The theory for the disperse structure of real crystals by Dimiter Balarew, as a predecessor of the nonclassical crystallization of mesocrystals

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The generally accepted classical theory of crystal growth, developed by Kossel and Stranski at the end of the 1920s, describes crystallization as a layer-wise deposition of atoms, ions or molecules on the surface of a crystal nucleus. At the same time, Dimiter Balarew developed the idea for colloid chemical growth of real crystals from salt solutions, which consists of aggregation of clusters sized about 0.01 μm (nanoparticles) into a disperse structure of real crystals. For many reasons, this theory remained in forgetfulness. However, in the last three decades an increasing number of examples were observed which could not be explained by the classical models. Finally, it was proven that the crystals can also grow by attachment of nanoparticles, a process known as nonclassical crystallization. So, Dimiter Balarew was perhaps the first scientist who raised the idea of self-organized agglomeration through oriented attachment of nanoparticles in salt solutions and formation of crystals with a disperse structure.
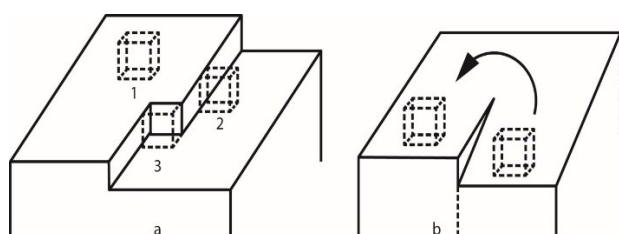
More than 80 years ago Dimiter Balarew created his theory of real crystal growth from salt solutions. On the basis of his experimental data accumulated in the 1930s, he launched the idea for colloid chemical growth of real crystals from salt solutions, resulting in a dispersed structure of the real crystals. In 1939 he summarized the data and published the monograph "The disperse structure of the solid systems" [1].

However, at that time the classical theory of crystal growth developed by Gibbs [2], Volmer and Weber [3], Kossel [4] and Stranski [5] was generally accepted. The classical theory describes crystallization as an adsorption process of atoms, ions or molecules on the surface of a crystal nucleus and their subsequent migration over the crystal surface until they reach edges and kinks where their attachment is energetically favorable (Fig. 1a). In this way, a layer-by-layer crystal growth is achieved.

Figure 1. Crystal growth: (a) Molecular-kinetic theory of Kossel-Stranski [4, 5]; (b) Screw dislocations mechanism [6].

Burton *et al.* later developed a crystal growth model through screw dislocations and spiral growth (Fig. 1b) [6].

Considering the classical models of crystal growth by successive deposition of individual ions, atoms or molecules on the surface of a growing crystal, it is obvious that these models cannot be valid for the cases of salts crystallization from aqueous solutions. In aqueous solutions of salts free ions do not exist. The ions are always hydrated, forming ion pairs and complexes with each other. The latter are grouped into associates of different sizes depending on the composition of the solutions, the concentrations of the salts and the temperature.

According to the classical theories nucleation is considered to take place in a supersaturated solution by stochastic solute clustering. The earliest crystal precursor is considered to be a cluster of critical size [3]. Recently, it was shown that stable clusters play a dominant role in the prenucleation stage [7]. This means that nucleation is not a problem of critical size only, it can be speculated that entropic solvent effects intervene as well. It follows that the lowest critical supersaturation needed for nucleation is expected for those salts whose solutions contain sufficiently high concentration of complexes having crystal structure analogous with fragments from the structure of the crystallizing salt [8].

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Dimiter Balarew developed the idea for a colloid chemical growth of real crystals through agglomeration of particles sized about 0.01μm, which he called elementary crystals (i.e., nanoparticles according to modern terminology). The latter, almost equally oriented (self-organized), being three-dimensionally arranged, aggregate into a disperse structure of a real crystal [1]. On Figure 2, Dimiter Balarew showed the attachment of the elementary crystals for the formation of the real crystal on the example of $BaSO_4$.
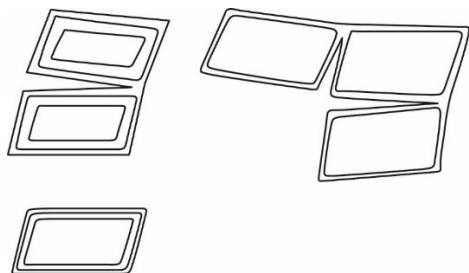
Figure 2. Attachment of the elementary crystals of $BaSO_4$ during the formation of the real crystal [1].

On Figure 3 he showed the morphology of crystals with well-formed faces, edges and corners (Fig. 3a), dendritic crystals (Fig. 3b) and amorphous particles (Fig. 3c), all of them obtained through attachment of the elementary crystals at different kinetics of crystallization: slow crystallization yields well-shaped crystals (a), faster crystallization yields dendritic crystals (b) while amorphous particles (c) are obtained under fast crystallization.
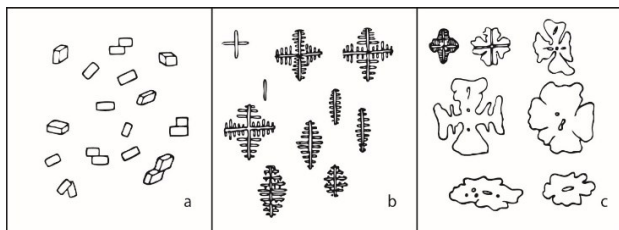
Figure 3. Structures obtained through attachment of the elementary crystals at different kinetics of crystallization: (a) Crystals with well-formed faces, edges and corners; (b) Dendritic crystals; (c) Amorphous particles [1].

