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Supramolecular assemblies in eutectic alloys

V S Pervov, I D Mikheikin, E V Makhonina, V D Butskii

Contents

I.	Main concepts and state-of-the-art in the theory of eutectics	759
II.	Main concepts and objects of inorganic supramolecular chemistry	762
III.	Static Frenkel – Kontorova model for finite systems	763
IV.	Supramolecular concept in the theory of eutectics	765
V.	Conclusion	767

Abstract. The main concepts of the theory of eutectics are analysed. The most essential results of investigations on eutectic alloys of inorganic compounds are surveyed. Evidence in favour of the supramolecular concept of eutectics is presented. This concept takes into account interactions of incommensurate substructures and gives an insight into the mechanisms of formation of supramolecular eutectic assemblies in boundary regions ('non-autonomous phases'). Using the static one-dimensional Frenkel – Kontorova model for finite systems, it is shown that the consideration of these mechanisms in terms of supramolecular chemistry simplifies analysis of the behaviour of inorganic eutectic systems in the course of crystallisation under conditions both close to and far from equilibrium, including crystallization upon quenching and under external actions. The supramolecular concept bridges gaps between the definitions 'compound', 'eutectic' and 'solution' in physicochemical analysis. The bibliography includes 83 references.

I. Main concepts and state-of-the-art in the theory of eutectics

Theoretical views of the nature of eutectic alloys were formed more than 80 years ago. Since then these views have gained wide acceptance. However, authors of a number of papers and monographs (see, for examples, Refs 1 and 2) stated their justified belief that the theory of eutectics is inconsistent with up-to-date knowledge. Thus, this theory fails to explain the fact that eutectics have low melting points, leaves unexplained the mechanism of the initial step of melting and gives no clear answer to the question as to why a 'mixture' of crystals of two compounds is molten and crystallises at the same temperature.[2] A sharp increase in the mutual solubility of components as the eutectic temperature passes through the liquidus line is inconsistent with the known data that melting leads to only small changes in interatomic distances (melting of many metals and salts is even accompanied by a decrease in interatomic distances [3]).

Numerous studies of eutectics can be divided into three main groups. The first group involves data on the structures and morphology of eutectics (including attempts to classify eutectics). The second group includes theoretical studies of possible mechanisms of solidification of eutectic materials of different types. Results of recent studies of interphase and intergrain boundaries and structures of melts belong to the third group. Micromorphological structural features of eutectic composites ('eutectic grains' or 'colonies' [4 – 6]) were most extensively studied in the 1920s – 1980s.

Different classifications of eutectic structures were proposed. These classifications were presented in many reviews (see, for example, Refs 1, 4 and 5). However, attempts to combine these classifications into a single system failed because all known reviews were based on phenomenological data, which, generally, ignore many important factors, such as the chemical nature and structures of individual compounds, the degree of their chemical interaction, temperature and concentration parameters, conditions of crystallisation and cooling. That is why much recent attention has been focussed on investigations of particular objects. Nevertheless, early studies revealed certain general formal tendencies. For instance, it was demonstrated [4] that crystal nucleation of eutectic phases occurs separately in organic systems solidified at relatively small supercooling: '...both crystals grow as though these processes were independent and crystal growth proceeds until the liquid completely disappears'.[4] The so-called 'rough conglomerate of phases' is thus formed. In the second mode of growth typical of inorganic systems, nuclei appear at the contact interface of both phases. In the latter case, the basic phase gives rise to a coupled growth of colonies on a bicrystalline base. Taran [1] believed that this idea carries 'the germ of correct understanding' of the whole process of formation of a eutectic colony, *e.g.*, the colony is a product of crystal formation occurring in contact, *i.e.*, of cocrystallisation of two eutectic phases.

The best known classifications are those proposed by Brady,[7] Portevin,[8] Scheil [9] and Hant and Jackson.[10] Scheil's classification has gained wide acceptance. In this classification, the author attempted to take into account both morphological features and the assumed differences in the mechanism of crystallisation of eutectic alloys. All structures are classified into three groups, *viz.*, normal, degenerate (or separated) and anomalous. All eutectics characterised by the ordered arrangement of phases, *viz.*, lamellar, rod and globular, are assigned to normal structures. These eutectics have a colony structure, and individual colonies can

V S Pervov, I D Mikheikin Moscow State University of Engineering Ecology, St. Basmannaya ul. 21/4, 105066 Moscow, Russian Federation. Fax (7-095) 261 49 61. Tel. (7-095) 267 19 47.
E-mail: pervov@igic.ras.ru (V S Pervov)
Tel. (7-095) 267 19 60 (I D Mikheikin)
E V Makhonina, V D Butskii N S Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky prosp. 31, 119991 Moscow, Russian Federation. Fax (7-095) 952 20 62.
Tel. (7-095) 952 20 62. E-mail: evma@igic.ras.ru (E V Makhonina)

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always be separated by boundaries. The order appears due to the coupled growth of phases. The eutectic class depends on the rate of cooling. Very slow cooling can lead to 'degeneration of coupled growth', and eutectic phases crystallise separately to form degenerate (or separated) structures. Finally, there are systems in which coupled growth cannot take place at all (anomalous eutectics).[9]

In recent years, the terminology proposed by Brady[7] has found ever-increasing application to the description of the eutectic morphology. Brady took the surface tension of components as the main classification criterion and classified eutectics as globular (both components have high but different surface tensions), lamellar (both components have high and approximately equal surface tensions), polygonal (one of the components has a substantially higher surface tension than another component) and crystalline (both components have low surface tensions). In the discussion of the morphology and structures of eutectic alloys, let us cite the conclusions made by Taran[1] after detailed analysis of the available classifications and abundant factual data. These conclusions concern not only the structures of eutectic colonies but also the mechanisms of their formation for interacting systems.

1. A colony can occur as a finely crystalline mixture of two phases (*i.e.*, a 'mechanical mixture of phases').

2. A colony can consist of a matrix built from the basic phase and inclusions of numerous crystallites of another phase. The basic phase is characterised by high entropy of melting and, correspondingly, by high surface tension at the interface with the melt. The development of a colony is accompanied by coupled growth of dispersed crystals and the matrix.

3. A colony contains two intergrown branched crystals of eutectic phases. The centre of the colony is the site of primary contact between the nucleated crystals. The formation of colonies occurs through their coupled growth.

As mentioned above, the structural features of crystallised eutectic alloys depend on the conditions of crystallisation of the system. The classical theory of crystallisation is based on studies by Gibbs and Volmer,[11–13] who introduced the notion of metastable systems and constructed the apparatus of thermodynamics of phase interfaces. This theory is beyond the scope of the present review because it has been outlined in numerous handbooks and monographs. Let us only note that the Gibbs–Volmer theory does not allow one to predict the structures of crystallised multicomponent alloys and determine the morphology of co-crystallised phases. This theory did not find application in the theory of eutectics, although the consideration of a eutectic alloy as a mechanical mixture of phases and the views of the separate crystal growth of each phase are seemingly consistent with the model implied in this theory. In our opinion, the reason is that the real crystallisation conditions very rarely satisfy the requirements of the thermodynamic model.

