

# CRYSTALLIZATION

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## Summary

Many factors can influence crystallization in food products. What makes foods somewhat unique are the complexities that arise in food composition, and the efforts that are made to control a product's crystallization for texture or appearance and not for separation. In many products, the goal of crystallization is to generate a certain texture or appearance to make the product acceptable. Thus, nucleating many of the crystals that remain small within the product itself is often the goal. A large number of crystals must have small mean sizes and narrow distributions. The crystals must also have proper shape and/or polymorphs to enhance stability of the product during storage and distribution. However, in other types of products, crystallization is undesirable even though the system is supersaturated. In these cases, techniques are used to prevent crystallization from occurring during storage, since this leads to unacceptable product quality.

## 1. Introduction

There are many components in foods that crystallize either partially or completely. The

most important are sugars (sucrose, lactose, glucose and fructose), ice, lipids, and starches. However, crystallization of salts, sugar alcohols, organic acids, proteins and emulsifiers may be important in certain applications. Table 1 lists some of the main crystallization components in foods with examples of products where control of crystallization is important.

<b>Component</b>	<b>Product Categories</b>	<b>Product Examples</b>
<b>Ice</b>	Frozen desserts	Ice cream, frozen yogurt
	Frozen foods	Meats, fruits and vegetables, entrees
	Freeze dried products	Instant coffee, dried fruits, rehydratable meals
<b>Sugars</b>	Confectionery products	Grained caramels, fudge, fondant, panned goods, chewing gum
	Cereals	Frosted cereals, glazed cereals
	Dairy products	Whey and milk powders
	Other	Icings, frostings
<b>Sugar alcohols i.e., sorbitol</b>	Confectionery products	Chewing gum, sugar-free products.
<b>Lipids</b>	Spreads	Butter, margarine.
	Confectionery products	Chocolate, compound coatings, toffee.
	Baked goods	Croissants, puffed pastries, cookies, pie crust
	Other	Peanut butter, frostings
<b>Salts</b>	Table salt	NaCl, salt substitutes
	Dairy products	Milk, cheese
<b>Starches</b>	Baked goods	Bread, cookies, cakes, crackers
	Extruded products	Snacks, crackers
<b>Proteins</b>	Additives	Lysine
<b>Organic acids</b>	Powdered additives	Citric acid
<b>Emulsifiers</b>	Additives	Lipid-based products, dressings

Table 1. Typical food products where controlling crystallization is important to quality and shelf life.

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In many food products, the crystalline structure within is important to product quality, texture, and stability. It is this structure, along with other structural elements (emulsions, air cells, etc.), that determines product appearance (e.g., frosted cereal coating), mechanical properties during handling (e.g., spreadability of butter), mouthfeel during consumption (e.g., smoothness of ice cream), and shelf stability (e.g., fat bloom in

chocolate). The nature of the crystalline structure is controlled by manipulating the products composition and processing conditions.

Crystallization is also important during the processing of certain food components, as a purification or separation step. Examples of where a separation process is important include refining of sugars (sucrose, lactose, glucose, etc.), salt, and organic acids (citric acid, etc.), fat fractionation (palm oil, milk fat, tallow, etc.), and freeze concentration. In these situations, crystal formation is controlled for efficient separation from the liquid phase.

No matter what the application, crystallization involves the following steps. First, the liquid must attain a level of supersaturation or supercooling. This is accomplished through cooling or evaporation. Once a critical supersaturation has been exceeded, nucleation occurs. Nucleation involves formation of a crystalline state from the supersaturated liquid state. Once nuclei form, they grow into product-sized crystals through incorporation of additional molecules into the crystal lattice. Crystallization continues until equilibrium is achieved between the liquid and crystalline states and an equilibrium phase volume (of the crystal) is produced. Further changes in crystalline structure can occur during storage, especially as temperature and moisture content fluctuate, due to further equilibration of the crystals' surface free energy or internal energy. This ripening of crystals is often called recrystallization.

Controlling crystallization to generate a desired crystalline structure requires an understanding of how formulation and processing factors influence the kinetics of nucleation, growth, and recrystallization. In some cases, nucleation must be inhibited to allow the formation of only a few crystals, which can then grow to a large size for efficient separation. In many cases, however, it is desirable to promote massive nucleation to inhibit their growth - a large number of crystals will provide a smooth texture in many food products (See *Sensory Evaluation*, and *Texture in Solid and Semi-solid Foods*).

