Phase/State Transitions of Confectionery Sweeteners: Thermodynamic and Kinetic Aspects

Richard W. Hartel, Roja Ergun, and Sarah Vogel

Abstract: It has been said that the key to making high-quality candy is understanding and controlling the transitions of sugar. Whether found as crystal, glass, or fluid solution, sugars impart the texture necessary to distinguish one confection from another and to provide a unique experience to the consumer. In principle, the phase/state transitions of sugars are best understood through careful application of the phase diagram. However, many, if not all, confections are not at equilibrium, meaning that the phase diagram is simply a starting point for understanding and controlling the state of sugars. An understanding of the thermodynamic driving forces that push a confection towards equilibrium and the kinetic constraints that control the rate of approaching that equilibrium are key elements to creating products with the desired texture, quality, and shelf life. In this review, we summarize the thermodynamic and kinetic aspects of controlling phase/state transitions in sweeteners, with particular emphasis on applications to confectionery products.

Introduction

In confections and many other food products, controlling the state of sweeteners is critical to attaining the desired characteristics, from appearance to texture. Sweeteners may be found dissolved in the water in a food, dispersed as a crystalline phase, immobilized in the amorphous or glassy state, or various combinations of these states. For example, confections may be characterized according to the nature of the sweetener as shown in Table 1. During processing, sugars in confectionery formulations typically go through one phase transition, or more, depending on the nature of the product. Changes in phase behavior may also occur during storage, usually with a negative effect on shelf life.

Phase transitions are often categorized according to first-order, second-order, or higher-order transitions (Roos 1995; LeBail and others 2003). In a first-order transition, there is change in enthalpy, $H$, of the material (heat is either released or accepted) as the molecules go from one state to the other. In contrast, in a second-order transition, there is no enthalpy change associated with the transition, just a change in heat capacity, $C_p$. For example, when studied in a calorimeter (such as a differential scanning calorimeter [DSC]), a crystal melting (first order) is observed as an endothermic heat flux associated with the enthalpy change as heat is removed from the environment, whereas a glass undergoing a transition to the liquid state (second order) in the calorimeter exhibits only a small shift in the baseline at the glass transition (Roos 1995). Crystallization and glass transition are the 2 main phase/state transitions exhibited by sweeteners.

As noted in Table 1, the physical state of the sweetener can have a critical influence on the attributes of the confection; that is, crystals affect both appearance and textural properties. For example, the glassy state of a hard candy contains colors and flavors that are uniformly dispersed throughout the confection rather than being only on the surface as in colored rock (crystal) candy. Also, the chewy characteristics of a nougat or caramel, for example, can be moderated through formation of small crystals to impart a short texture to the confection.

Controlling phase/state transitions in sugar-based foods like confections requires knowledge of equilibrium considerations and kinetic effects. The equilibrium conditions, as described by the phase diagram, define what phase/state to expect if the food product attains phase equilibrium. However, kinetic constraints prevent many foods from attaining phase equilibrium, meaning that they remain in a metastable state during their entire span (acceptable...

Table 1—Categorization of sugar-based confections based on the state of sugar (from Ergun and Hartel 2009).

<table>
<thead>
<tr>
<th>Category</th>
<th>Examples</th>
<th>Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noncrystalline</td>
<td>Liquid</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td></td>
<td>Syrup candies</td>
<td>Chewy, solid-like structure due to hydrocolloids</td>
</tr>
<tr>
<td></td>
<td>Gummies and jellies</td>
<td></td>
</tr>
<tr>
<td>Amorphous</td>
<td>Ungrained caramel</td>
<td>Chewy</td>
</tr>
<tr>
<td></td>
<td>Chewy nougat</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Marshmallow</td>
<td></td>
</tr>
<tr>
<td>Glassy</td>
<td>Cotton candy</td>
<td>Floss</td>
</tr>
<tr>
<td></td>
<td>Hard candy</td>
<td>Hard and brittle</td>
</tr>
<tr>
<td></td>
<td>Brittles</td>
<td></td>
</tr>
<tr>
<td>Crystalline</td>
<td>Rock candy</td>
<td>Hard crystals</td>
</tr>
<tr>
<td></td>
<td>Candy powders</td>
<td>Free-flowing powder</td>
</tr>
<tr>
<td></td>
<td>Tablets or lozenges (wafers)</td>
<td>Compacted or fused powder</td>
</tr>
<tr>
<td>Partially crystalline</td>
<td>Grained (after dinner) mints</td>
<td>Variable texture depending on crystal content; with increasing “short” texture as crystal content increases</td>
</tr>
<tr>
<td></td>
<td>Fondants and creams</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Grained caramel and fudge</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Grained nougat and marshmallow</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hard and soft panned shell candy</td>
<td></td>
</tr>
</tbody>
</table>

MS 20100588 Submitted 5/28/2010, Accepted 8/25/2010. Authors are with Univ. of Wisconsin-Madison, Madison, WI, U.S.A. Direct inquiries to author Hartel (e-mail: rwhartel@wisc.edu).
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shelf life). Often it is the changes associated with the approach of these metastable states to thermodynamic equilibrium over time that lead to the end of shelf life. Thus, knowledge of the rate processes associated with phase/state transitions is also important for controlling microstructure, texture, and shelf life in foods.

Phase/State Diagram

The phase diagram for a sweetener in water describes the equilibrium conditions between 2 phases. Equilibrium in this case is defined as when the chemical potential of molecules in one phase is equal to the chemical potential of molecules in the second phase. For example, at the solubility concentration, sweetener molecules dissolved in the liquid phase have the same chemical potential as the sweetener molecules within the crystalline phase (Hartel 2001). The 2 most important equilibrium lines in highly concentrated sugar-based foods like confections are the boiling point elevation line and the solubility curve. A third equilibrium boundary, the freezing point depression curve, is important for frozen foods. These lines represent the equilibrium between water and water vapor (boiling point), dissolved sugar and crystals (solubility), and water and ice (freezing point).