Presently, the less known concept of the phase field is used in many studies (including those devoted to the mechanisms of crystallisation of eutectic alloys). This concept has been proposed approximately simultaneously with the classical Gibbs–Volmer theory of phase interfaces. The phase-field approach is based on the assumption that a liquid-solid interface is determined as a gradual change in extensive quantities (continuous continuum[14,15]).

For the solid and liquid phases in the system to be distinguished at any instant, the so-called order parameters describing the 'phase field' are introduced. The concept of the phase field was developed for modelling processes of solidification of two-component systems. According to these models, the free energy of the system depends on the temperature, phase field and concentrations of all components (*i.e.*, on the phase diagram). Computer simulations of solidification of eutectic alloys with different morphology (dendrite,[16] lamellar,[17–21] *etc.*[18,21]) demonstrated that the theoretical model is in satisfactory agreement with experimental data. The drawbacks of the cited studies are the cursory consideration of the morphology and lack of information on the structures of interphase boundaries. Besides, this model provides no clear explanation as to why the melting point of a eutectic is equal to its solidification temperature and it does not include parameters allowing for the description of distinctive specific properties of eutectic composites.

Obviously, the theories of phase interfaces and phase field, which include thermodynamic potentials as the initial parameters, can be used only if the system under consideration is close to thermodynamic equilibrium. Taking into account that an alloy can occur under conditions far from equilibrium (quenching), physical schemes were developed, which relate the morphological features of an alloy to diffusion processes. Considerations are carried out within the framework of stationary and non-stationary problems of diffusion. According to Chalmers and Weingard (Fig. 1),[22,23] the appearance of periodic structures of eutectics (lamellar or rod) is determined by distances between the phase interface OA and two solid–liquid interfaces OB and OC in the vicinity of the point O. The width of lamellae depends on the rate of their growth and the influence of two opposite tendencies. One of these tendencies consists in the fact that the thicker is the lamella OB, the larger is the distance for which the structural components of the phase OC, which diffuse in the cross direction, should be moved and, correspondingly, the stronger is the driving force of diffusion. The latter is equal to $\Delta G^T(\text{melt}) - \Delta G^T(\text{cr})$, where $\Delta G^T(\text{melt})$ and $\Delta G^T(\text{cr})$ are the Gibbs free energies in the melt and crystal, respectively. At the same time, the thinner is the lamella, the stronger is the resistance to this force (determined by the contact surface OA). Therefore, diffusion is favoured by a small thickness of lamellae, whereas the principle of minimisation of the energy of the phase interface, by contrast, facilitates thickening of the lamellae. It can easily be concluded that a change in the rate of cooling should lead to a change in the mechanism of crystallisation due to the difference in the diffusion rate. Evidently, the above-considered mechanism is consistent with the Brady–Scheil classification (see above) and conclusions made in the studies.[11,12]

In recent years, the Jackson–Hunt theory of formation of periodic structures upon crystallisation of eutectics[24,25] has gained recognition. This theory takes into account the parameters of a phase diagram, surface tension and the rate of motion of the interphase boundary. Many studies were devoted to the development of the Jackson–Hunt model (see, for example, Ref. 26). Among these studies, noteworthy are investigations on the application of this theory to calculations of particular systems.[27] In a number of studies, account was taken of differences in the phase density,[28] the presence of external pressure,[15] temperature gradient,[29] effect of electromagnetic fields[30] and differences in thermal conductivity of both components.[31]

An analogous approach was used in the study of the mechanisms of crystallisation of eutectics with rod or dendrite structures.[32]

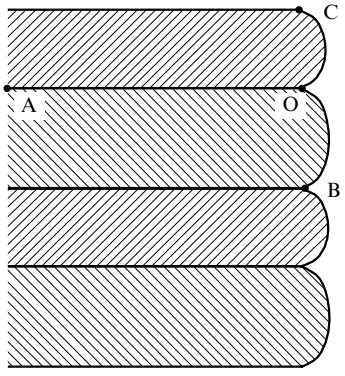


Figure 1. Mechanism of formation of lamellar eutectics according to Chalmers and Weingard.[22,23]

The effects of rapid cooling (diffusion retardation) upon crystallisation of eutectics were investigated.[20, 32, 33]

In spite of the fact that the results of calculations of particular eutectic structures with the use of the above-described models are in good agreement with the experimental data, it can be stated that the essential drawback of the available approaches is that they poorly describe interactions between components at the interface. In the review,[2] it was noted that it is this presence of an interface and solid–liquid interactions that are responsible for specific properties of eutectic alloys: 'In a liquid eutectic alloy, the 'structural complementarity' between the dispersed medium and dispersed phase (the dimensional compatibility of the atomic arrangement at the interface) is better than that in a solidified alloy'. And later: 'The eutectic composition corresponds to the phase ratio self-established in the melt at which the dispersed medium (melt) occurs in the state of solvation shells of dispersed particles. This specific nature of eutectics is responsible for their melting and crystallisation at a certain and constant temperature. A sacrifice in the dimensional compatibility of the atomic arrangement that occurs upon crystallisation is responsible for the elastic deformation of conjugated crystal lattices and a high elastic energy of the interphase surface'.[2]

These conclusions are confirmed by theoretical statements made by various authors at different periods of time. Commenting on the study by Bochvar,[4] Taran [1] emphasised that 'the fundamental idea is that two different crystals must be in contact with each other'. Based on the results of analysis of the structures of numerous eutectic alloys, Taran assumed that in the case of 'the crystal-chemical difference between phases typical of the vast majority of eutectics,... the consideration of one of the phases as the basic one seems to be justified'.[1] This phase should possess '...a more complex crystal-chemical nature... The surface tension at the interface between this phase and the melt is high, which provides the possibility of nucleation and growth... of the second phase...'.[1] This basic phase can be determined with the use of the theorem of minimum entropy production in non-equilibrium processes. It was confirmed that this theorem is also applicable to particular simple eutectic structures, for example, to lamellar structures.[34] However, in a number of studies, this criterion was demonstrated to be insufficient. In the investigation,[35] the latter was attributed to the fact that characteristics of 'pure' phases are considered, whereas the presence of the second component is ignored, in particular, the entropy of mixing, which depends on interactions between the molecules of the components, is not taken into consideration. To characterise these interactions, new parameters, for example, the 'parameter of surface roughness' were introduced.[35]

It should be noted that processes attendant on melting of crystals of different types (ionic, molecular, with different structures, *etc*.) were studied and described in detail.[36] The complexity of these processes in the pre-melting period (for example, positional and orientational disorder, the dependence on the type of unit cell of the initial crystal and its imperfection) suggests that the situation can become strongly complicated in the case of a mixture of interacting phases. In our opinion, all these changes should concern primarily the model of positional disorder because disordering of interacting structural units upon melting can be accompanied by their self-organisation giving rise to associates or something resembling a compound.[36]

