

## Poster Sessions

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### MS35.P18

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#### The growth morphology of gypsum crystals: an experimental study

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Gypsum (calcium sulfate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is the most abundant sulfate mineral throughout natural earth systems and is also present in a wide range of industrial processes (e.g. construction material, fertilizer) where the morphology and size of the crystals determines the final characteristics of the product. But despite its importance in natural and artificial processes neither the growth nor equilibrium morphology of gypsum crystals are properly understood [1]. A series of crystallization experiments were conducted to identify the key parameters that control the growth morphology of gypsum crystals.

When gypsum precipitates from a supersaturated  $\text{CaSO}_4$  solution, single crystals, twins and spherulites are formed. All of them present the same trend in growth morphology as a function of temperature and supersaturation. At low temperatures ( $\approx 4^\circ\text{C}$ ) mainly plate like crystals are formed and morphology varies little with supersaturation. At higher temperatures ( $\geq 20^\circ\text{C}$ ) crystals with needle habits are dominant, becoming more elongated as supersaturation increases. When supersaturation surpasses a critical value crystal size starts to decrease. The influence of temperature and supersaturation on the growth morphology can be, roughly, explained in terms of changing growth kinetics with varying temperature [2] and increased nucleation at higher supersaturation. Although it should be mentioned that crystals grown under the same experimental conditions always present a large variation in growth morphology (except at  $4^\circ\text{C}$ ). Transmission Electron Microscopy was used to observe the growth morphology of crystals at the early stages of crystallization and this large variation in morphology was also observed (Figure 1). These results indicate that the nucleation stage and/or the early stages of growth have a large influence on the growth morphology of gypsum.

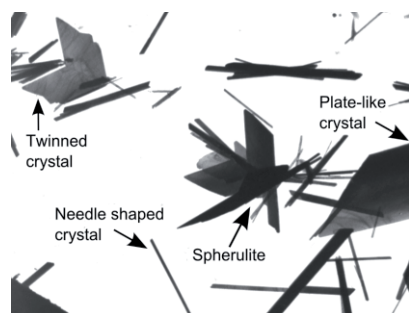


Figure 1. TEM image of gypsum crystals grown at room temperature (Saturation Index  $\text{gypsum} = 0.73$ ). Chemical reaction stopped after 4 minutes since reagents are in contact.

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#### Crystallization of acetaminophen on a polymer surface

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Polymorphic control has long been desired. One of the ways to achieve this control is by heterogeneous nucleation. Recently the use of polymers as heteronuclei has been investigated and the results suggest that the polymers to some extent are able to facilitate selective growth of polymorphs [1]. Furthermore heterogeneous nucleation can be a way to obtain polymorphs, which have not been produced before because of a large kinetic barrier in the aggregation step.

In this study the mechanisms behind heterogeneous nucleation on a noncrystalline polymer surface are investigated. An important factor in the initial aggregation of molecules on a surface could be the roughness of the surface. In addition to the roughness the polarity of the surface is too suspected to contribute to the selective growth.

The roughness of spin-coated polymer surfaces is determined by AFM, and the polymorphic form and orientation of acetaminophen crystallized on the surface is determined by powder X-ray diffraction.

In addition to the experimental work a theoretical approach is also taken. Because of the substantial size of acetaminophen interaction with the surface, it is not feasible to treat the whole system quantum mechanically. The system is therefore treated with quantum mechanics/molecular mechanics. This implies that the system is divided into a smaller part treated by quantum mechanics and a part treated by molecular mechanics.

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### MS35.P20

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#### In situ study of temperature effects on protein crystallization

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Despite the number of protein structures solved by X-ray diffraction increases exponentially, the quality of the single crystal samples obtained from standard crystallization procedures still limit structural studies and results obtained. The classical theory for crystallization some nuclei may become crystals when they exceed the free energy barrier and the critical size. Physical-chemical parameters such as temperature, pH and concentration alter the height of the free energy barrier and consequently the critical nuclei size and the growth rate. Indeed the physical-chemical changes in the protein solutions during the crystallization process are complex and far from well understood [1].