The glass transition curve is often overlaid on the phase diagram to provide what is more properly called a state diagram (Roos and Karel 1991; Slade and Levine 1991; Roos 1995), so-called because the glassy state is metastable and not in an equilibrium condition. The state diagram, as defined by the boiling point elevation curve, solubility curve, and glass transition curve, provides a unique opportunity for understanding and controlling sweeteners in confections. Figure 1 shows the portion of the sucrose state diagram of importance for controlling the sugar phase transitions pertinent to confections—evaporation, crystallization, and glass transition (Hartel 2001). State diagrams of the sweetener systems in confections are obtained by combining solubility, boiling point elevation, and glass transition curves. These curves divide the diagram into various regions that allow prediction of the physical state and stability of confections depending on the temperature and solid/water content. For example, in Figure 1 the region between the sucrose solubility and glass transition curves is the crystallization zone; temperature and composition must fall within this zone if crystals are to be formed either during processing or storage (Hartel 1993). The region beyond the glass transition curve is the glassy state. Even though the glass region is not an equilibrium condition, molecular mobility is low enough to limit crystallization for a reasonable time scale (years). So the glass transition curve can be used to determine the storage temperature at which glassy-state sweeteners are stable.

In the following sections, available data for boiling point elevation, solubility, and glass transition of various sweeteners in confections are reviewed. Methods to estimate or measure these parameters are also discussed.

Boiling point elevation

Many confections are made by cooking a sweetener–water solution to a specified temperature to bring about the desired water content in the finished product. Due to the rapid rate of mass transfer during evaporation, the cooking process generally follows the boiling point elevation curve, which means that cooking to a certain temperature indicates specific water content as long as the boiling point elevation is known for the mixture of sweeteners. Thus, knowledge of the boiling point elevation curve for the sweetener mixture in a formulation is important for control of manufacturing and specification of product characteristics (texture, shelf life, and so on).

Numerous sources of boiling point elevation curves exist for various sweeteners, with sucrose, corn syrup, and invert sugar (and their mixtures) being the most available (Pancoast and Junk 1980; Mageean and others 1991). However, the data available in the literature can vary quite widely and are notoriously inaccurate at higher temperatures. For example, Mageean and others (1991), in their summary of all published data on boiling point elevation of sugars, cite one publication that says the boiling point temperature for a 94% sucrose concentration is 127.5 °C (261.5 °F), whereas another study gives a value of 135.6 °C (276.1 °F). The differences among the cited literature get larger as sucrose concentration increases.

There are several reasons for this lack of agreement in the literature. First, measuring the water content associated with a certain cook temperature is more difficult than it seems. When sugar syrup is cooked to a very high temperature, it has to be immediately cooled before measurement of water content. There are no good methods of measuring water content directly at elevated temperatures (which is why candy makers measure temperature in the first place). And, since the evaporation rate is extremely high at elevated temperatures, cooling the sample quickly enough to avoid continued evaporation and water loss is extremely difficult. This leads to lower water content than expected. Second, cooking sugars to very high temperatures (140 °C and higher) causes changes in the composition that can alter the boiling point. For one, inversion of sucrose into glucose and fructose occurs rapidly at elevated temperatures, introducing monosaccharides that change the boiling temperature according to Rault’s Law (Peacock and Starzak 1995). Then, further breakdown of monosaccharides, particularly fructose, occurs readily at elevated temperatures, resulting in lower molecular weight components that further raise the boiling point. Boiling must be extremely rapid (such as thin-film cookers) to prevent these compositional changes.

Starzak and Mathlouthi (2006) have reviewed all early data, based in part on previous compilations (Starzak and Peacock 1997, 1998), for water activity, solubility and boiling point elevation for the sucrose–water system, and clearly document the scatter in the data. They use a weighting method to collapse all the data into a single equation predicting water activity as a function of concentration and temperature. Peacock (1998) used a neural network approach to predict boiling point elevation for sucrose-water based on the earlier compilations.
The boiling point elevation curves for 3 sweeteners (sucrose, glucose, and 43 DE corn syrup) are compared in Figure 2. For consistency, data from Hoynak and Bollenback (1966) are used for comparison since different studies have obtained widely disparate results (see Starzak and Mathlouthi 2006). As expected, based on the concept of colligative properties, the boiling point increases with increasing concentration and with decreasing molecular weight of the sweetener. Note that the data for 43 DE corn syrup begins to show a steeper increase in boiling point at 90% dissolved solids concentration, probably due to errors in the original measurements. In the original reference (Hoynak and Bollenback 1966), the boiling point of 43 DE corn syrup increased well above that of sucrose. This indicates a potential breakdown of sucrose and monosaccharides during cooking, which would lead to the anomalously high measured boiling points.

Corn syrups with different dextrose equivalent (DE) values have different boiling point elevation curves due to their inherent differences in average molecular weight. High-DE (such as 63 DE) corn syrups contain more low-molecular-weight saccharides and so have a higher boiling point elevation than lower-DE corn syrups. However, 2 corn syrups with the same DE may also have slightly different boiling point elevations if their saccharide profiles are significantly different. For this reason, each specific corn syrup should be evaluated for differences in boiling point elevation prior to use in confections. A candy manufacturer who changes corn syrup suppliers may experience slight differences in moisture content in their finished product even though all other conditions (especially cook temperature) are kept the same.

Binary mixtures of sweeteners generally have boiling point elevation curves that fall between those of the 2 components, with the actual value being dependent on the relative weight percentages of each component. For example, a 50 : 50 mixture of sucrose and corn syrup will have a boiling point elevation curve approximately half-way between the individual curves for sucrose and corn syrup. Pancoast and Junk (1980) and Mageean and others (1991) provide boiling point data for various mixtures of sucrose and corn syrups of different DE. However, due to the high viscosity, boiling point elevation data for corn syrups and their mixtures with sucrose are highly suspect at concentrations above 90% to 95% sweeteners (on a solids basis).

Knowledge of the boiling point elevation curve for a specific sweetener mixture is important since this relationship governs final water content of the confection and, thus, product texture, quality, and shelf life. This relationship was explored in more detail by Ergun and others (2010).