The concept of 'interacting phases' was supported by abundant experimental evidence. For example, interatomic interactions at the interface in crystallised eutectics were investigated. Analysis of X-ray emission and photoelectron spectra of eutectic alloys in the Al–Ge, Ag–Si, Ag–Ge (see Ref. 37) and Fe(Co,Ni)–Ge (see Ref. 38) systems demonstrated that the energy state of atoms in boundary layers of eutectic phases differs substantially from the state of atoms in the bulk of these phases and in the corresponding individual crystals. This specific state of boundary atoms is said to be 'chemically active'.[36] These conclusions were made in studies of thin layers of eutectic alloys on substrates.[39]

Let us discuss in more detail the remarkable and reliable experimental fact, *viz*., the orientational structural preference upon crystallisation of lamellar eutectics (the detection of this phenomenon was the aim of many investigations). In particular, it was proved [40] that the contact of phases along two crystallographic planes, *viz*., (111)Al–(211)$CuAl_2$ and (101)Al–(120)$CuAl_2$, is favourable for Al–$CuAl_2$ eutectics in the course of growth of a lamellar single crystal upon very slow cooling.

The consequences of interactions between components of eutectics in a molten state were also studied in sufficient detail. Thus, it was established [41–47] that melts of eutectic systems in a particular temperature range above the liquidus line are characterised by 'dynamic inhomogeneity' manifested in the presence of ordered microregions, which are similar in composition and structure to eutectic colonies that form a structure of an alloy in the solid state. These ordered regions are called clusters, microgroups, cybotaxes, associates, dynamic short-lived complexes, heterophase complexes of atoms (or molecules), quasimolecules and fragments.[2] Hereinafter, we shall use the term 'non-autonomous phase' to refer to these ordered regions.

Many liquid alloys with eutectic compositions were studied by X-ray diffraction methods, which confirmed the presence of such non-autonomous phases. Studies of eutectic systems containing an intermediate phase revealed microgroups of atoms, which are similar in composition and structure to a chemical compound existing in the solid state (in the Tl–Te,[42] Mg–Bi,[43] Fe–Si,[44] In–Sb,[45] *etc*. systems). For some binary amalgam systems, the substantiated conclusion was made that ordered structures, which are similar to chemical compounds, are retained in a melt.[47] In several studies, continuous series of solid solutions or metastable intermediate phases were detected in simple eutectic alloys obtained upon melt quenching.[2] These results are consistent, for example, with the conclusions [48] that eutectic melts are difficult to devitrify as well as with the data [49, 50] that metastable solid solutions or compounds can exist after mechanochemical activation of eutectic alloys.

At the same time, it is known that microregions self-organised in a melt (non-autonomous phases) can be destroyed by external actions. For example, it was reported that the concentration in a eutectic melt changed under the action of centrifugal forces.[2]

When discussing the current state of the theory of eutectics, it should be noted that analogies between eutectics and chemical compounds were found. For example, Antipin and Vazhenin [51] analysed two points of view, which are, in their opinion, of most importance. The first and most justified point of view consists in that eutectics are similar in nature to chemical compounds. The main argument is that most of eutectics obey the law of multiple ratios. The compositions of eutectics in melts of selected salts are given in Table 1.[51]

Table 1. Compositions of eutectics in molten salts.[51]

System	Chemical formula of the eutectic	Content of the second component (mol.%)	
		experiment	calculations
NaF–NaCl	NaF·2 NaCl	66.6	66.6
NaF–SrF_2	2 NaF·SrF_2	33.3	33.3
$SrCl_2$–NaCl	$SrCl_2$·NaCl	50.0	50.0
LiCl–$BaCl_2$	3 LiCl·$BaCl_2$	25.0	25.0
KF–KI	KF·2 KI	66.0	66.0
NaF–KF	2 NaF·3 KF	60.0	60.0
NaF–LiF	2 NaF·3 LiF	61.0	60.0
KCl–KPO_3	3 KCl·KPO_3	20.0	20.0
KBr–KOH	KBr·3 KOH	75.0	75.0

It should be mentioned that Antipin and Vazhenin [51] noted that more complex ratios (for example, $NaCl \cdot 14\,NaNO_3$, $2\,NaF \cdot 9\,NaI$, $NaCl \cdot 6\,LiNO_3$, *etc.*) were observed in some cases. These ratios could be considered as artificially selected. They referred to the data obtained by Geveling, who calculated that of 22 potassium halides, which form eutectics with other salts, 12 substances exactly correspond to multiple molar ratios. For three substances, the discrepancy is several tenths of a molar percentage. The remaining eutectics are not described by simple formulae. The authors of the cited monograph noted [51] that 'this fact does not provide reason to reject certain stoichiometric ratios but can be indicative of their complexity' and believed that upon heating of a mechanical mixture of compounds forming eutectics, the liquid phase corresponding to the composition of the eutectic appears at a specified temperature only if certain ratios and conditions for contact between crystallographic planes of both substructures occur at the contact site. Antipin and Vazhenin [51] concluded that, unlike chemical compounds characterised by the closest packing, a eutectic can be considered 'as the most weakly packed combinations of its constituent ions and atoms' and, hence, external actions, in particular, the pressure, 'can make the packing denser, *i.e.*, can, in the limit, give rise to a specific structure of a chemical compound'.[51] In addition, studies were cited in which phase diagrams of either a eutectic or a chemical compound were obtained by varying the crystallisation conditions. Figure 2 illustrates the disappearance of a chemical compound and the appearance of a eutectic in the 2-chloronaphthalene – antimony trichloride system under certain experimental conditions.[51]

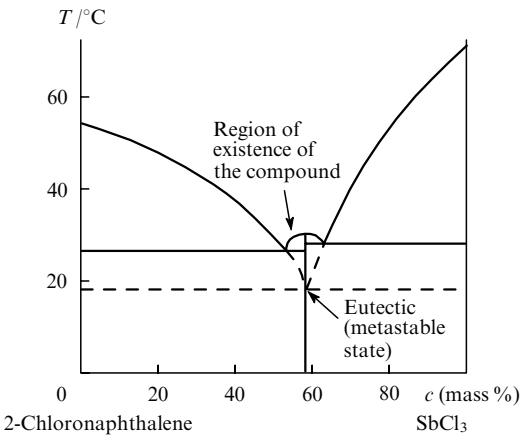


Figure 2. Phase diagram for the 2-chloronaphthalene – antimony trichloride system in the case of equilibrium and non-equilibrium crystallisation (c is the concentration of $SbCl_3$).[51]

Recently, the composition of a vapour over a eutectic melt was investigated.[52, 53] Complex molecules of the $MLnCl_4$ and M_2LnCl_5 types (M = Rb or Cs) were reliably detected in the vapour by high-temperature mass spectrometry. These results indicate that interactions in a melt, whose eutectic composition corresponds to the simple component ratio of 1 : 1, can be strong to an extent that congruent evaporation of the compound corresponding to the eutectic composition becomes possible. Therefore, the results of the above-mentioned studies can be considered as important experimental evidence in support of the proposed concept.