## **2. Crystallization Principles**

Several fundamental principles are critical to an understanding of crystallization. These include: (1) the nature of the phase diagram and generation of a supersaturation; (2) nucleation, or formation of the crystalline phase from the supersaturated state; (3) growth of nuclei until all supersaturation is depleted and a phase volume equilibrium attained; and (4) recrystallization or ripening, where crystals rearrange, minimizing either surface free energy or internal energy.

### **2.1. Phase/State Behavior**

The phase diagram represents the equilibrium conditions that exist in a system (see *Phase Transitions*). In order to understand crystallization in a food product or process, it is important to know the phase boundaries of the system. From the phase diagram, one can obtain information about the driving force for crystallization during processing, as well as the final relationship between the crystalline and liquid phases after equilibration. For a simple binary system of solute and solvent, the phase diagram

shows the equilibrium curves for each component. For example, the phase diagram for sucrose-water can be seen in Figure 1. Equilibrium between the sucrose (the solute) molecules in liquid form and those in crystalline form is defined by the solubility line. Equilibrium between the water (solvent) in both liquid and crystalline forms is defined by the freezing point depression curve in Figure 1.

For many components, solubility increases with temperature, as seen with sucrose in water (Figure 1). However, some salts (i.e., Ca and Mg bicarbonates) have an inverse solubility relationship. These may be important in the heating of hard water during which they precipitate out as scale. Solubility curves for several sugars and polyols are shown in Figure 2. Some important solution systems in the food industry include sugars (sucrose, lactose, glucose, etc.), salts, organic acids and some specialized lipid systems where fat is dissolved in an organic solvent.

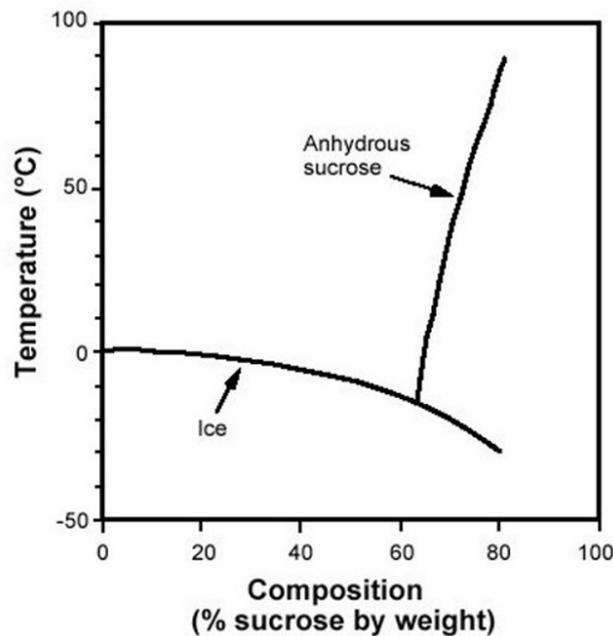


Figure 1. Phase diagram of sucrose-water system.

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In many systems of importance to the food industry, including sugars and organic acids, it is also important to note the transition from a liquid state to a glassy state as concentration increases and/or temperature decreases. For example, a sucrose syrup concentrated rapidly and then cooled rapidly to room temperature does not have sufficient time to crystallize before passing into a glassy state. This glass transition temperature depends on the concentration of solute. A glass transition line can be drawn on the binary phase diagram, which is often called a state diagram to denote the inclusion of non-equilibrium state transition between liquid and glass. Figure 3 shows the state diagram for sucrose-water and displays regions where crystallization can take place. Solute crystallizes only within the boundary between the solubility and the glass transition curves. Systems with lower concentration than on the solubility curve are under-saturated and do not crystallize. Systems with concentrations above the glass

transition point (at a given temperature) also do not crystallize, due to molecular mobility constraints. Solvent crystallizes only in the region below the freezing point depression curve.

