Crystallization in dense food systems

1. Company information

NIZO food research is an independent contract research institute for the international food industry. Turnover 20 MEuro; 150 FTE. Research is core activity, ranging from applied to fundamental, in the areas of the physical chemistry of food, microbiology of food, health and food processing.

2. Problem

The problem which may profit from fundamental/theoretical consideration is in our view the process of crystal formation in dense systems (low solvent activity) or porous systems (high solvent activity but high tortuosity).
In practical systems of relevance are in our case food systems such as:

- Ripened cheese (tyrosine and lactose crystals)
- Protein bars (sucrose crystals)
- Milk powder (lactose crystals)
- Ice cream (ice crystals)
- Chocolate (triglyceride [fat] crystals on the surface, also known as 'blooming')

In most cases (except in chocolate) the solvent of the crystallizing material is water.
From this short list in becomes clear that the issue of crystallization plays a role in various food products of economic importance. In most cases crystallization is not wanted, and poses therefore a quality issue. For instance, sugar containing matrices (e.g. protein bars) become tough or even hard during shelf life due to crystallization of sucrose. In ripened cheese, a white gloss is often seen on cutting surfaces due to the formation of Ca-lactate crystals. This is mistaken for mould by the consumer, and the product is thrown away. On the other hand, in old cheese (e.g. Old Amsterdam) visible crystals of tyrosine, an amino acid formed during hydrolysis of proteins by flavour-producing microbes, are a signature of quality and their growth should be stimulated.
Lactose crystallization in spray-dried milk powder (including infant formula) is a huge problem in industry, because during storage it may cause caking and eventually solidification of the bulk of powder.
The 'mouldy' appearance of chocolate which was stored at a too high temperature due to recrystallization of the low molar mass fat fraction is well known.
In ice cream, a too high storage temperature causes roughness of the ice cream due to the formation of large ice crystals.

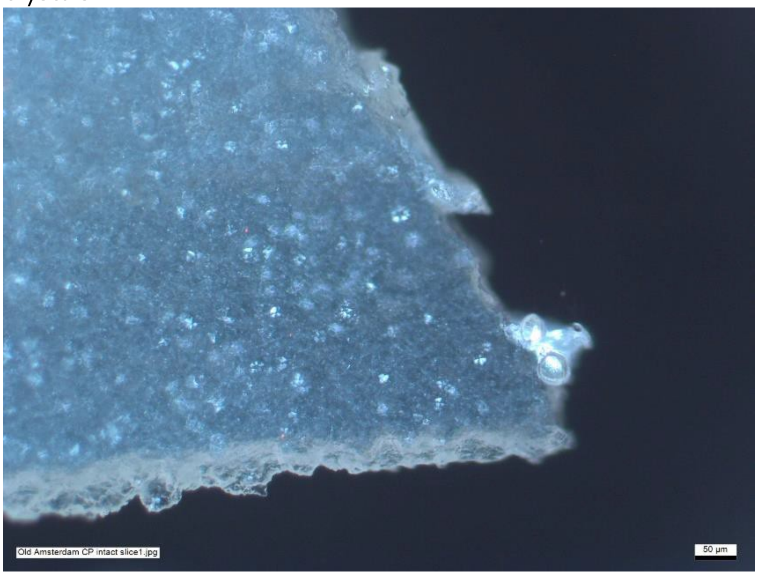

Figure 1 Crystals (probably Ca-lactate) in old cheese. Taken between crossed polarizers, highlighting the crystals.

The common properties of these systems are:

- supersaturation (obviously)

- a high concentration of non-inert interface
- a matrix with a certain modulus, (possibly) suppressing the growth of (standard) crystals
- a low diffusivity
- a possibility of preferential adsorption of specific crystal planes on elements in the matrix

The question is whether there is a set of parameters, measurable in non-complex conditions (such as wettability of the matrix, relative sizes of different crystal planes, diffusion of crystallizing molecules in non-saturated conditions, modulus of the matrix) which can be used to predict, suppress or promote crystallization of small molecules such as sugars and amino acids in dense, and several respects restricted systems. The processes at play may to some extent be similar to geological processes.
A relevant observation is shown in Figure 2, the state diagram of a frozen water-sucrose system. The freezing of water concentrates the sugar in an increasingly smaller volume. If the sugar concentration exceeds a certain value, the sugar solution becomes a glass. Further freezing of water is slowed down, or completely arrested, possibly because of the mechanical resistance of the sugar/water glass, or because the diffusion of water towards the ice frontier is slowed down by the glass formation. One of the outcomes of this work shop is envisaged to be a quantitative estimate of these effects.

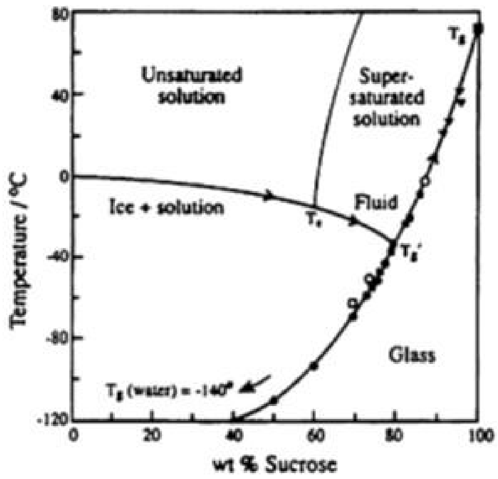

Figure 2 State diagram of a sucrose/water system. Figure taken from F. Franks, Eur. J. Pharm.Biopharm 24 221 (1998)

Further fundamental questions that might be addressed in the work shop:

- Which soluble polymer length is needed for a (small) fraction of insoluble monomers to become unnoticeable?
- How can we estimate which stress a growing crystal can overcome?
- How does the crystal shape change when there is an adsorbing matrix around?

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