An alternative point of view consisting in that eutectics are heterogeneous mixtures, in the opinion of Antipin and Vazhenin,[51] is based on two facts. First, the dependence of the eutectic composition on the external action, for example, on the pressure, can be attributed to a 'weak packing'. Second, a strong effect of the composition of impurities on the properties of eutectic alloys cannot be explained within the framework of the concept presented in the monograph.[51] However, it should be noted that the influence of impurities on the properties of eutectics has been considered in detail by Rebinder,[54] who explained this influence using the classical Gibbs – Volmer postulates and concepts of colloid chemistry.

To conclude this section, we cite one of the most recent definitions of the phenomenon of eutectics: 'The eutectic is a specific alloy (solution), whose components are partially miscible in the solid and liquid states and spontaneously form a thermodynamically equilibrium lyophilic dispersed system at certain temperatures. This system is characterised by substantial interphase interactions and solvation as well as by sedimentation stability. The composition of a eutectic corresponds to the ratio between eutectic phases, which is self-established in the melt and at which the dispersed medium completely occurs in the state of solvation shells of dispersed particles'.[2] It can be seen that the specific features of the formation of non-autonomous phases in eutectic alloys are described with the use of the notion of lyophilic systems characterised by interactions between dispersed particles. The terminology of colloid chemistry can eliminate particular contradictions in the theory of eutectics but it does not give a clear understanding of the mechanisms of processes occurring during melting and crystallisation of eutectic alloys. In our opinion, it seems more logical to use concepts of supramolecular chemistry for the determination of the nature of eutectic alloys and processes taking place during their formation. The formal possibilities of this approach will be considered in the next section. The drawbacks of the available notions can be to a large extent eliminated, first, by taking into account interactions between incommensurate substructures and, second, by developing a model, which describes mechanisms of these interactions and in which possible deformations and defects upon self-organisation of non-autonomous phases should be considered as a product of these interactions.

II. Main concepts and objects of inorganic supramolecular chemistry

J-M Lehn described supramolecular chemistry as the next step toward complexation of systems under study from molecules to supramolecules and organised supramolecular systems held together by non-covalent interactions.[55] This field of science deals with the chemistry of supramolecular assemblies and intermolecular interactions. Lehn assigned coordination bonds with metal ions as well as Coulombic, hydrogen, van der Waals and donor-acceptor interactions to intermolecular interactions.[55] The main property of self-organised supramolecular systems is their ability to perform molecular recognition. Recognition of components implies complementarity, *i.e.*, the mutual correspondence, both geometric and at the level of formation of intermolecular bonds, between the participants of the assembly (substrate and receptor). Although supramolecular chemistry has its roots in organic synthesis, coordination chemistry and studies of bioorganic and complicated organometallic complexes, Lehn particularly noted some objects of inorganic supramolecular chemistry admitting that the situation observed for these objects is rather inhomogeneous. In the study,[55] it was emphasised that intercalates, clathrates and host – guest structures exist only in the solid state. In the strict sense of the word, these structures are not discrete supramolecules but belong to solid supramolecular assemblies. Extended supramolecular assemblies (guests in extended † host structures) and discrete supramolecules occupy a special place.

† By 'extended' structures are meant one-, two- or three-dimensional infinite or semi-infinite crystalline substances with ionic or covalent bonds.

A more detailed classification of objects of inorganic supramolecular chemistry was presented in the review.[56] Among these objects are intercalates containing guests of different sizes in the host lattice, clathrates, framework silicates and complex molybdenum and vanadium phosphates. Because of the lack of the commonly accepted definitions and notions, the range of these objects is outlined very roughly.

In the present review, we restricted ourselves to the discussion of host – guest compounds as objects of inorganic supramolecular chemistry. These compounds allow one to study supramolecular assemblies in which the guest molecules form rather strong bonds with extended structures, factors influencing their complementarity (in particular, the geometric and topological complementarity between the components) and characteristic features of self-organisation. Extended assemblies enable one to consider the consequences of possible violations of the principle of complementarity and reveal the structural features of assemblies resulting from these violations. As will be demonstrated below, investigations of such objects can help in elucidating the mechanisms of formation of eutectic alloys.

It is known that formation of inorganic supramolecular assemblies can lead to violation of the principle of geometric and topological complementarity. Layered intercalates (in layered dichalcogenide matrices, graphite or clays) were particularly noted [56] as typical host – guest compounds examined in inorganic supramolecular chemistry. In all the above-mentioned cases, layers in the host lattice are linked by van der Waals interactions. Upon incorporation of guest molecules, the layers are pushed apart. It is known [57] that a change in the interlayer distance is an indication of the formation of an intercalate. This change depends on the size of the guest and can be 3 – 5 times larger than the initial crystallographic parameter of the host lattice. However, the ratio between the sizes of the guest molecules and cavities in the host lattice is not the only factor responsible for the limiting stoichiometry of an intercalate. It was demonstrated [58, 59] that the limiting stoichiometry of the intercalates A_aMX_2 (A is metal and MX_2 is a layered dichalcogenide matrix) is determined by the conditions of the matrix conduction band filling with electrons of the donor A (*i.e.*, by electron stabilisation of the A_aMX_2 structure as a whole). The geometric factors are of secondary importance, as unambiguously evidenced by the small sizes of the M atoms in the A_aMX_2 systems, the absence of changes in the interlayer distances, the small limiting value of the parameter a and the dependence of a on the valence states of the A and M atoms.

The synthesis schemes for suprastructures developed in the study [56] consist in the following: the structure of a host should be constructed in such a way that it can be adapted to the structure of a guest. Successful examples of these retrosyntheses were cited in the study.[60] It should be noted that the so-called matrix crystals, which belong to a new type of inorganic supramolecular assemblies, have been discovered very recently.[60] Single crystals of synthetic opal were grown. These crystals contain cavities of a certain size, which form a regular cubic sublattice. The cavities were filled (from a melt under pressure) by crystalline and amorphous selenium as well as by sodium chloride. It was established that guest molecules always form quasilattices with unusually large parameters. Therefore, the geometric incommensurability of the sublattices is compensated by deformation of one of them (in this case, by deformation of the guest sublattice). Misfit compounds, which are a variety of intercalates in a layered dichalcogenide matrix, provide another example of incommensurability between the guest and host. Such compounds can also be assigned to objects of supramolecular chemistry. These are complex chalcogenides of the general formula $(AX)_{1+x}(MX_2)_y$ (A = Sn, Pb, Bi, Sb, Ln; M = Ti, V, Nb, Ta, Cr; X = S, Se; $x = 0.08 - 0.28$; $y = 1, 2, 3,...$) consisting of layers of two substructures, *viz.*, AX (guest) and MX_2 (host). The guest layer (Q layer) forms a pseudocubic NaCl-type lattice. The host layer (H layer) occurs as a sandwich composed of hexagonal networks of the X atoms in which the M metal atoms have a trigonal-prismatic (Nb, Ta) or octahedral (Ti, V, Cr) environment formed by the X atoms. The Q and H layers are incommensurate along one of the crystallographic directions (along one of the axes of the layer plane), the incommensurability being determined by the limiting value of x (at $y = 1$). Data on misfit compounds were generalised in the review [61] in which it was noted that high thermodynamic stability of such compounds calls for revision of the topochemical laws of construction of supramolecular structures.‡ Besides, it was hypothesised that in the process of organisation of supramolecular assemblies with incommensurate elements, the forces responsible for the retention of substructures (and their molecular recognition) compete with the forces linking these substructures.[61] This can lead to morphological distortions of crystals and the appearance of different structural defects. The widespread opinion that the properties of misfit compounds are additive with respect to the properties of their constituent substructures was disproved in the study.[63] Numerous phase transitions were observed by measuring thermal capacity. The authors of the cited study [63] believed that these phase transitions are caused by temperature- and incommensurability-dependent defects of suprastructures.