### Solubility

Sweeteners are generally quite soluble in water, although the solubility of different sugars can be dramatically different, as seen in Table 2. These differences are due to the specific molecular interactions between the sweetener and water. For sucrose in water, the solubility and temperature relationship is given by Pancoast and Junk (1980) as:

\[
S = 64.397 + 0.0725T + 0.0020569T^2 - 9.035 \times 10^{-6}T^3
\]

Here, \( T \) is temperature in °C and \( S \) is sucrose solubility in % sucrose by weight. Sucrose solubility at room temperature (22 °C) is about 67% (g sucrose/100 g of solution), whereas lactose is much less soluble (approximately 17%) and fructose is much more soluble (approximately 80%).

To measure solubility of sweeteners in water, 2 methods are generally used (Hartel 2001). In the first method, a dilute solution, at a concentration slightly less than the expected solubility concentration, is loaded with excess crystalline material and allowed to equilibrate under agitation at controlled temperature. Crystals dissolve until equilibrium is attained at the solubility concentration at which solid and liquid sweetener molecules have the same chemical potential. The concentration of the liquid phase is measured to denote the saturation concentration at that temperature. The second method requires preparation of a supersaturated solution, at a concentration slightly above the expected saturation concentration. Again, crystals are added, but in this case crystallization is allowed to proceed to equilibrium, at which the solution desuper saturates to the equilibrium concentration. Solution concentration is again measured to denote the saturation concentration at that temperature. In both cases, sufficient time is needed to ensure equilibrium has been reached. This may take days or even weeks, especially for measurements at low temperatures. Ideally, solubility concentration is measured with both methods and equilibrium is assured when identical saturation concentrations are obtained.

In most confections, the sweetener phase is actually a combination of different sugars, each of which influences the solubility concentration of the others. For example, the presence of invert sugar and/or corn syrup causes a substantial decrease in sucrose solubility (Pancoast and Junk 1980; Mageean and others 1991) due to the competition among the sugar molecules for water. Therefore, the addition of corn syrup or invert sugar to a sucrose solution results in a decrease in solubility of sucrose, as shown in

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**Table 2—Solubility of various sweeteners.**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Solubility (%) (at 20 °C)</th>
<th>Solubility (%) (at 50 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose</td>
<td>66.5</td>
<td>72.1</td>
</tr>
<tr>
<td>Glucose</td>
<td>47.8</td>
<td>70.9</td>
</tr>
<tr>
<td>Fructose</td>
<td>78.9</td>
<td>86.9</td>
</tr>
<tr>
<td>Lactose</td>
<td>16</td>
<td>30.3</td>
</tr>
<tr>
<td>Maltose</td>
<td>44</td>
<td>58.3</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>73.0</td>
<td>83</td>
</tr>
<tr>
<td>Mannitol</td>
<td>20</td>
<td>31</td>
</tr>
<tr>
<td>Xylitol</td>
<td>63</td>
<td>80</td>
</tr>
<tr>
<td>Maltitol</td>
<td>60</td>
<td>70</td>
</tr>
<tr>
<td>Isomalt</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
<td>Lactitol</td>
<td>52</td>
<td>74</td>
</tr>
<tr>
<td>Erythritol</td>
<td>37</td>
<td>55</td>
</tr>
</tbody>
</table>

Sources: Zumbe and others (2001); Pancoast and Junk (1980).
Figure 3–Solubility of sucrose in the presence of invert sugar (data from Pancoast and Junk 1980).

Figure 3 for invert sugar. Higher addition levels of invert sugar result in less sucrose being dissolved at equilibrium. To study the effects of additives on solubility, the additive is added to water at a specific concentration (gram impurity per 100 g water) and solubility measured as previously mentioned (Liang and others 1988). The solubility concentration of the sugar can then be expressed in gram sweetener per 100 g water.

When corn syrup (or invert sugar) replaces sucrose in a formulation, 2 things happen. First, the amount of sucrose decreases, but at the same time, the solubility of sucrose in the presence of the added corn syrup also goes down. Table 3 shows the decrease in sucrose concentration when corn syrup is added at different ratios. Table 3 also shows that, despite this decrease in sucrose content, the system is still supersaturated (sucrose content is greater than solubility concentration). Mixed systems of sucrose and corn syrup may still be supersaturated, at a decreasing extent with increasing corn syrup concentration and, thus, are potentially prone to crystallization.

One requirement to form sweetener crystals in a confection is that the solubility concentration of the graining sugar must be exceeded at some point in the process (or during storage). Thus, knowledge of the solubility concentration, and its dependence on temperature, is necessary. Further, from the solubility concentration, the amount of crystalline material expected can be calculated from a mass balance, assuming that phase equilibrium has been attained (Ergun and Hartel 2009). This topic will be explored in greater detail in a later section.

Although a supersaturation is required for crystallization, the supersaturated state is not sufficient by itself for crystallization to occur if there are kinetic constraints preventing nucleation. Crystallization of a supersaturated system may not occur either because inhibitors (doctoring agents like corn syrup) prevent sweetener molecules from coming together to form nuclei or due to limited molecular mobility, as found in sugar glasses. Further details on the kinetics constraints that can inhibit crystallization will be discussed in a later section.

**Glass transition**

Solid confections can either be in a crystalline state or in a thermodynamically unstable amorphous state (Ergun and others 2010). Amorphous confections, or noncrystalline candy with high viscosity, are formed by subcooling a supersaturated sugar solution (Kitt 1993; Jeffery 2001). The amorphous state can exist either as a viscous fluid-like rubbery state or as a high-viscosity glassy state with low molecular mobility (Roos 1995). Amorphous glasses are characterized by a random arrangement of molecules with no long-scale ordering. The glass transition occurs when the glassy state converts to the rubbery state (or vice versa), with the temperature of this transition being called the glass transition temperature ($T_g$) (Slade and Levine 1991). The glass transition is a second-order state transition that results in changes in various material properties, including specific heat, dielectric constant, viscosity, molecular mobility, and mechanical properties (Sperling 1986; Roos and Karel 1993; Roos 1995). Thus, the glass transition can be measured by tracking changes in these properties. Most often, this involves use of calorimetry, mechanical analysis, or measurement of dielectric constant.

