approach involving LDH is not limited to preparation of the above-mentioned nanomaterials. The availability of the starting compounds, simplicity and low cost of synthetic procedure, ease of control of the composition of both intermediates and end products, as well as the possibility of intercalating the LDH structure with various cations and anions make this method rather promising for the preparation of virtually all classes of nanocomposites.

Yet another method for the synthesis of nanocomposites is based on matrix stabilisation of metal and metal oxide nanoparticles of size less than 50 nm as a result of the polymerisation reaction proceeding within the solid phase.[272, 273] In other words, the technique combines the formation of both nanoparticles and polymer matrix to stabilise them. The process proceeds as copolymerisation of metal-containing monomers that form the polymer matrix. Supramolecular organisation of nanocomposites is achieved as a result of controlled thermal transformation of the metal-containing monomers in an inert atmosphere. The main stages of this transformation are dehydration and thermal copolymerisation including self-propagating frontal polymerisation and controlled pyrolysis of the product obtained.

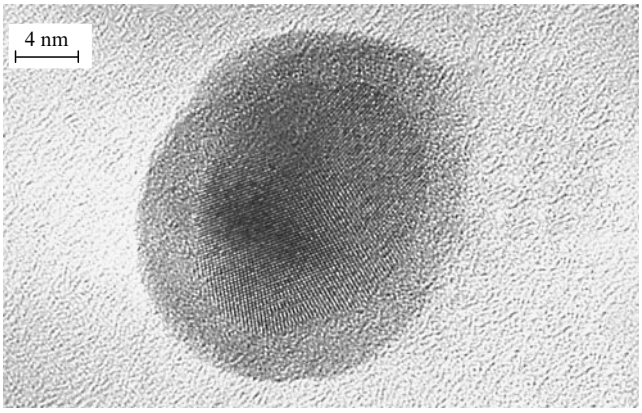


Figure 36. High-resolution electron micrograph of a PbS – amorphous sulfur core – shell nanoparticle in a LDH matrix.

By varying the copolymerisation conditions and pyrolysis temperature it is possible to prepare both nanoparticles of desired size and the necessary particle size distribution within the polymer matrix with controllable composition and thickness. The nanoparticles thus obtained are chemically bound to the polymer matrix in which they are present. Typical monomers are methacrylate, maleate and acrylamide complexes of d-metals (Co, Ni, Fe, Mn, Ti, Zr, Hf, *etc*.).

When preparing nanocomposites possessing synergistic properties, particular emphasis is placed on co-polycondensation of one or more monomeric metal complexes including both main-group (Ba, Zn, Cd, Pb) and rare-earth (Eu, La, Nd) elements. In particular, controlled thermolysis of Fe_2CoAcr_5 causes amorphisation of the starting crystalline phases, while the magnetic product ($CoFe_2O_4$) is formed in the last stage of the process. The nanocomposite thus obtained exhibits unusual properties (*e.g*., a non-symmetric hysteresis loop and anomalous coupling between the antiferromagnetic and ferrimagnetic phases). Each magnetic particle of the nanocomposite is comprised of a spherical ferrimagnetic core (8 – 12 nm) and a spin glass shell 8 to 10 nm thick; ensembles of such particles can be an efficient magnetic medium.

A particular group of compounds comprises hybrid nanocomposites, which are formed from organic molecules or macromolecules (templates) and inorganic components containing optically active molecules or ions. Using methods of 'soft chemistry' and self-assembly at nanolevel, it is possible to create highly complex hierarchical structures with unique optical properties including high light emissive power and photochromic and electroluminescent effects.[274]