Theoretical analysis [64, 65] confirmed the possibility of self-organisation of suprastructures from structures incommensurate along one crystallographic direction. Mechanisms of this self-organisation were proposed in the studies.[64, 65] The results of these investigations are briefly surveyed in the next section. Here it should be noted that (as will be demonstrated below) a consideration of eutectics, which, in the limiting case, are incommensurate along all three crystallographic directions, in terms of supramolecular chemistry allows one to answer many questions and eliminate unclear facts, which we have mentioned in the discussion of the available concepts of eutectics.

III. Static Frenkel – Kontorova model for finite systems

Interactions between substructures characterised by one-dimensional incommensurability (misfit compounds) were proposed to be considered as the behaviour of an elastic and less strong chain of finite length (guest) in the field of a rigid substrate (host) inducing a periodic potential (U) [64, 65] for elements of the chain (Fig. 3). This approach is a static version of the known Frenkel – Kontorova model.[66]

A method was developed [64, 65] for the numerical solution of the problem of a search for energy minima of systems, which are composed of an elastic chain consisting of $N + 1$ atoms (*i.e.*, containing N bonds) and a substrate, provided that the position of the chain on the substrate is determined by only one parameter (position of its end or beginning), whereas all other geometric elements of the chains are calculated according to recurrent equations. In calculations, the incommensurability parameter of subsystems $\gamma = b/h$ (b is the bond length in the free chain) and the ratio between their characteristic energies $z = 2\pi A/(kh^2)$ ($kh^2/2$ is the energy of stretching of the bond in the chain by a period of the substrate) are used as parameters of the problem. For convenience of discussion, the dimensionless potential energy (E) of chain – substrate systems (in units $kh^2/2$) per degree of freedom was introduced in the form $\varepsilon = E/(N + 1)$. In calculations, the incommensurability parameter of subsystems (γ) was varied within 0.5 – 1.5, and the optimum region of variation of the dimensionless

‡ It should be noted that the term 'misfit' is rather widely used in the literature. In particular, misfits between the parameters of crystal lattices of components of alloys are generally considered in metallurgy. For instance, in the study devoted to the development of compositions of high-temperature nickel alloys,[62] the misfit characteristics were determined and the influence of these characteristics on processes of ordering and liquation depending on the morphological structural features were investigated.

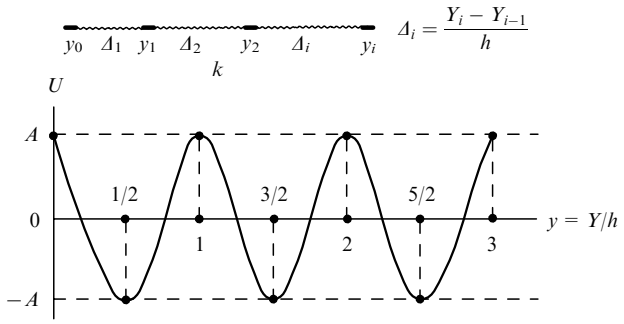


Figure 3. Frenkel – Kontorova model for a chain of a finite length;[66] y_0 is the position of the beginning of the chain; y_i is the dimensionless coordinate of the ith element of the chain ($i = 0, 1, ..., N$) in units h, where h is the period of the potential of the substrate; Y_i is the absolute coordinate of the ith element of the chain; Δ_i is the length of the ith bond in the chain in units h; k is the rigidity of the bonds in the chain; U is the potential energy; A is the amplitude of the potential of the substrate.

energy parameter z was determined from the real values of the corresponding constants for inorganic compounds. Leaving aside mathematical procedures (analytical and numerical solutions of this problem were reported in detail in Refs 64 and 65), let us consider the most important conclusions drawn from the dependences obtained.

1. For different z and γ, the energy of the system in the ground state per degree of freedom (ε) increases as the number of bonds (N) increases. This indicates that beginning with a particular number of bonds, fragmentation (cleavage of the chain) becomes favourable. Obviously, in each particular case, the gain in energy upon fragmentation must be compared with the real bond energies in the corresponding substructure. Typical plots of the relative maximum bond deformations for a chain in the ground state [$\delta = (1/\gamma - 1) \times 100\%$] and the corresponding energies per degree of freedom (ε) *vs.* the number of bonds (N) at different incommensurability parameters γ and energy parameters z are shown in Figs. 4 *a–f*. It can be seen that an increase in N leads to a change in the configuration of the ground state. For example, if $\gamma = 1.1$ (see Fig. 4 *a*) and $z = 0.030$, the rigid chain is strongly stretched (or cleaved) on going from $N = 12$ to $N = 13$. If $\gamma = 0.9$ (see Fig. 4 *c*), a strong chain contraction occurs at the same parameters of the system.

2. The probability of fragmentation sharply increases as the initial incommensurability increases as well as upon the formation of strong chain – substrate bonds. For example, if $\gamma = 0.6$ (see Fig. 4 *e*), the deformation of one bond reaches 20% already at $z = 0.15$.