DSC is one of the most commonly used methods for measuring the glass transition temperature. DSC involves comparing the relative heat flow to a sample pan compared to an empty reference pan as temperature is changed at constant rate. When a glassy material is subjected to a uniform temperature increase in a DSC, there is a change in the heat flow at the glass transition. As a second-order transition, the glass transition does not result in an enthalpic peak, but is seen only as a change in specific heat of the material. In a DSC scan, this is observed as a step change in the heat flow from the value associated with the glass to that of the amorphous fluid-like material (Roos 1995). The glass transition generally occurs over a range of temperatures, rather than at a single temperature, with more complex mixtures of sweeteners (for example, corn syrup, invert sugar, and sucrose) exhibiting a broader temperature range for the transition. The $T_g$ value is often reported as the temperature of the inflection point of the change, although midpoint, onset, and/or endset temperatures may also be reported to indicate the range.

Sugar glasses are not completely static or unchanging (Angell 2002). Many exhibit a phenomenon known as enthalpic relaxation (Finegold and others 1989; Schmidt and Lammert 1996; Bhandari and Hartel 2008), which might loosely be defined as rearrangements of the sugar molecules while in the glassy state. When a sugar glass that is more than a few days old is heated in a DSC, a small endothermic peak is seen close to the shift in baseline associated with the glass transition. This endothermic peak is attributed to enthalpic relaxation of the sugar molecules in the glassy state. To measure a true $T_g$, sugar glasses must be scanned twice, the first time to extinguish the enthalpic relaxation peak so that the true $T_g$ can be assessed in the second scan after the sample has been cooled again below the glass transition. These changes can be seen in Figure 4, where both first and second scans of a sugar glass are shown. The first scan shows the enthalpic relaxation, while in the second scan, the enthalpic relaxation peak is gone and the

**Table 3–Effects of corn syrup replacement for sucrose on sucrose supersaturation, calculated for a solution containing 12% water.**

<table>
<thead>
<tr>
<th>Sucrose/corn syrup (% by weight solids basis)</th>
<th>$C_s^0$ (g sucrose/100 g water)</th>
<th>$C_s^0$ (g sucrose/100 g water)</th>
<th>$\Delta C_s^0$ (g sucrose/100 g water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>733.3</td>
<td>210.4</td>
<td>522.9</td>
</tr>
<tr>
<td>90/10</td>
<td>660.0</td>
<td>185.3</td>
<td>474.7</td>
</tr>
<tr>
<td>80/20</td>
<td>586.7</td>
<td>160.2</td>
<td>426.5</td>
</tr>
<tr>
<td>70/30</td>
<td>513.3</td>
<td>135.1</td>
<td>378.2</td>
</tr>
<tr>
<td>60/40</td>
<td>440.0</td>
<td>110.0</td>
<td>330.0</td>
</tr>
<tr>
<td>50/50</td>
<td>366.6</td>
<td>84.9</td>
<td>281.7</td>
</tr>
<tr>
<td>40/60</td>
<td>293.3</td>
<td>59.7</td>
<td>233.6</td>
</tr>
<tr>
<td>30/70</td>
<td>220.0</td>
<td>34.6</td>
<td>185.4</td>
</tr>
<tr>
<td>20/80</td>
<td>146.0</td>
<td>9.5</td>
<td>136.5</td>
</tr>
</tbody>
</table>

$A_i$ = initial dissolved sucrose content; $C_s^0$ = sucrose solubility concentration in the presence of specified amount of corn syrup solids; $C_s^0$ = actual sucrose supersaturation.

Source: Calculated from data by Jonathon (2004).

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actual glass transition is evident. Measuring $T_g$ for many sweeteners requires this 2-scan approach.

The glassy state is metastable due to the limited molecular mobility so that diffusion-based chemical reactions and physical changes (such as crystallization) are severely limited. From a kinetic perspective, reactant molecules must exhibit a minimum degree of mobility to collide with, orient toward, and react with one another (Sherwin and others 2002; Sherwin and Labuza 2006). Since molecular mobility is strongly restricted in the glassy state due to the close proximity of the molecules (Hartel and others 2008), transformations occur only at dramatically reduced rates when the product is held below $T_g$ (Levine and Slade 1992; Bhandari and Howes 2000). Thus, even though a glass is thermodynamically unstable, crystallization is unlikely to occur due to the low mobility (and high viscosity). That is, the amorphous state is kinetically metastable (Frick and Richter 1995). With an increase in temperature and the resulting increase in molecular mobility (decrease in viscosity), amorphous materials may exhibit time-dependent structural transformations such as stickiness, collapse, and crystallization when $T_g$ falls below ambient temperature (Roos and Karel 1993; Roos 1995; Labuza and Labuza 2004). For these reasons, $T_g$ is often seen as an indicator of product properties, stability, and safety of foods (Levine and Slade 1992).

$T_g$ is governed by molecular composition, degree of polymer cross-linking, and plasticizer (such as water) concentration (deGraaf and others 1993). Carbohydrates with low molecular weight generally have low $T_g$ and $T_g$ generally increases with an increase in molecular weight of the sweetener, although there are exceptions to the rule (White and Cakebread 1966; Levine and Slade 1992; Roos 1995). Table 4 shows $T_g$ values for a variety of sweeteners used in confections. Among the disaccharides, $T_g$ varies from 65 to 70 °C for sucrose to over 100 °C for lactose, whereas the monosaccharides glucose and fructose have $T_g$ values of about 31 and 5 to 10 °C, respectively. Note the significantly lower $T_g$ for most, but not all, polyols. Maltitol and isomalt, in particular, have $T_g$ values above room temperature, making them suitable for use in sugar-free hard candies.

