

# MORPHOLOGY AND GROWTH UNIT OF CRYSTALS: AN INTRODUCTION

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Nicolaus Steno (1638–1687) was the pioneer of the science on morphology of crystals. In his treatise “*De solido intra solidum naturaliter contento dissertationis prodromus* (1669)”, he correctly argued that quartz crystals take on various external forms because growth rates of the faces are anisotropic. Anisotropy in growth rates forms the core of the problem, although in the time of Steno it was not understood why anisotropy is present.

During the 17th to 19th Centuries, classic geometrical crystallography was established and structural crystallography started to develop. The latter has developed gloriously since 1912. However, we had to wait until 1930th before we have atomistic models of crystal growth, such as two-dimensional nucleation growth model by Volmer-Kossel-Stranski, and later spiral growth model by Burton-Cabrera-Frank.

Important concepts that were formalized before the birth of atomistic crystal growth models were

Equilibrium form, a form that can be expected in equilibrium under a given  $P$ ,  $T$  condition.

Structural form, a form that can be expected on the basis of geometry of a lattice or a structure, and thus is not directly related to thermodynamic parameters.

Growth forms, various forms that can appear as transient forms before a given crystal attains equilibrium.

It is to be noted that morphologies of polyhedral crystals and dendrites were separate problems in these days. It is also interesting to note that the equilibrium form has recently attracted revival interests and have been experimentally studied because of He crystals, and structural form has been modernized by incorporating modern concept of crystal growth and interface roughness.

After the birth of atomistic models of crystal growth, studies on

morphology of crystals have made a remarkable progress. Morphology of crystals became to be investigated in relation to crystal growth mechanisms. Thus the concept of interface roughness and roughening transition became the core of the problem. Extensive computer simulations have been made to demonstrate how a smooth interface transforms to a rough interface as  $\alpha$  values decrease or as driving forces increase. Step pattern morphology has been investigated extensively. Also internal morphologies such as growth sectors or growth banding have become a subject of investigation. In Table 1, the important concepts emerged through these investigations are summarized.

Another important concept that emerged during these days was morphological stability of solid-liquid interfaces. Through these advancements, morphologies of dendritic and polyhedral crystals became consistently

TABLE 1.

STRUCTURE	GROWTH	SYNTHESIS	INTERN. CONF.
Kepler, 1611 snow flakes <i>Packing</i>	Steno, 1669 quartz crystals <i>Growth Rate Anisotropy</i>	Alchemist  Flux method	
Hauy, Bravais <i>Primitive Form, Lattice</i>	habit variation <i>Morphology-Lattice</i>	Verneuil method (ruby)	
Geometrical Crystallography			
Laue, 1912 X-ray diffraction	diffusion, convection <i>Diffusion Layer</i>	BS CZ (optical)	
Crystal chemistry	VKS, 1930th <i>Layer Growth</i>  BCF, 1949, 1951 <i>Spiral Growth</i> surface microtopography <i>R-<math>\sigma</math> relation</i>	Hydrothermal (piezo)  (semiconductor)	Faraday Society, 1949
Automation	Jackson, 1958 <i>Interface Roughness</i> Mullin & Sekerka, 1968 <i>Morphological Instability</i> Bennema, Gilmer, 1971	LEC EFG  Thin film Epitaxy	Cooperstown C., 1958  Nancy Coll., 1965 ICCG-1, 1966
Protein structure	Computer simulation <i>Roughening Transition</i>  In-situ observation	LPE MBE MOCVD	ICCG-4, 1974 ICVGE

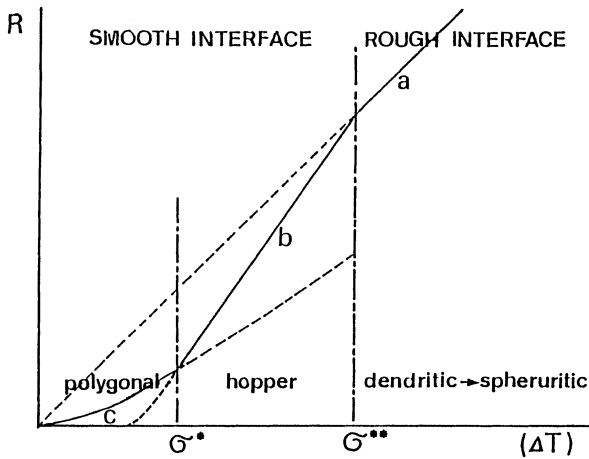


FIG. 1. Morphologies to be expected in different  $\Delta\mu/kT$  or  $\sigma$  regions. Schematically shown on  $R$  vs.  $\Delta\mu/kT$  diagram.

understood. In Fig. 1, a schematic diagram is shown, which represents only a section of events but can be utilized as a standard. Depending on phases, materials, sizes, the positions of  $\sigma^*$  and  $\sigma^{**}$  in Fig. 1 may change.

Although morphology of crystals attaining a certain size has been the main subject of study, it is interesting to know whether ultra fine particles as small as 50 Å or less in diameter will take the same morphology as or different morphology from larger crystals. We will see in this Seminar the behaviour of ultra fine particles.

Although in all theoretical models of crystal growth, atomic or ionic entities are assumed as growth unit, experimentalists have argued the possible existence of larger growth unit, which will certainly modify the growth morphology. It appears to the present author that experimental evidences supporting this argument have been increasingly reported in different fields of research. Identification of quasi-crystal, polymerization in complicated silicate melts, observation of dense sub-layer within the boundary layer around a growing crystal may be taken as such examples.

How various morphologies appear and what is the relation between morphological variations and growth parameters are not only a subject of mere curiosity, but also are closely related to applied fields, including geological science, atmospheric physics, metal and alloy solidification, quality control of semi-conductor or optoelectronic crystals, industrial crystallization and further to biomineralization. Since morphology of a crystal represents the whole growth process, we may say that those who understood morphology

have understood crystal growth and thus can apply the principle correctly. We need co-operation among scientists from different fields, but interested in the same subject, to solve these problems.

It is the convenor's pleasure that a forum is provided in a form of Oji International Seminar to discuss the problem, internationally and interdisciplinary.