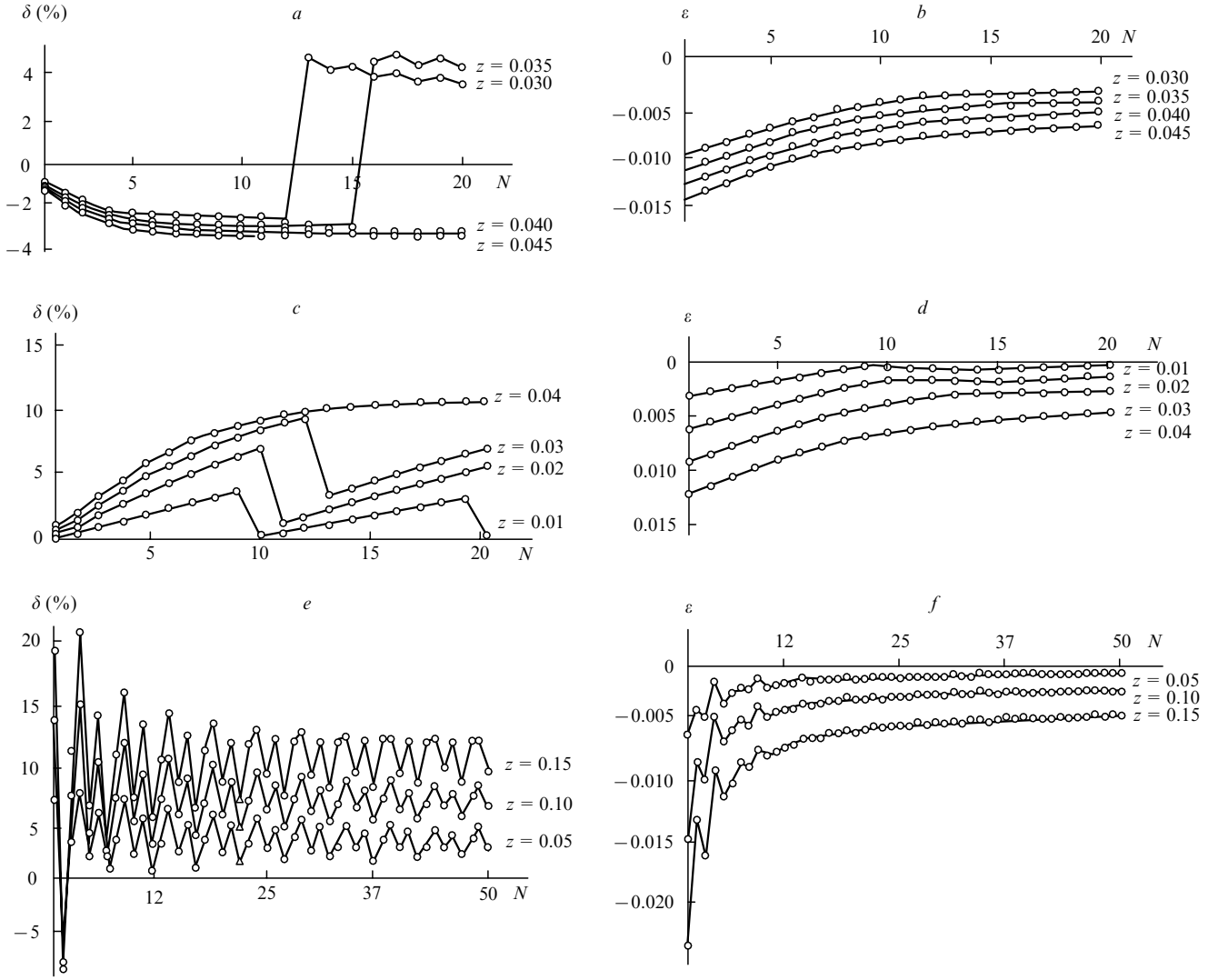


Figure 4. Plots of the maximum relative bond deformation (δ) in the chain in the ground state (*a*, *c*, *e*) and the energy per degree of freedom (ε) of the system (*b*, *d*, *f*) *vs.* the number of bonds (N) in the chain for $z < z^*$ and $\gamma = 1.1$ (*a*, *b*); 0.9 (*c*, *d*); 0.6 (*e*, *f*).[65] See comments in the text.

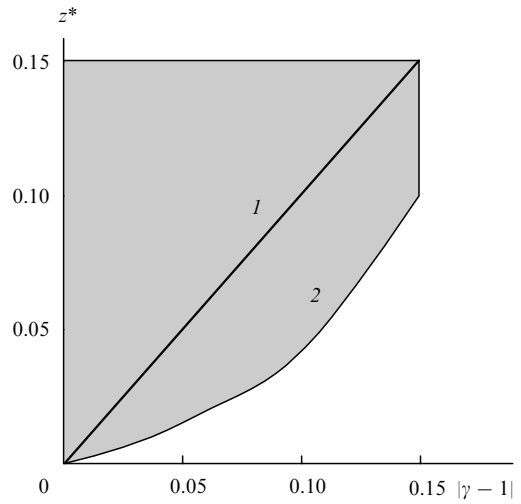


Figure 5. Estimation (*1*) and calculated (*2*) plots of z^* *vs.* γ. The region in which the ground state of the chain has the 1 : 1 configuration is dashed.[65]

3. For chains with any rigidity and for a given incommensurability between the chain and substrate, there is the energy parameter z^* such that if $z > z^*$, the system occurs in the ground state (corresponding to the ratio of 1 : 1), *i.e.*, $\gamma = 1.0$ (Fig. 5).

4. Excited metastable states of the system (conformers) also possess some interesting features. Calculations demonstrated that these states should be very stable. Regions of contraction or stretching in incommensurate systems are developed analogously to those in commensurate systems ($\gamma = 1.0$). This fact allows one to state that the deformation and fragmentation of substructures in real eutectic alloys depend substantially on the conditions of the synthesis (crystallisation).

5. The proposed one-dimensional model provides the answer to the question as to the mechanisms of mechanochemical actions on interacting substructures. The preliminary longitudinal contraction or stretching of the chain influences the incommensurability parameter γ, whereas the forces acting in the perpendicular direction affect the parameter z (*via* the dependence of the parameter A on the chain – substrate distance). The above-mentioned changes can lead to the formation of a suprastructure in the metastable state for non-excited γ and z.

Although these conclusions were made based on the results of investigations, which were far from completion, it is believed that they are of importance for an understanding of the mechanisms of formation of eutectic suprastructures from elements, which are, in the limiting case, incommensurate along all three crystallographic directions.

First, calculations demonstrated that the formation of assemblies from incommensurate elements cannot differ substantially from the formation of assemblies from commensurate elements if the synthesis conditions imply the presence of excited states. This is yet another argument in favour of the statement that the topological and geometric complementarity between the guest and host is not necessary, and, consequently, eutectics can be assigned to objects of supramolecular chemistry.

Second, one can follow the changes in the parameters of the model (as yet one-dimensional) depending on the external conditions (the effect of the temperature on the interaction potential, rigidity and bond energy, mechanical actions, *etc.*)

Third, the mechanism of fragmentation of interacting incommensurate substructures, *i.e.*, the formation of thermodynamically stable nanocomposites, was established. In our opinion, the conclusions made for a one-dimensional model can be used for explaining certain phenomenological results of studies of eutectic alloys.

IV. Supramolecular concept in the theory of eutectics

As mentioned above, poorly defined terms in inorganic supramolecular chemistry arise from the fact that intercalated host – guest compounds are assigned to solid supramolecular structures according to the available nomenclature. Therefore, the term 'compound' is set equal to the term 'supramolecular assembly'. At the same time, in solid-state chemistry it is generally agreed that compounds have individual structures. In our opinion, there is an approach eliminating these uncertainties. If an interaction between the initial substructures leads to their destruction giving rise to a new structure typical of a particular compound, conditions for the molecular recognition are violated. These objects fall outside the scope of supramolecular chemistry and the problems considered in the present review. However, if the energy released upon interaction between the initial structural elements is insufficient for their radical rearrangement, it can be used for production of various structurally less stable supramolecular assemblies. We believe that any alloys (eutectics, solid solutions, *etc.*) can serve as examples of such supramolecular assemblies. This provides the basis for our approach. Undoubtedly, these assemblies are consistent with the principle of molecular recognition because the initial structures are not destroyed. Evidently, the Gibbs energies of such assemblies should depend on their architecture and mutual arrangement of sublattices. For example, the fulfilment of the principle of complementarity depends to a lesser or greater extent on the incommensurability and rigidity parameters, the presence of defects and analogous factors. In syntheses under different conditions (for example, under different temperature modes of alloy solidification), the self-organisation of a suprastructure should be accompanied by the emergence of hierarchy of assemblies of different types. The main type (possessing the lowest energy under particular thermodynamic conditions) should correspond to the case of the limiting self-organisation, whereas all other types are non-equilibrium or metastable. A change in the synthesis conditions should lead to a change in the energy hierarchy of suprastructures.