An increase in water content leads to lower $T_g$ values, as the water molecules plasticize the sugar glass (Roos 1995). The $T_g$ of pure sucrose, for example, drops below room temperature (22 °C) when water content is greater than about 5.5%. That is, sucrose does not form a glass at room temperature when water content is above this value. In glassy confections, water content is generally less than 3% to 4%; however, other ingredients in confections typically also affect $T_g$.

Candies manufactured with mixtures of sugars have $T_g$ values somewhere between those of each component sugar in the mixture, depending on the relative ratios (Finegold and others 1989). In principle, the Gordon–Taylor equation can be used to predict $T_g$ of binary mixtures of sweeteners or sweetener and water. The Gordon–Taylor equation is given as (Roos 1995):

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}$$

(2)

Here, $w_1$ and $w_2$ are the weight fractions of components 1 and 2, while $T_{g1}$ and $T_{g2}$ are the glass transition temperatures for each component. The constant, $k$, can be calculated from the difference in specific heat values for the 2 components between glass and fluid states ($k = \Delta C_p1/\Delta C_p2$). For example, the effect of water on $T_g$ of sugar–water mixtures has been shown to correlate well with the values estimated from the Gordon–Taylor equation (Roos 1993; Khalloufi and others 2006).

Glass transition temperatures for more complex mixtures of sweeteners, as generally found in confections, are typically more difficult to estimate. Because of the numerous components found in confections (sugars, corn syrups, water, and so on), it is difficult to accurately predict $T_g$ values based on knowledge of the composition. Although general trends have been documented, for example, Figure 5 compares $T_g$ values for mixtures of sucrose and corn syrup (Gabarra 1996), such data do not account for changing water content or for changes in composition during processing (for example, inversion during cooking). For commercial products, measurement of $T_g$ is highly recommended since the saccharide distribution in the finished candy may be quite different from the initial mixture.

The different saccharide distribution in confections also leads to different patterns of moisture uptake. For example, the effects of water content on $T_g$ of 2 commercial hard candies are shown in Figure 6 (Nowakowski 2000). In all cases, $T_g$ decreased as water content increased, as expected; however, the slopes were quite different due to the differences in saccharide composition. $T_g$ values for Brand 2 above about 6% water were not measurable due to the onset of sucrose crystallization at those levels. From this, each combination of sweeteners in a commercial product behaves uniquely, dependent on the contributions of the individual components.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fructose</td>
<td>5 to 10</td>
</tr>
<tr>
<td>Glucose</td>
<td>31</td>
</tr>
<tr>
<td>Galactose</td>
<td>30</td>
</tr>
<tr>
<td>Lactose</td>
<td>101</td>
</tr>
<tr>
<td>Maltose</td>
<td>87</td>
</tr>
<tr>
<td>Sucrose</td>
<td>62 to 70</td>
</tr>
<tr>
<td>Raffinose</td>
<td>70</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>-9</td>
</tr>
<tr>
<td>Xylitol</td>
<td>-29</td>
</tr>
<tr>
<td>Maltitol</td>
<td>39</td>
</tr>
<tr>
<td>Isomalt</td>
<td>63.6</td>
</tr>
<tr>
<td>42 DE corn syrup solids</td>
<td>79</td>
</tr>
<tr>
<td>20 DE corn syrup solids</td>
<td>139</td>
</tr>
<tr>
<td>Polydextrose</td>
<td>90.8</td>
</tr>
<tr>
<td>Hydrogenated starch hydrolysate (MW 504)</td>
<td>54.6</td>
</tr>
<tr>
<td>Hydrogenated starch hydrolysate (MW 644)</td>
<td>75.0</td>
</tr>
</tbody>
</table>

Sources: Roos and Karel (1991); Noel and others (1991); Roos (1995, 2002); Fennema (1996); Raudonius and others (2000); Hartel (2001)
Phase/state transitions of confectionery sweeteners

Glass transition principles have also been applied to various candies, particularly sugar-based (Gabarra and Hartel 1998; Nowakowski and Hartel 2002) and sugar-free (Raudonus and others 2000; McFetridge and others 2004) hard candies. Other confections where the principles of glass transition have been applied include cotton candy (Labuza and Labuza 2004), marshmallow (Lim and others 2006), caramel (Chung and others 1999; Car- doso and de Abreu 2004; Ahmed and others 2006), toffee (Kilcast 2000), and date paste (Ahmed and others 2005).

Interpreting the state diagram

The state diagram has been widely recommended as a means for controlling phase/state transitions in foods (Roos and Karel 1991; Roos 1995; Rahman 2006). However, due to the complex nature of real foods, its actual application to practical circumstances has been somewhat limited. Often, the exact locations of the transition lines are unknown and only approximate values must be used. In general, however, the state diagram provides a guide for conditions (temperature and solids concentration) where crystals may be expected to form.

However, some progress has been made in recent years in applying the state diagram approach to sweeteners, particularly related to confections. For example, the manufacture of certain candies can be followed on the state diagram to provide perspective on what state might be expected from any process (Hartel 2001; Ergun and Hartel 2009). Figure 7 shows process trajectories on approximate state diagrams for the manufacturing steps required for fondant (highly crystallized) and hard candy (glassy).