Both the oriented self-organization of the elementary crystals and their subsequent attachment are due to the following specific physicochemical properties of the elementary crystals:
- the high values of their surface-to-bulk ratio;
- their fine building composition differing from the stoichiometric one and the different characteristics of the faces, edges and corners of the elementary crystals;
- their ability for ordering in common crystallographic orientations and aggregation as a

result of electrostatic and anisotropic van der Waals forces.

By the term "fine building composition of the crystals" Dimiter Balarew implies crystals with a composition different from the stoichiometric. So, if we suppose, for instance, that we have a CaF_2 crystal with the dimensions of a crystallographic unit cell, it consists of 14 Ca^{2+} ions and 8 F^- ions, i.e., the Ca/F ratio is 1.75 (Figure 4).
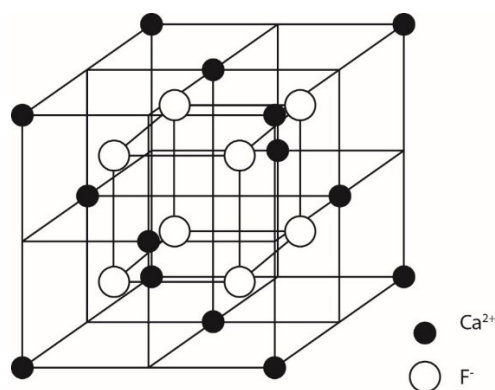
Figure 4. Unit cell of the CaF_2 structure (Ca/F ratio = 1.75) [1].

As the size of this crystal increases, the Ca/F ratio decreases, as shown in Figure 5, and at a sufficiently large crystal size it reaches the stoichiometric composition. This range of crystal sizes actually corresponds to nanoparticle-sized crystals.
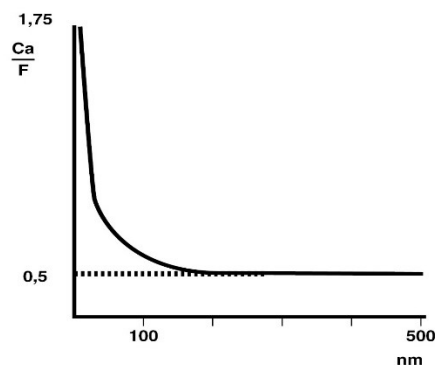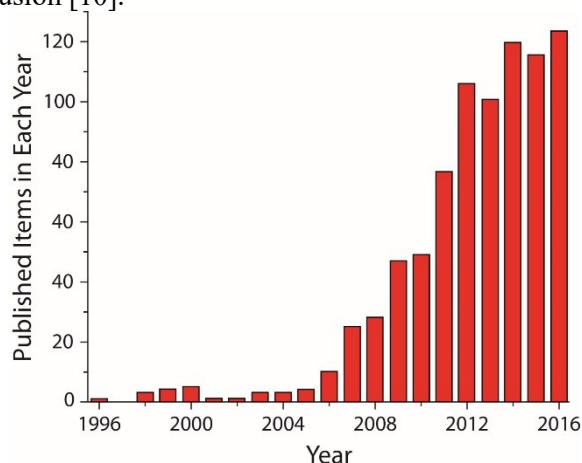
Figure 5. Dependence of the composition of the crystals on their size as numbers of the unit cells [1].

Through formation of the actual crystals by aggregation of the nanocrystals, internal surfaces remain in the bulk of the macrocrystal, which are hydrated, also containing adsorbed admixtures from the mother liquid. Dimiter Balarew called this occurrence "an internal adsorption process".

The theory of Dimiter Balarew remained more or less in forgetfulness. However, in the last three decades an increasing number of examples were observed, which could not be explained by classical models. Finally, it was proven that a crystal can grow

not only by attachment of atoms, ions or molecules, as in the classical models but also by attachment of particles, a process known as nonclassical crystallization. The idea for the occurrence of a self-assembly process of agglomeration of nanoparticles as a structure-generating process of formation of macrocrystals, close to the idea developed by Dimiter Balarew, was created in the early 2000s by Cölfen and Antonetti [9] who named the crystals obtained according to this mechanism mesocrystals (shortened name for mesoscopically structured crystals). Cölfen defined the mesocrystals as superstructures composed of nanoparticles, being arranged three-dimensionally in crystallographic register. Mesocrystals are often only intermediate structures in a nonclassical crystallization pathway leading to a final single crystal by nanoparticle fusion [10].

Since mesocrystals have high crystallinity, as well as high porosity, they are promising substitutes for single-crystalline and/or porous polycrystalline materials in many applications such as catalysis, sensing, and solar-energy conversion [11]. Figure 6 shows the growing interest in mesocrystals in the years 1996 - 2016 [12].

Figure 6. Papers published per year on mesocrystals as numbered by Sturm *et al.* [12] by the search of word *mesocrystal* in the Web of Science by the end of 2016.

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