X. Biomimetism as route to advanced materials

One of the most attractive avenues in design of advanced materials involves the use of biomimetic approaches.[275, 276] A living organism is a complex dynamic system, which exists due to continuous exchange with the environment. The exchange occurs by breathing, nourishment and excretion. In other words, dissipative self-organisation is intrinsic in any living organism.[277] However, this does not exclude conservative self-organisation processes in certain regions of a complex system. And though the processes of conservative and dissipative self-organisation are to some extent the reverse of each other (conservative self-organisation is a result of the evolution of the system towards a decrease in the Gibbs free energy, which is achieved at high temperatures due to an increase in entropy, while dissipative self-organisation is a result of the evolution of the system towards a decrease in entropy), they likely co-exist and make different contributions to the vital activity of the complex system.[30, 31]

Undoubtedly, both geological and biological evolution of matter obey the laws of nonlinear dynamics, but the interrelation between the processes of conservative and dissipative self-organisation changes in favour of the latter on going from inanimated to organised matter.[278] Clearly, the pre-biological or geological evolution associated with transition from plasma to molecules, condensed phase and then to formation of simple and complex minerals is determined by processes of conservative self-organisation,[279] whereas the phenomenon of life is intimately associated with dissipative self-organisation.[280] Time is also of paramount importance for evolution.[281] Creating more or less complex artificial inorganic or organic structures, researchers accelerate particular processes by varying the temperature, pressure, chemical potentials of reagents, *etc*. Illustrative examples are provided by fabrication of synthetic diamonds, opals, complex oxides with spinel, perovskite, pyroxene, *etc*. structures. Considerable progress has been made towards hydrothermal synthesis of natural minerals,[282] which demonstrated high efficiency of approaches based on geomimetism.[283] Some efforts have been undertaken, aimed at 'adjusting' nature by creating more perfect biological systems or their fragments by, *e.g*., cloning. In the course of pre-biological evolution any system tends to reach a state that is most stable towards faults or fluctuations. At the same time, an increase in the complexity of a system accelerates the exchange of matter and energy, *i.e*., biological evolution. This statement to some extent contradicts inferences about slowing down metabolism during the evolution of living systems in the course of natural selection. Nevertheless, approaches developed to create models of evolution can be employed for chemical engineering of various materials.[284]

One of the simplest methods involves the use of biomineralisation processes, in which the conditions for nucleation and crystal growth of inorganic phases are determined by the organised surface of an organic matrix. Biomineralisation processes allow preparation of various inorganic materials with nearly identical crystallites of particular compositions and structure at moderate supersaturations and temperatures.[285, 286] A classical example is provided by the formation of oriented chains of monodomain magnetite crystals [287] or metastable ferromagnetic based on iron sulfide involving magnetic bacteria.[288, 289] This opens up a way towards cryochemical synthesis of advanced magnetic materials. As a rule, particles of the magnetic material are similar in size to one another and often have an unusual metastable structure.

Yet another feature of biomimetism is preferred crystallographic orientation of inorganic material relative to the organic matrix,[290] which often represents a supramolecular structure and is comprised of polypeptide layers, polysaccharide matrices or protolipid membranes. Subsequent ordering of such organised inorgano-organic composites often causes formation of hierarchical structures,[291, 292] which can be exemplified by mollusk shells. For instance, the shell of *Atrina sp*. comprises a layer of calcite crystals coated with an organic sheath and ordered with formation of a coherent structure. This structure is typical of many types of bioceramics and characterised by unusual structural properties. For instance, the tensile strength of bioceramics is several orders of magnitude higher than that of a material of the same composition prepared in a conventional manner.