The progress of the state of a sugar solution during manufacture of fondant, a highly crystallized sugar matrix (Jeffery 2001), is shown in Figure 7A (Hartel 2001). Typically, corn syrup content (on a solids basis) in fondant is 10% to 20%; thus, Figure 7A shows the state diagram for a mixture of 90% sucrose and 10% corn syrup solids (42 DE). The boiling point elevation temperatures and solubility concentrations are decreased slightly while glass transition temperatures are increased slightly in the presence of 10% corn syrup solids, compared to the pure sucrose state diagram. The general process for making fondant can be followed on the state diagram to indicate the phase/state conditions assuming equilibrium. A dissolved sucrose and corn syrup solution is heated to boiling. Water evaporates during boiling as heating continues. In general, evaporation is quite rapid, so it is likely that the boiling process follows along the boiling point elevation curve. This relationship between boiling temperature and solids content (inversely, water content) allows the candy maker to determine the final moisture content of the confection by control of cook temperature. When the desired water content is reached, the cooked sugar syrup is removed from the heat and cooled quickly under static conditions (to avoid nucleation) to a point about midway between the solubility curve and the glass transition curve. This point is the optimal temperature for crystallization, where there is a balance between the 2 competing forces—increased supersaturation (promoting crystallization) and decreased molecular
mobility (inhibiting crystallization). For fondant, maximal crystallization is desired to create numerous tiny crystals that provide the desired texture and smoothness during eating. Thus, conditions that promote crystallization (minimal addition of inhibitors, optimal beating temperature, high beating intensity, and so on) are used (Lees 1965; Hartel 2001). As the sugar mixture crystallizes and sucrose molecules are removed from the dissolved state, the concentration of dissolved solids remaining in the liquid phase decreases. Crystallization continues until the solution concentration reaches the equilibrium state, at which sucrose saturation occurs in the presence of the added corn syrup solids. This is seen in Figure 7A as a decrease in dissolved solids content in the liquid phase (in reality, the temperature increases slightly during the crystallization stage of fondant making). After exiting the fondant beater (Minifie 1999), the fondant cools to room temperature, with additional crystallization taking place to ensure equilibrium solubility conditions are maintained in the solution phase.

In contrast, Figure 7B compares the progress of the state of a sugar solution during manufacture of hard candy (Hartel 2001). Hard candy is an amorphous glass (Kitt 1993; Minifie 1999) and crystallization is not desired. In part, graining is inhibited by addition of sufficient doctoring agent (corn syrup). Thus, Figure 7B shows the state diagram for a mixture of 70% sucrose and 30% corn syrup solids (42 DE). Compared to Figure 7A (10% corn syrup solids), the boiling point elevation temperatures and solubility concentrations are considerably reduced while the glass transition temperature increases slightly. In hard candy manufacture, a relatively dilute solution of dissolved sucrose and corn syrup is heated to the boiling point. During cooking, evaporation occurs and the concentration increases, generally following the boiling point elevation curve. As it becomes more concentrated, the sugar mixture crosses the solubility curve at some point, following the boiling point elevation curve into the supersaturated region. Upon reaching the desired cook temperature (300 °F) to give very low moisture content (2% to 3%), the traditional process involves cooling the candy mass to the plastic state where it is sufficiently viscous that it can be formed. Once the final shape has been formed, the candy mass is cooled to room temperature where it becomes a stable glass. As seen in Figure 7B, in hard candy manufacture, the concentrated sugar syrup spends considerable time within the zone where crystallization may take place. In this case, sufficient crystallization inhibitors, like corn syrup and/or invert sugar, must be present to retard crystallization long enough so that the glass state can be attained prior to massive crystallization. Once the glassy state has been achieved, crystallization cannot occur due to restricted mobility and, as a result, hard candy can have extended shelf life when stored properly.

As seen with these 2 examples, the phase/state diagram is helpful for understanding which phase/state is likely to be found. State diagrams can be drawn for any crystallizing sweetener matrix, including sugar-free ingredients. For example, Gharsallaoui and others (2008) have documented the state diagrams for maltitol and trehalose.

Crystallization Kinetics

Although phase/state behavior is important, the second piece to understanding and controlling phase transitions of sweeteners is kinetics, or the rate at which crystallization (nucleation and growth) takes place. Primarily, the rate of formation of nuclei is the most important aspect for controlling crystallization since nucleation rate determines the total number of crystals present in the final product. However, the rate of crystal growth can influence final properties as well. The rate of crystallization is governed by a supersaturation driving force, but is also influenced by external conditions such as heating or cooling rates, evaporation rates, and shear or agitation rates. Furthermore, a supersaturated state may exist but not lead to formation of crystals due to other constraints. The effects of doctoring agents to moderate crystallization in confections and the inability of the highly supersaturated glassy state to grain are 2 examples where kinetic constraints act to retard or completely inhibit crystallization.

The rate of crystallization is an important factor since it determines the nature of the crystalline phase, whether there are numerous small crystals or fewer larger crystals (Hartel 2001). The nature of the crystalline dispersion influences numerous properties of the food, including texture and appearance. For example, improper crystallization in fondant leads to the occurrence of large crystals that impart an undesirable coarse texture (Lees 1965).

Crystallization mechanisms

The general principles of crystallization have been covered in great detail elsewhere (Dirksen and Ring 1991; Mullin 2001). Crystallization in foods and sweeteners has also been reviewed in detail (Hartel and Shastry 1991; Hartel 2001). In this section, we briefly review the general principles and add recent citations on mechanisms of sweetener crystallization.

Nucleation. Nucleation is the first and the most important step of crystallization. Since the number and extent of nuclei determine the amount and size of crystals in the finished product, controlling crystallization starts with controlling nucleation (Hartel 2001).

Crystals can form only from a supersaturated solution, in which the sweetener concentration exceeds the solubility concentration. At a molecular level, nucleation occurs when enough sugar molecules come together in an arrangement that minimizes their free energy, leading eventually to formation of a crystal lattice. While in the liquid state, sugar molecules associate with water molecules through hydrogen bonds, with the number of molecules of solution water depending on the chemical structure of the sugar and concentration of the dissolved sugar. For nucleation to occur, these water molecules (the hydration layer) must de-solvate from the sugar molecules to allow sugar-sugar molecular interactions, which happen with increasing frequency as concentration increases above the solubility concentration. A stable nucleus is formed when a cluster of sugar molecules reaches the critical size, which decreases with increasing supersaturation (Mullin 2001). The propensity of different sugars to nucleate can be quite different; for example, mannitol and maltitol nucleate readily compared to sucrose and xylitol (Bensouissi and others 2010). How easily nucleation occurs depends on the physicochemical properties of the sweetener, such as solubility, viscosity (diffusivity), surface tension, and hydration number (number of water molecules associated with the sweetener molecule) (Bensouissi and others 2010).