According to Marseille Protein Crystallization Database crystallization essays have been performed in two preferential temperatures: 277K or 293K [2]. Results presented in the literature

suggest that the temperature may influence the nucleation and growth by changing the supersaturation level or by inducing liquid-liquid phase transitions [3].

In this study the effects of temperature in the nucleation and in the growth of crystals of different proteins were investigated. Protein crystals grown using batch technique over a temperature range from 277K to 297K were measured and counted. The preliminary results indicate that under the same crystallization conditions, a remarkable change in the number of crystals is observed when the crystallization temperature is modified. Dynamic Light Scattering experiments were performed for *in situ* determination of the size of aggregates during the crystallization process [4]. According to the fluctuation theory, the diffusion coefficient(s) of the sample solution can be obtained from the correlation times of the second order Auto Correlation Function (ACF) of the scattered light intensity. In this application, the ACF decays like the square of sum of exponentials [5] and the size distributions are determined using the Einstein-Stokes relation for diffusion when polydisperse aggregates are considered rigid spheres moving through the sample with low Reynolds number. Data analysis was performed using the program SEDFIT and according to the maximum entropy [6] the square of sum of two exponentials better adjust the data.

The results of DLS experiments indicated no temperature dependence of the growth rate of the scatters (crystals, nuclei) in the investigated temperature range. However, the scattered light intensity during the crystallization essays suffers a crucial change with temperature. Thus, temperature seems only to affect the crystallization process by altering the number of nuclei exceeding the critical size.

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### Growth kinetics of the {100} face of potassium chloride crystals

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There are different kinds of particles (atoms, molecules, molecular clusters, etc) in the solutions but it is not known exactly what particles are the building units of the ion crystals. The work [1] suggests a theory which connects the growth rate with the Kossel or non-Kossel models of growth. So, the study of the dependence of the step velocity on supersaturation and other parameters may help to verify the models of ionic crystal growth.

The growth kinetics of the {100} faces of potassium chloride crystals was studied by atomic force microscopy (AFM) and Michelson laser interferometry.

Interferometric observations have shown that potassium chloride exhibits skeletal growth morphologies. Solution inclusions and segmented faces have appeared even at low supersaturation. The growth steps mostly came from the edges and quickly gained domination over growth hillocks on the face. At higher supersaturations of solution the growth hillocks appeared on the face, as well, but they often overlapped.

According to [2] the growth rate of potassium chloride decreases in the presence of lead chloride. Also PbCl<sub>2</sub> additive makes more stable the {100} faces of KCL crystal, preventing them from segmentation, and stimulates the appearance of growth centers on the surface.

Lower growth rates of the {100} faces in PbCl<sub>2</sub> doped solution allowed *in situ* study of surface crystallization processes by AFM. These experiments showed that lead chloride influenced significantly surface morphology of potassium chloride crystals.

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**Keywords: crystal, surface, kinetics**

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### Crystal growth using low temperature gradient sublimation

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Many organic compounds are known to exist in different crystalline forms both as polymorphs and solvates [1]. Since processing steps in pharmaceutical industry raise many opportunities for phase transformations or solvate formation which may affect their physico-chemical properties it is important to be able to obtain pure crystalline forms.

A method for growing high quality single crystals in the gas phase has been developed. The combination of low (and very low) temperature gradients with vacuum sublimation has several important advantages over other crystallization techniques. Sublimation (which is also a purification technique) can give good quality single crystals in few hours without the necessity of using solvents. The crystalline form and morphology of crystals grown from gas phase are far less affected by solvents and impurities than crystals grown from solution.

The method has been successfully applied to several different classes of compounds. These include systems which exhibit polymorphism, pseudo-polymorphism (sulfathiazole, carbamazepine), have difficulties with crystal packing (stanazolol and ethinyl estradiol [2]) or have problematic morphologies when grown from solution (4-hydroxy-N-phenyl-benzenesulfonamide).

All compounds were analyzed using single crystal X-Ray diffraction, X-Ray powder diffraction, FT-IR spectroscopy and differential scanning calorimetry.

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### Effect of cooling rate on thermal crystallization of energetic materials

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