The mechanism of the effect of an organic matrix on crystallisation of inorganic compounds was initially described in the framework of epitaxial relationships based on crystallographic similarity.[293] More recently,[294 – 296] it was shown that the mechanism of the influence of ordered organic matrix on the nucleation of inorganic compounds is more complicated, being a combination of at least three interfacial processes including adsorption and ordering of charged particles on the surface of the organic matrix, transcription of geometric information through ordered cations and the appearance of stoichiometric complementarity between the cations bonded to the head groups of adsorbed monolayer and

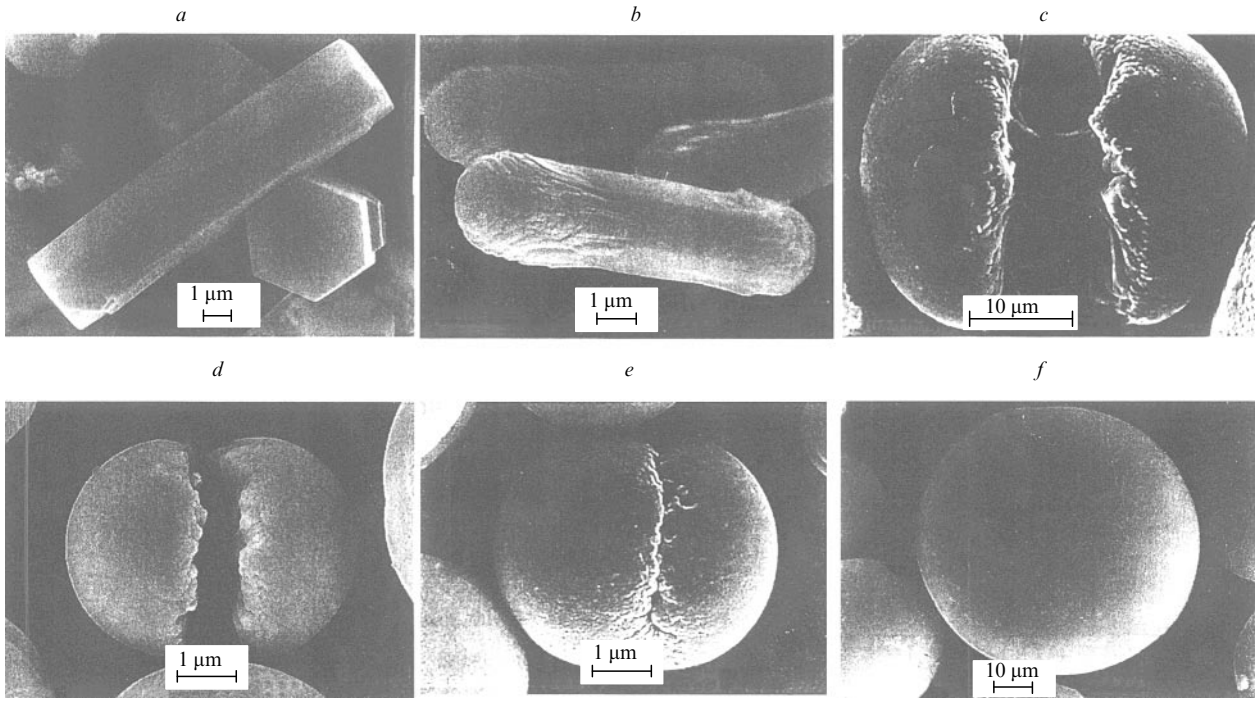


Figure 37. Electron micrographs obtained in different stages of morphogenesis of fluoroapatite aggregates.
Initial stage, elongated hexagonal prismatic seeds 10 μm long (*a*); intermediate stages (dumb-bell aggregates) (*b*–*d*); and final stages (spheroaggregates) (*e*, *f*).[301]

the local coordination environment of ions in the crystal structure of nuclei. Oriented nucleation of inorganic compounds is controlled by molecular recognition of the two-dimensional organic template and the nuclei of inorganic crystals.[297]

