

## 結晶の成長と溶解およびその形態

## Formation of patterns in growth and dissolution of crystals

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This talk is concerned with fundamental aspects of formation of pattern of crystals in undersaturation. The formation of patterns in crystal growth is a free-boundary problem in which the interface that separates the crystal from an associated solution or vapor phase moves under the influence of non-equilibrium conditions. The formation of patterns in crystal dissolution/evaporation is also a free-boundary problem. The topics of dissolution/evaporation pattern of crystals, however, have been neglected in comparison with the study of growth morphology of crystals except a few studies [1].

The growth patterns depend markedly on conditions in the solution/vapor phase, such as temperature and concentration, which influence the growth speed of each element of the interface. The growth speed of the interface also depends on the local geometry of the interface, specifically on the interface curvature and the orientation of the interface relative to the crystal axes. Although the dissolution/evaporation forms diminish with time, the patterns could also depend on conditions in the solution/vapor phase under the small deviation from equilibrium conditions.

The local motions of interface can, in principle, be determined by solving the transport equations that take into account the following elementary processes:

- 1) a diffusion process for the transport of latent heat liberated or absorbed at the interface,
- 2) a process for diffusing molecules through the solution/vapor phase toward or from the interface, and
- 3) an interface kinetic process for incorporating/decorporation molecules into/from a crystalline phase at the interface[2].

We consider the asymmetry of normal speed at interface relative to the equilibrium point from supersaturation to undersaturation. We shall term the positive normal speed the growth rate of crystallization and the negative normal speed the dissolution/evaporation rate. Both local normal speed  $V$  of the interface can be proportional to the deviation from local equilibrium conditions  $\Delta$ , which depend on interface curvature:

$$V = \beta \Delta,$$

where  $\beta$  is a kinetic coefficient that can depend on interface orientation and the degree of supersaturation or undersaturation at the interface. In general,  $V$  includes the Boltzmann factor  $\exp(-E/kT)$ , where  $E$  is an activation energy,  $k$  is the Boltzmann constant and  $T$  is temperature. Since the factor  $\exp(-E/kT)$  causes enhancement of the dissolution/evaporation rate for  $T > T_e$  but reduction of the growth rate for  $T < T_e$ , the behavior of  $V$  relative to  $T_e$  is asymmetric. On the other hand if  $V$  is controlled by the undersaturation and the factor  $\exp(-E/kT)$  does not work, the dissolution rate can approach a limiting value. This is because the degree of undersaturation has a minimum limit, e.g., pure solvent without solute.

In this talk, we show the patterns during growth or dissolution/evaporation of a two-dimensional crystal under conditions such that the transport of heat and/or solute is so rapid that growth is controlled by interfacial processes. Furthermore, we discuss the formation of both patterns in the point of view of the asymmetry of normal speed at interface relative to the equilibrium point.

## references

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