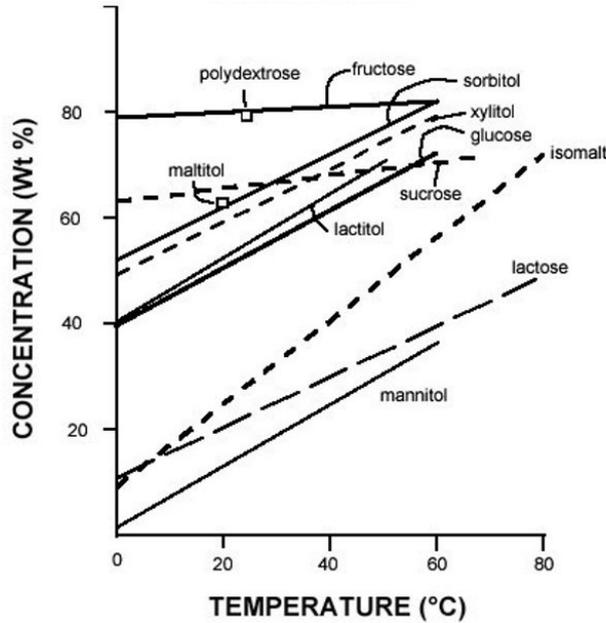


Figure 2. Solubility curves for sugars and sugar alcohols.  
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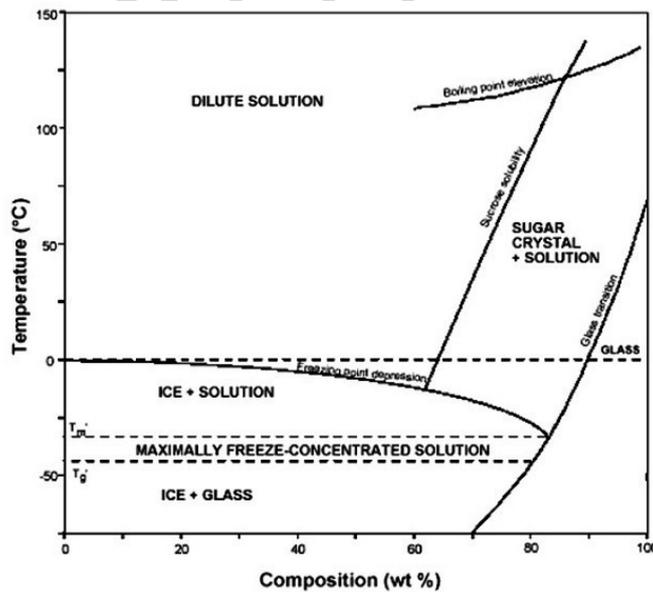


Figure 3. State diagram for sucrose-water system.  
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The driving force for crystallization of the solute is the extent of supersaturation. This is

often defined as the excess in concentration in the actual solution above the saturation or solubility concentration. Thermodynamically, the driving force is based on the difference in chemical potential between the supersaturated liquid and equilibrium solid states. This chemical potential difference is best defined as the difference in chemical activities between the supersaturated liquid and the equilibrium states. However, activity values are not often available for systems of interest in foods and are difficult to measure. Thus, the approximation of using concentration in place of activity is made to describe the supersaturation driving force. For solutes, the thermodynamic driving force increases as the difference in concentration of solute above the solubility concentration increases. However, crystallization rates do not necessarily increase as the supersaturation driving force increases, especially in systems that easily form glassy states. In this case, as concentration increases (or temperature decreases) and approaches the glass transition region, mobility of the molecules decreases, that is, the molecules are no longer able to move (either translation or rotation) with sufficient freedom to allow formation of the crystalline lattice. Thus, as glass transition is approached, crystallization rates decrease.

The driving force for crystallization of the solvent is simply the temperature sub-cooling below the thermodynamic freezing/melting point. In order to freeze ice in a sucrose-water system, for example, the solution must be cooled below the freezing point for the given solute concentration (Figure 1). The rate of freezing is generally proportional to the driving force (sub-cooling), although temperatures too low also result in decreased crystallization since decreased molecular mobility inhibits freezing. For natural lipids, the situation is more complex, since no single freezing/melting point exists. When a natural fat is heated, it melts over a range of temperatures dependent on the chemical composition and polymorphic variations. This melting range for fats is most often shown either as enthalpy changes measured by Differential Scanning Calorimetry (DSC) or as a decrease in solid fat content (SFC) measured by pulsed Nuclear Magnetic Resonance (NMR). SFC profiles for several natural fats are shown in Figure 4. Cocoa butter, which contains relatively few triacylglycerol components, melts over a narrow temperature range (25 to 35°C), whereas milk fat, which contains hundreds of different triacylglycerols, melts over a range from -40 to 40°C. Thus, it is nearly impossible to define a single melting point when defining a thermodynamic driving force for lipid crystallization.