Nucleation can occur by either homogeneous or heterogeneous mechanisms. Homogeneous nucleation occurs when a sufficient number of molecules come together to form a 3-dimensional, stable nucleus, whereas in heterogeneous nucleation, a solid substrate replaces a portion of the molecules needed to form a stable cluster. Due to the natural presence of nucleating sites (such as dust particles, other impurities, and so on), heterogeneous nucleation is generally the predominant form of nucleation in foods. The energy required for the formation of crystal volume and surface (Dirksen and Ring 1991; Mullin 2001) needs to be overcome by the driving force, or supersaturation. In heterogeneous nucleation, foreign nucleation sites (dust and so on) decrease the energy
Nucleation rate, or the number of crystals formed (per unit time per unit volume), for a given sugar is dependent on both internal and external factors. As noted above, each sweetener has a propensity for nucleation based on its physicochemical nature, but external heat and mass transport conditions (such as temperature, cooling rate, and agitation) can also influence the ability of a supersaturated state to nucleate. In some sugars, a fairly wide zone of supersaturation exists where nucleation is limited; in this metastable zone, sweetener molecules do not attain the critical cluster size for conversion to a stable nucleus. The width of the metastable zone of sucrose, mannitol, maltitol, and xylitol correlates with the propensity of these sweeteners to crystallize (Benouissi and others 2010). That is, systems with a lower metastable zone are faster nucleating than those with a large metastable zone.

Measuring nucleation rate has generally proven difficult—nuclei are defined as the initial crystal forms, before the crystals grow to a size where they can be observed, and counting the number of nuclei formed over time is difficult. Because of this difficulty, many studies have investigated the induction time for nucleation and then assumed an inverse relationship between induction time and nucleation rate; however, this relationship does not work under all circumstances, especially when near the glass transition region (Levenson and Hartel 2005). Furthermore, measurement of induction time is also difficult since the time required for nuclei to reach a detectable size is often longer than the true induction time required for initial onset of formation of nuclei.

Although numerous methods have been used over the years to measure nucleation rate or induction time, most of these methods make assumptions and introduce errors that limit their accuracy. One of the simplest methods of characterizing nucleation rate is to count the number of crystals that form as a function of time. However, the time required for nuclei to grow to detectable size may introduce significant errors depending on the sensing measurement. Besides visual and microscopic observations, tools such as calorimetry, turbidity, x-ray, and other spectroscopic tools have been used. Sensing methods that get closest to the actual measurement. Besides visual and microscopic observations, tools such as calorimetry, turbidity, x-ray, and other spectroscopic tools have been used. Sensing methods that get closest to the actual nucleation rate; however, this relationship does not work under all circumstances, especially when near the glass transition region (Levenson and Hartel 2005). Furthermore, measurement of induction time is also difficult since the time required for nuclei to reach a detectable size is often longer than the true induction time required for initial onset of formation of nuclei.

To further compound the difficulties of studying nucleation, the natural variability inherent in formation of the crystal lattice generally results in hugely variable results. A classical study on sucrose nucleation by Van Hook and Bruno (1949) documented this variability. Under carefully controlled conditions, a supersaturated sucrose solution poured into 4 different vials varied in induction time from as short as a few hours to as long as 24 h. Only slight differences in the nucleating capability of heterogeneous nuclei sites are sufficient to give such variable nucleation results. Experimental measurement of induction time for nucleation of a sucrose and corn syrup mixture (based on microscopic evaluation of the presence of crystals) showed that the variability in time for onset of nuclei formation was greatest when induction times were at their highest (Figure 8). That is, at the optimal temperature for nucleation, induction time was shortest and so was the variability in nucleation rate.

Because of the variability in nucleation, seed crystals are often added to bypass the nucleation step. For example, seeding of nougat, fudge, or marshmallow with a small amount of fondant or powdered sugar circumvents the need for controlling nuclei formation (Minifie 1999). Rather than carefully cooling and agitating the mass to induce graining, the fudge maker can elect simply to add fondant to the mass after cooking. The seed crystals that remain after adding fondant simply dissolve or grow until the saturation concentration has been reached. However, the trade-off with seeding is that the crystal size in the finished product is only as small as the size of the seed crystals added; thus, slightly coarser product is generally obtained from seeding.

Factors that affect nucleation. The formation of crystals from the liquid state requires that molecules come together and organize into a uniform lattice. The ability of molecules to form into nuclei depends on numerous factors, including both environmental influences and the effects of other ingredients used in a formulation.

Supersaturation. A supersaturated state is necessary for nucleation to occur, with higher nucleation rates (shorter induction times) seen at higher supersaturations, but only up to a point (Hartel and Shastry 1991). When concentration is so high that molecular mobility is reduced, the nucleation rate also decreases and induction time increases. Ultimately, when molecular mobility is so low that the matrix is in the glassy state, nucleation is effectively reduced to zero and the matrix is metastable, meaning that nucleation does not occur (at least over a very long time period) (Lees 1977; Vink 1998).

Temperature. In general, as temperature goes up, the rates of most chemical and physical processes also increase. Early research on sucrose nucleation by Van Hook (1971), among others, has documented that sucrose nucleation follows classical nucleation theory (Mullin 2001), at least in principle, with nucleation rate increasing exponentially as temperature increases. Furthermore, the activation energy for the temperature dependence of nucleation is approximately equal to the activation energy for the change in diffusivity with temperature, which suggests that the nucleation event is a diffusion-controlled process.

In confections, total solids content (or inversely, water content) is held constant and a decrease in temperature also leads to an increase in supersaturation due to the decreased solubility as temperature goes up. Thus, cooling of a solution with constant sweetener concentration results in a nucleation profile dependent on the competing phenomena of increasing supersaturation and
decreasing molecular mobility. The result is that at some “optimal” temperature, the rate of nucleation is at a maximum and induction time is the shortest (Hartel and Shastry 1991). At temperatures both higher and lower than this optimal temperature point, nucleation rate is slower (induction time is longer). In fondant manufacture, the optimal temperature for maximum nucleation (shortest induction time) typically falls between 48 and 50 °C (Lees 1965; Hartel 2001). This effect is seen in Figure 8, where samples were cooked to the desired initial water content and cooled rapidly to each temperature for study. After the desired temperature was attained, the mixture was agitated and samples were taken periodically for observation with a polarized light microscopy. The difference between the last time when no crystals were observed and the first sampling when crystals were evident was taken as the induction time.

