

## MS49.P17

*Acta Cryst.* (2011) A67, C539**Stochastic formalism for nucleation under unsteady conditions**

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Kinetics of nucleation are relatively well understood under steady-state conditions, the main problem still unsolved being the large uncertainties introduced by the stochastic nature of nucleation. To tackle this problem, a probabilistic formulation for nucleation kinetics is required instead of the deterministic formulations currently available. Some approaches in this direction have been presented mainly related to the derivation of kinetic information from experimental data [1], but a general formalism for stochastic nucleation is still incomplete at best.

A Langevin-type stochastic differential equation (LT-SDE) is proposed to model the fluctuating behaviour of the cluster radius in the spherical shape approximation. Indeed, an analytical solution for the probability density function of induction time is obtained not only for steady but also unsteady work of cluster formation. The latter condition allows for the study of time-dependent (supersaturation, pressure, temperature, etc.) nucleation processes from a stochastic point of view.

Crystallization under unsteady conditions are getting very important in mainstream fields like protein crystal growth, where the small volumes involved and the wide metastable area in the phase diagram imposes the use of large supersaturation values induced by diffusion of the precipitant. In such conditions, the stochastic effects in nucleation are largely controlled by unsteady kinetics and can be responsible for the selection of the supersaturation at which nucleation happens (which is central for the quality of the crystals obtained) and, more importantly, the kinetic selection of polymorph.

[1] A. F. Izmailov, A. S. Myerson, S. Arnold, *Journal of Crystal Growth* **1999**, 196, 234-242.

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## MS49.P18

*Acta Cryst.* (2011) A67, C539**Nucleation and growth of crystals within the frames of the quataron concept**

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The problem of crystals nucleation has come into scientific use in XIX century as a problem of the origin of a new phase in the course of phase transition. More or less finished theory has been formed by the beginning of XX century. According to the classical molecular-kinetic theory of phase-formation, the nucleus of a new phase is formed as a result of consecutive joining of atoms to each other. With that, that grouping of atoms or molecules which has reached such sizes that can exist in equilibrium in the environment is called a critical nucleus. We alternatively suggest another two-step mechanism of crystals nucleation. According to this mechanism nucleation is preceded by the stage of clusterization of substance which results in the formation of special nano-size clusters in crystal-forming media (clusters of "hidden" phase or quatarons). Formation of clusters of hidden phase occurs on the mechanism of self-organization and is conditioned by specific behaviour of substance at nano-level. The top radius boundary of spontaneously formed clusters of "hidden" phase is limited by size

$4\delta$  where  $\delta$  – approximately corresponds to diameter of cluster-forming atoms, molecules or other structural units. Namely clusters with radius  $r \geq 4\delta$  are potential centers of crystallization. They, at observance of some not severe conditions, are transformed to crystal nuclei.

As to crystals growth, corresponding theoretical concepts in general were developed by mid of last century on the basis of solution of the problem on the nature of building units. The key competitive ideas for concepts development were:

1. Crystals grow by joining of separate atoms (ions) or molecules (Kossel-Stransky concept).
2. Building units at crystals growth are separate crystal blocks (Fedorov-Balarev concept).

In principle, realization of these two extreme variants does not contradict the general laws of physics and chemistry. The majority of modern models of crystals growth are built within the frames of these concepts. However every year collects more and more experimental data obtained, first of all, on the basis of direct researches of the structure of crystal-forming media by spectroscopic methods and observations over growth of crystals by means of atomic-force microscopy, testifying to more difficult character of crystal-forming and to existence of differently organized atom-molecular groupings in crystal-forming media. In this connection the idea on building units as particles of larger, than separate atoms or molecules, but not crystal particles is discussed and finds more and more proofs. The ideas on the multi-route and combined character of growth of crystals become dominating. As to our quataron concept, the mechanism of crystals growth lying in its basis is trivial and simple. Quatarons, appearing on a growing surface of a crystal, either break up to separate atoms (further - atomic growth) or form two-dimensional nuclei (layer-by-layer growth). In rare cases they can form fractal structures on the surface (fractal growth) or inhibit growth. On their fundamental properties quatarons appeared to be ideal structures as building units. Among the advantages of the quataron concept is that only it operates with nonequilibrium structural units at description of crystals growth, which, in turn, also takes place only in nonequilibrium conditions. The basic laws of formation and growth of crystals find explanation within the frames of the quataron concept.

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## MS49.P19

*Acta Cryst.* (2011) A67, C539-C540**Direct AFM-observations of Dissolution Processes on Dioxydine Crystal Defects**

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Presented here are the results of *in-situ* AFM (atomic-force microscopy) investigations of the crystallization in solution. It is shown that dissolution of the crystal surface of the organic compound of dioxydine ( $C_{10}H_{10}N_2O_4$ ) simultaneously follows two fundamentally different mechanisms: 1) the mechanism of formation of hollow nucleus on the crystalline defects; 2) the layer-by-layer mechanism activated by screw dislocation. It is the first time when we have received successive images of dioxydine surface dissolution on dislocational spirals of different type. We have studied the differences in sculpture and behaviour of multifilar spirals formed by screw dislocations located at distance more and less than  $2\pi r_c$  ( $r_c$  – the radius of the critical nucleus). We show how the form of complex dislocation canal depends on position of canals of single dislocations. It has been established that growth and dissolution on the screw dislocations on the face (100) of dioxydine