Organisation of suprastructures from incommensurate elements can proceed according to three schemes. In the first scheme, we deal with rigid substructures, which rather weakly interact with each other. Since the energy effects are small, the self-organisation § is also insignificant. In a certain approximation, we arrive at the term 'mechanical mixture of phases' whose properties are additive with respect to the properties of its consituent structural elements.

According to the second scheme, non-rigidity of interacting substructures or external mechanical actions compensate insignificant incommensurability between these substructures upon the formation of a suprastructure. In this case, stresses giving rise to a change in the crystal morphology should appear in the resulting suprastructure, and the non-additivity of the thermal capacity and some other physicochemical properties can be observed. Apparently, this scheme can be used for explaining the formation of limited solid solutions. It is worthwhile to cite the reasoning of the authors of the study [69] who believed that the regions of existence of solid solutions in phase diagrams cannot be described in the context of classical thermodynamics because of their imperfection. These phases are non-equilibrium and, consequently, they must decompose as the system approaches equilibrium. It has long been noticed that some alloys quenched from a solid-solution region appear to be decomposed (the so-called 'tweed' or modulated structure is formed).[70–73] In the study,[74] this phenomenon was interpreted as follows: 'The concentration at which noticeable

§ The meaning and differences of the terms 'self-organisation' and 'self-assembling' are extensively discussed in the literature. Cases when the initial components have different incommensurability and rigidity parameters were also described.[67,68]

deviations from perfection take place in a particular solution depends substantially on the nature of the compounds involved in this solution. Solutions for which deviations from perfection cannot be observed throughout the concentration range are exceptionally rare and exist only if their components have similar chemical structures, possess similar thermodynamic characteristics, similar atomic sizes, identical crystal structures, *etc*. If atoms differ in size by more than 14%, a solid solution cannot be formed because the deformation energy of the crystal lattice substantially increases'. It was also noted that if only two types of interactions, *viz*., attraction (tendency to ordering) and repulsion (tendency to phase separation), occur between components, two types of regions in which these tendencies are manifested should be observed in phase diagrams.[74, 75] In the studies,[76, 77] the thermodynamic, kinetic and morphological aspects of decomposition of substitution solid solutions characterised by either the positive or negative energy of ordering were considered. Using a model of free energy relaxation for separation and ordering, a method was developed [76] for the computer simulation of such transformations, including calculations of the effects of induced elastic stresses.

Therefore, the problems discussed in the present review, *viz*., the possibility of self-organisation and defect formation in systems with interacting incommensurate structural elements, are directly related not only to eutectic alloys but also to solid solutions. Based on the available data, it can be assumed that the difference between the eutectic type of formation of an alloy in a binary system and the formation of a solid solution consists in the following.

In the case of small incommensurability, the molten components A and B are mutually soluble. The release of thermal energy responsible for the conditions of formation of a solution can be favoured by mechanical actions (thus, it was experimentally demonstrated [78] that these actions allow one to extend sharply the concentration region of existence of single-phase alloys; the mechanochemical synthesis of metastable solid solutions from eutectic phases was carried out in the studies [49, 50]). If the components A and B have more substantial incommensurability and do not interact with each other (the negative energy of ordering), they undergo phase separation.

However, if the components A and B interact with each other, it is worthwhile to consider the third scheme associated with the mechanisms of structural compensation in the course of active self-organisation of assemblies, which are composed of incommensurate substructures, in eutectic alloys. This is true for cases when the potential of interactions between substructures is rather high and their non-rigidity and incommensurability lead to critical deformations or fragmentation of one of the substructures. The formation of assemblies can be accompanied by the appearance of various defects, nanocomposite structures, non-additivity of properties and morphological changes during crystal growth.

Evidently, eutectic supramolecular assemblies are generated as non-autonomous phases, *i.e*., as phases formed in the vicinity of the contact surface of interacting substructures. However, under certain conditions, this non-autonomy can, in principle, turn into the organisation of the structure as a solid solution. Therefore, the proposed concept allows one to bridge the gap between the terms 'eutectic' and 'solid solution'. Obviously, non-autonomous phases in a molten state differ from those in the solid state because processes of self-organisation of substructures depend substantially on the temperature (crystal lattice parameters,[79] bond energies, interatomic distances [2] and rigidity are changed). Consequently, like in the case of solid solutions, the ground states of a supramolecular system and a set of excited states are functions of the temperature. In our opinion, estimation of the changes in the parameters of the system in the proposed one-dimensional theoretical model will enable one to predict the characteristic features of eutectic suprastructures formed in the quenching mode. As mentioned above, alloys prepared by quenching can retain the structure of assemblies formed at high temperature as long as is wished due to thermodynamic stability of the conformers. Stability of eutectic suprastructures is responsible for the necessity of the constancy of their compositions and melting – solidification temperatures. The fact that eutectics have low-melting points and possess specific physiochemical properties can easily be explained taking into account that interactions between incommensurate structural elements are associated with bond deformation and considering that under particular conditions the total amount of defects in a non-autonomous phase should be approximately constant.

Measurements of heat capacities and the determination of their temperature dependences for a series of oxide eutectic alloys provided evidence that these non-autonomous phases play different roles in such systems. The $GaSe-GaSe_{1.5}$ system was studied in the Se concentration range of 50% – 60%, where the homogeneity region of gallium monoselenide and simple eutectics occurred.[80] For this purpose, samples, which were quenched from a melt and slowly cooled, were used. We studied the temperature dependences of the heat capacity [81] for the PbO – ZnO (eutectic, 89 mol.% of ZnO, $T_m = 1134$ K),[82] $PbO-Y_2O_3$ (eutectic, 95 mol.% of Y_2O_3, $T_m = 1103$ K) [48] and MoO_3 – PbO (eutectic, 59 mol.% of MoO_3, $T_m = 933$ K) systems.[83] A special procedure was developed, which made it possible to decrease an error of the measurements of heat capacity to approximately 0.5%. The crystallographic characteristics of substructures and eutectic alloys were studied. It appeared that the heat capacities of eutectics, like those of misfit compounds, deviated toward the values calculated according to the additive scheme (by 4.0% – 4.5% for PbO – ZnO and by 9% – 10% for $PbO-Y_2O_3$ and $PbO-MoO_3$). The devitrification and crystallisation temperatures in the region of eutectic compositions and in the nearby concentration regions were also investigated. The results of these investigations demonstrated that there are no substantial difference between the structures of the 'host – guest' type, which fall into the category of supramolecular compounds and are consistent with the principle of molecular recognition, and eutectic assemblies.