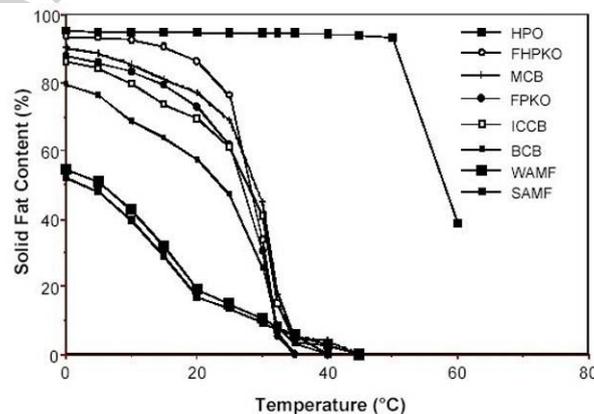


Figure 4. Solid fat content melting profiles obtained by pulsed nuclear magnetic

resonance. HPO: hardened palm oil; FHPKO: fractionated, hydrogenated palm kernel oil (PKO); FPKO: fractionated PKO; MCB: Malaysian cocoa butter (CB); ICCB Ivory Coast CB; BCB: Brazilian CB; WAMF: winter anhydrous milk fat (AMF); SAMF: summer AMF.

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In foods, other constituents often exist that influence the solubility and/or glass transition conditions. For example, adding corn syrup to sucrose alters both the amount of sucrose dissolved and the glass transition curve of the mixture.

Another example that is important in several foods (caramel, ice cream, etc.) is the mixture of lactose and sucrose. Figure 5 shows the effect of each component on the phase behavior of the other.

The addition of sucrose depresses the solubility of lactose, and vice versa. Since sucrose and lactose have different glass transition temperature curves, a mixture of the two has a glass transition curve somewhere between the lines representing the pure components.

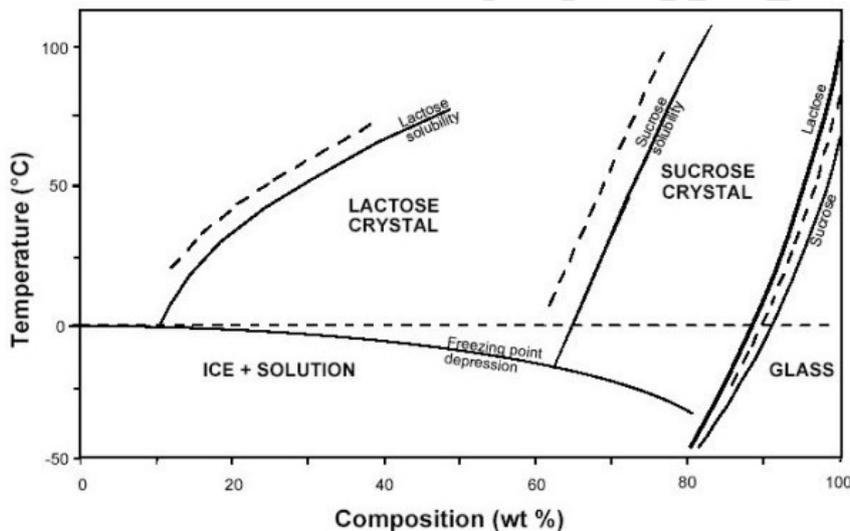


Figure 5. Mixtures of lactose and sucrose cause changes in phase/state behavior. Solid lines represent behavior of sucrose, dashed lines represent behavior of lactose and dotted line represents a mixture of sucrose and lactose.

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As foods become more and more complicated, with higher numbers of interacting ingredients, a quantitative description of phase behavior becomes more and more difficult. Nevertheless, the phase diagram contains useful information for quantifying the driving force for crystallization and the amount of crystalline phase volume produced at a given condition as the system approaches equilibrium. Further research is needed to clarify the interactive effects of mixtures of ingredients on the phase behavior of the crystallizing species.

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### **Biographical Sketch**

**Richard W. Hartel, Ph.D.**, currently a Professor of Food Engineering, has been with the Department of Food Science at the University of Wisconsin-Madison since 1986. After receiving a Ph.D. degree in Agricultural and Chemical Engineering at Colorado State University, Dr. Hartel spent four years as a Research Chemical Engineer at Eastman Kodak, Co. His current research interests include structure development during manufacture and storage of frozen desserts, the physical chemistry of lipid mixtures, lipid crystallization in foods, and sugar crystallization in foods. He teaches classes in Food Engineering, Food Processing, Phase Transitions and Lipid Chemistry.