Of crucial interest are the results obtained in a study [298] on the morphogenesis of fluoroapatite in denatured collagen (gelatin) matrix, which is in many ways similar to the growth of bone tissue and dentin.[299, 300] The sequence of morphogenesis stages is shown in Fig. 37. The process begins with elongated hexagonal prismatic seeds, which are then transformed into dumb-bell structures by a fractal self-similarity mechanism, and is completed by the formation of spheroaggregates of size 150 μm. It is noteworthy that the surface of the spheroaggregates is comprised of needle-shaped fragments. Figure 38 presents the results of a two-dimensional computer simulation,[301] which clearly illustrates the possibility of fractal growth of the system from a seed to a closed fluoroapatite spheroaggregate. The fractal mechanism of morphogenesis of the fluoroapatite particles was related to the assumption of the existence of intrinsic electric fields that control the crystal growth. This means that both crystalline seeds and products of morphogenesis are permanent dipoles. The polarity of collagen and the structural features of apatites $Ca_5X[PO_4]_3$ ($X = F^-$, Cl^-, OH^-),[302] in which the distribution of the anions X can be varied from centrosymmetrical to non-centrosymmetrical, confirm this model. It should be taken into account that extremely mild biomimetic growth conditions, which must favour a high degree of atomic ordering, cause an asymmetric displacement of the anions X from the equilibrium positions in the mirror plane [303] and a (possible) reduction of symmetry from the centrosymmetrical point group $6/m$ to the pyroelectric point group 6. Finally, the polar organic component and inorganic crystals can exhibit synergism, thus forming an ordered composite structure in

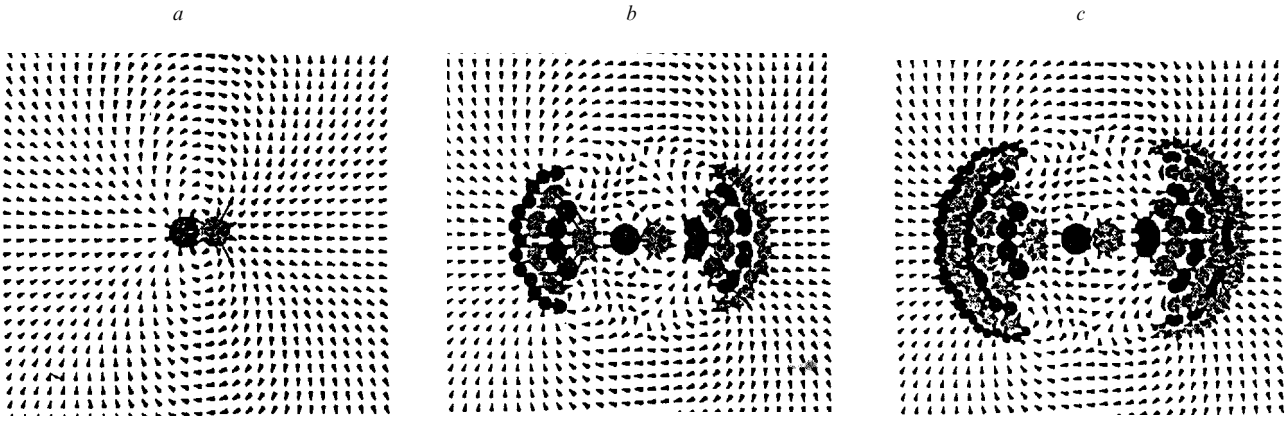


Figure 38. Two-dimensional evolution models of an intrinsic electric field around a growing fluoroapatite spheroaggregate.
Each permanent dipole is represented by a combination of black and gray circles denoting the positive and negative charge, respectively; seeds (*a*); the growing spheroaggregate: seed + 2 generations (*b*) and seed + 3 generations (*c*). Arrows denote the directions of the electric field lines.[301]

