

# Some general remarks on crystallisation in the presence of additives

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## *Résumé*

Le présent article résume les données de base de la physique de la cristallisation, les équations essentielles qui expliquent la nucléation et la cinétique de croissance, ainsi que les modes d'action d'un additif sur les propriétés du système et son influence sur le déroulement de la cristallisation. L'application au cas particulier d'un film d'une solution de chlorure cuivrique en présence d'additif est envisagée : le système est hétérogène dans le temps et l'espace. L'incidence de facteurs expérimentaux, tels les phénomènes de mouillage et de démouillage en rapport avec l'état de surface du support, la vitesse d'évaporation et les phénomènes de convection, est discutée. Ces facteurs sont à contrôler pour obtenir des résultats reproductibles et permettre ainsi de nouvelles possibilités quant au pouvoir prédictif de cette technique.

## *Summary*

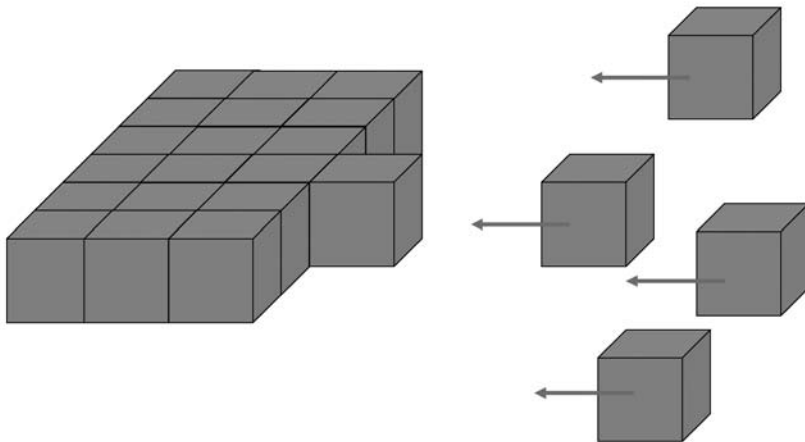
This paper summarises the basic physical principles of crystallisation, the fundamental equations which explain nucleation and growth kinetics as well as the effect of an additive on the properties of the system and the course of crystallisation. Application to the special case of a film comprising a copper chloride solution containing an additive is considered. This system is temporally and spatially heterogeneous. We also discuss the experimental factors, as well as the wetting phenomena in relation to the surface properties of the support, the speed of evaporation and convection phenomena. These factors should be controlled so that reproducible results can be obtained and thus allow new possibilities to arise regarding the predictive value of this technique.

## *Zusammenfassung*

Der vorliegende Artikel ist eine Zusammenfassung der Physikgrundlagen der Kristallisation, der grundlegenden Gleichungen, die die Nukleation und die Wachstumskinetik erklären, sowie der Wirkung eines Zusatzes auf die Eigenschaften des Systems und den Kristallisationsablauf. Die Anwendung auf den besonderen Fall eines Films, bestehend aus einer Lösung von Kupferchlorid im Beisein eines Zusatzes, wird in Betracht gezogen: Das System ist heterogen in Zeit und Raum. Diskutiert werden auch die experimentellen Faktoren sowie die Benetzungphänomene in Bezug auf die Oberflächeneigenschaften des Trägers, die Abdunstungsgeschwindigkeit und die Konvektionsphänomene. Diese Faktoren sollten unter Kontrolle gebracht werden, damit wiederholbare Ergebnisse erhalten werden können, um neue Möglichkeiten in Bezug auf das Voraussagevermögen dieser Technik zu erlauben.

## 1 Introduction

At first glance, forming a crystal starting from individual molecules seems to be an easy task. One simply has to assemble these molecules according to the ‘construction manual’ defined by the characteristic parameters of the unit cell of the crystal. However, if the crystallisation process advances at a finite (i.e., non-zero) growth rate, complications arise due to the necessary transport of the molecules towards the ‘construction site’ and the time needed for the integration into the crystal (Fig. 1). The growth front becomes unstable and the resulting crystals are less perfect in the sense that their morphology is no longer reflecting the form of the crystal lattice. Fascinating patterns are created, as can frequently be seen in Nature, for example snowflakes (cf. [snowcrystals.com](http://snowcrystals.com))



*Fig. 1:* Schematic representation of the formation of a two-dimensional crystal by transporting molecules (indicated by cubes) towards the crystal front. The site closest to the reservoir of free molecules has the highest probability of ‘capturing’ free molecules. Thus, this site will grow faster than the neighboring sites, giving rise to an instability of the growth front.

Such instabilities of the growth front can be reduced in number, or eliminated completely, if the growth process proceeds at low rates. Then, each molecule arriving at the front will have enough time to ‘examine’ the crystal surface and to find the ‘ideal’ location for its integration in the crystal. ‘Ideal’ means that the growth front stays smooth, as in such a case each molecule will profit from having the maximum possible number of neighbouring molecules, thereby reducing the free energy of the system.