In the context of the proposed concept, the orientational ordering in eutectic alloys (see above) can easily be explained. If the system is incommensurate along two or three crystallographic directions and the incommensurability parameter γ along different directions has different values, energetically most favourable positions will be chosen upon interaction between substructures of two components (A and B) in the course of self-organisation of assemblies.

Mechanochemical treatment of substructures can also lead to changes in the parameters of the system determining the self-organisation of assemblies.

Finally, the proposed concept provides an alternative insight to the mechanisms of modification of eutectics by adding the third component.

The known descriptions of quasi-equilibrium crystallisation of melts are based on the genetic relations between the phase diagrams of eutectics and solid solutions. A scheme of formation of a eutectic-type phase diagram after superposition of two phase diagrams of solid solutions is shown in Fig. 6. Weingard believed [23] that at the solidification temperature (T_{cr}), a melt with eutectic composition can be considered as if it were present on two liquidus lines. The liquid is in equilibrium with the solid phase with composition C_1 and another solid phase with composition C_2. Both solid phases are formed from the liquid with composition C_E. This mixture of two different solid phases is called a eutectic. It should be noted that the genetic relation between the state of a solid solution and eutectics is consistent with the conclusions drawn from the proposed theory. Recall that the results of analytical and numerical studies of the static one-dimensional Frenkel – Kontorova model eliminate sharp differences between commensurate and incommensurate substructures upon the formation of excited states of a suprastructure. At the same time, the supramolecular concept involving this theory

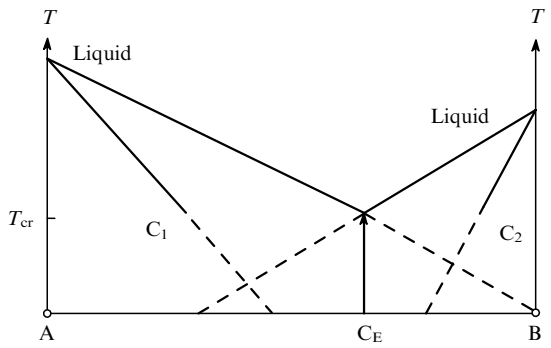


Figure 6. Scheme of formation of a eutectic-type phase diagram after superposition of two phase diagrams of solid solutions. See comments in the text.[23]

bridges the gap between the notions of compound and solution by introducing a 'supramolecular eutectic assembly' as an intermediate.

As can be seen from Fig. 7, different composites can occur in a two-component (consisting of the phases A and B) eutectic alloy depending on the parameters of the system and external actions. This can be a mechanical mixture of phases (see Fig. 7, line *1*), an associated solution (curve *2*) or a supramolecular assembly (curve *3*). The minimum of the potential corresponds to the ground state. The presence of excited states (conformers; region *4*) implies an uncertainty in the composition and structure of the assembly. The exact concentration ratios can take place only upon the formation of a compound with an individual structure (point *5*).

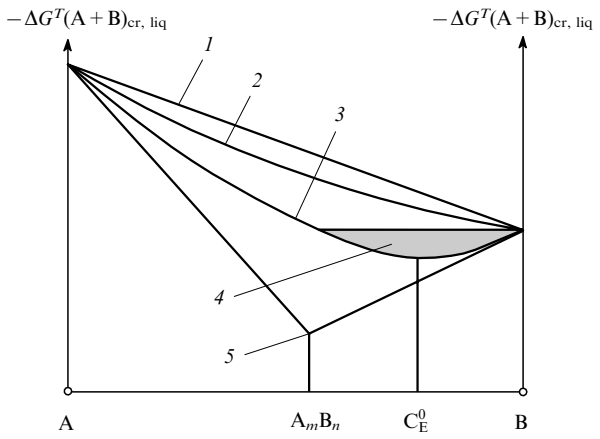


Figure 7. Types of interactions in a two-component A + B system; (*1*) a mechanical mixture of components, (*2*) an associated solution, (*3*) a supramolecular assembly, (*4*) a region of existence of metastable conformers (C_E^0 is a eutectic, the ground state), (*5*) a compound with an individual structure.

It can be stated that the proposed supramolecular concept in the theory of eutectics does not reject the classical views. The only difference is that the abstract thermodynamic criteria, such as the surface energy or surface tension, are changed for real parameters of interacting substructures, *viz*., the incommensurability, rigidity and interaction potential. These parameters are generally not used in supramolecular chemistry but are included in the static Frenkel – Kontorova model, which we propose for the description of different modes of self-organisation of systems characterised by one-dimensional incommensurability.

It should be noted that some of the notions used in the present review are discussed not for the first time. Thus, the terms 'assembly', 'size dimensionality factor' and 'crystallographic factor' have been used by Hume-Rothery *et al*.[5]

One would expect that the further development of theoretical approaches (primarily, the development of the two-dimensional static Frenkel – Kontorova model for finite systems) and the target studies of the dependences of the parameters of the model and structural features of the resulting suprastructural eutectic assemblies will allow one to accumulate data, which will make it possible to predict unambiguously properties of eutectic alloys.

V. Conclusion

The results surveyed in the present review provide evidence in favour of the supramolecular concept in the theory of eutectics. This concept is based on the assumption that a eutectic alloy containing the autonomous phases A and B (in a two-component system) must be studied with consideration for interactions between these phases. These interactions can be responsible for the formation of ordered microregions (non-autonomous phases) analogous to supramolecular assemblies. Depending on the interaction potential, incommensurability between the crystal lattices of the substructures A and B, their rigidity and extension, external mechanical actions, the conditions can be provided for the formation of defect composites, *viz*., non-autonomous phases with changed lattice parameters. The existence of such phases is confirmed by the data published in the literature and our experimental results. The mechanisms of self-organisation of such assemblies are discussed using the one-dimensional static Frenkel – Kontorova model. It was demonstrated that a change in the parameters of the model can lead to the formation of limited solid solutions. The relationships between the mechanisms of formation and ordering in metastable solid solutions and processes of formation of supramolecular assemblies in eutectic alloys are discussed. Along with the ground state of a non-autonomous phase (corresponding to the maximum level of self-organisation), there are a large number of excited states (conformers), which are similar in energy and whose transitions to the ground state should be kinetically hindered. At low interaction potentials and in the case of substantial rigidity of substructures A and B, eutectic alloys should be similar in properties to mechanical mixtures of the phases. The specific properties of eutectic alloys and the dependence of their structures on the synthesis conditions (temperature, rate of cooling, mechanical actions) depend on the amount of a non-autonomous phase and the degree of its organisation. Analysis of the results of investigations devoted to the structures and properties of eutectic alloys provided evidence that the proposed concept is consistent with abundant phenomenological data and is not contradictory to the classical theoretical notions.

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