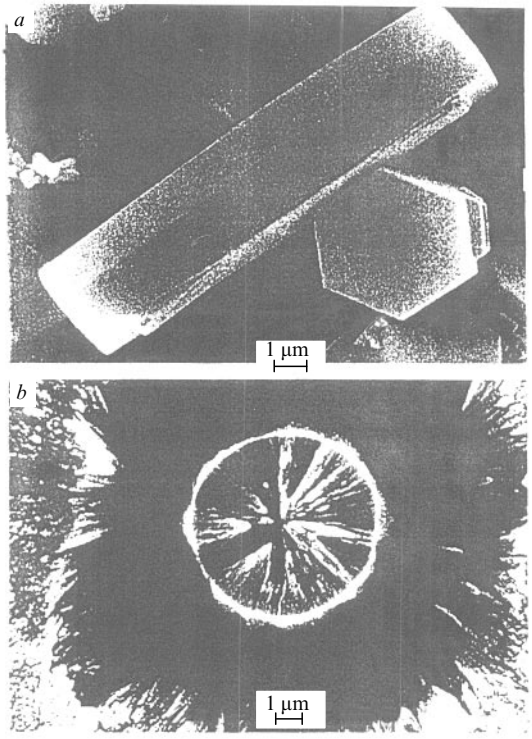


Figure 39. Electron micrographs of a hexagonal prismatic fluoroapatite seed (*a*) and its fracture area perpendicular to the seed axis (*b*).[298]

which the *c* axis of apatite crystals is oriented parallel to the long axis of collagen fibres.[275]

Returning to the morphogenesis of fluoroapatite, it should be noted that completion of the fractal growth (formation of spherical particles) is followed by formation of concentric shells comprised of elongated prismatic fluoroapatite seeds with nearly parallel orientation (the maximum diameter of the core + shell particle is 1 nm) and that the structure of the particle has much in common with the structure of dentin. Hexagonal prismatic seeds of fractal aggregates (see Fig. 39) are not single crystals, as is clearly demonstrated in the micrograph of the fracture area perpendicular to the seed axis. The cross-section shows that formation of the hexagonal prism begins with the central seed, which can be formed due to rearrangements of the gelatin molecules, which can serve as active nucleation centres of apatite. The size of apatite crystallites was not exactly determined, it can lie between nanoscale and mesoscopic levels. Thus, the hexagonal prismatic macroscopic seed is an inorgano-organic composite with an ordered hierarchical supestructure rather than a single crystal.

XI. Conclusion

Modern revolutionary changes in chemistry and technology of materials are closely related to the changes in the fundamental concepts of spatio-temporal evolution of materials.[304]

Self-organisation processes in the physicochemical systems used as precursors are of great importance for the design of advanced materials, since usually their evolution occurs under strongly nonequilibrium conditions. Conservative and dissipative self-organisation, which best manifest themselves in isolated and open systems, respectively, can accompany each other, thus making the description of the evolution of corresponding physicochemical systems much more complicated. Nonlinear patterns of evolution from precursor to the target solid-phase product complicates the optimum organisation of the reaction zone. Ideally, the precursor or the solid-phase intermediate from which the solid-phase product is formed must be a composite comprised of a highly homogeneous amorphous matrix and a nanotemplate, which provides a necessary direction of bulk crystallisation.

Application of dissipative chaos models to poorly reproducible physicochemical systems allows valuable information on their dynamics to be obtained. Of crucial importance are the self-organisation processes with formation of supramolecular ensembles and supramolecular materials bonded through noncovalent intermolecular bonds.[305]

Research on self-organisation phenomena in nanosystems [147] provides an insight into the conditions for formation of various structures (from nanocrystals to nanocomposites). Particular emphasis should be placed on the formation of fractal, epitaxial and template structures as well as nanocomposites that are used in the design of functional materials.

The use of models of bio-evolution, biomimetism and biomineralisation opens up attractive prospects for the creation of smart materials that will be highly competitive with natural materials and in some cases be superior to them.[306–308]

The author of this review would consider the goal sought in writing this review attained if he was able to show that the most promising and 'stylish' avenues of research in the field of materials science, which are associated with the design of seemingly quite different materials, have much in common. This first of all concerns the algorithm of description of complex open physicochemical systems, which exchange energy and matter with the environment but allow control of the evolution from precursors to target solid-phase products.

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