**Molecular mobility/viscosity.** Molecular mobility is primarily dependent on concentration and temperature, with increasing concentration and decreasing temperature both contributing to lower diffusivity (Hartel 2001). In fact, lower diffusivity correlates with higher viscosity; the 2 terms are often considered inversely proportional, even though this proportionality may not apply under all circumstances (Levenson and Hartel 2005). In particular, at high solids concentrations and low temperatures, this inverse relationship between diffusivity and viscosity no longer applies (Debenedetti and Stillinger 2001).

Moreover, addition of small amounts of hydrocolloids, like gelatin or protein, can cause a large increase in viscosity but may not have a substantial effect on nucleation. Even though the hydrocolloid provides thickening behavior, even to the point of forming a gel, sugar nucleation within the gel structure will still occur unless formulation factors (for example, corn syrup ratio) are appropriate to inhibit grain formation. Specifically, unless the sucrose-to-corn syrup ratio is properly balanced, sugar grain formation in gummy and jelly candies can still occur (Gordon 2007).

Sugar glasses provide another barrier to nucleation. As noted previously, the glassy state is not an equilibrium state, yet formation of nuclei does not occur because the necessary molecular rearrangements are kinetically inhibited by the low molecular mobility (which results in high viscosity) (Slade and Levine 1991). For nuclei to form, the molecules must have sufficient translational and rotational mobility to organize into a lattice. In the glassy state, the molecules are constrained by the close proximity of other molecules in the glass (Hartel and others 2008) and, thus, cannot form into the crystal lattice. Despite the high supersaturation found in a sugar glass, nucleation does not occur as long as the glassy state is maintained (Levenson and Hartel 2005).

**Agitation.** As a general rule of thumb, if nucleation is not desired (as in hard candy), supersaturated solutions must be handled very gently, with a minimum of agitation or shear. Any energy input into a supersaturated solution is likely to initiate crystal formation. Conversely, if many crystals are desired (as in fondant), extreme agitation (beating) is needed to induce massive nucleation (Lees 1965; Hartel 2001; Jeffery 2001). Mechanical energy is thought to enhance mobility of sugar molecules, bringing them in close proximity to form a stable nucleus.

Ultrasound energy input has been shown to enhance crystal nucleation, including nucleation of sugars (Ruecroft and others 2005). For example, Stasiak and Dolatowski (2008) have shown that ultrasonic energy input enhanced nucleation of sucrose under conditions of importance for sugar refining. No studies on the application of ultrasonic energy to enhance nucleation in confectionery products have been published.

**Formulation factors.** In confections, dissolved ingredients generally either have no effect or act to retard nucleation of sweeteners. For example, Van Hook (1971) showed that dissolved glucose, fructose, and lactose, as well as tartaric acid and calcium carbonate did not enhance nucleation of sucrose; indeed, most dissolved sugars have an inhibitory effect on sucrose nucleation (Van Hook 1961).

Specific additives, often called doctoring agents, are commonly used in confections to control sugar crystallization. In early confectionery history, the addition of cream of tartar or a small amount of acid caused inversion of sucrose (Vink 1998). The low pH and high cook temperatures result in inversion of some of the sucrose, with the glucose and fructose formed serving to moderate crystallization of the remaining sucrose. In addition, polymerization of the monosaccharides during cooking under acidic conditions, a reaction called reversion, further moderates sucrose crystallization. Specifically, polyfructose molecules, or fructose polymers with degree of polymerization between 2 and 4 are formed during acidic cooking of sucrose (Sabbagh and Fagerson 1979). These longer-chain oligosaccharides likely provide nucleation inhibition to sucrose confections.

Based on the increasing knowledge of how acid worked to stabilize sugar in confections, invert sugar was developed as an ingredient that could moderate, or doctor, sucrose grain formation (Vink 1998). Instead of having to control the acid reaction during processing, candy makers could simply add the appropriate amount of invert sugar to their formulation and then process in such a way as to minimize further inversion (namely, adding acid after the cook). The advent of corn syrup, with its high-molecular-weight glucose oligosaccharides, gave further control over sugar crystallization and allowed candy makers greater flexibility in controlling product quality, texture, and shelf life. The use of corn syrup (or glucose polymers from any other starch source) as a doctoring agent in confections is now widely accepted in the industry.

Doctoring agents used in confections influence sugar nucleation in several ways. First, their effect on supersaturation driving force must be considered. As a replacement for sucrose, increased levels of doctoring agents result in a decrease in the sucrose concentration. However, doctoring agents like corn syrup and invert sugar also decrease the solubility concentration of sucrose, with less sucrose needed for saturation at higher addition levels. The net effect is that the supersaturation driving force for sucrose (actual concentration relative to saturation concentration) decreases with increasing addition levels of corn syrup or invert sugar (Table 3). Thus, based on the decreased supersaturation driving force, the addition of invert sugar or corn syrup would be expected to decrease nucleation of sucrose. Further, since these are doctoring agents, the second effect of these molecules on sucrose also helps to prevent nucleation. That is, the molecules of corn syrup and invert sugar serve to interfere with the ability of sucrose molecules to join together into a crystal lattice. Thus, nucleation is retarded quite effectively with addition of doctoring agents like fructose and glucose (Bhandari and Hartel 2002) and corn syrup (Shastry 1991).

The same general principles as discussed above for the effects of ingredients on sucrose nucleation also apply to other sweeteners used in confections. For example, McFetridge and others (2004) quantified the inhibition of hydrolyzed starch hydrolysates (maltitol syrup) on isomalt and lactitol crystallization. Unfortunately, very little quantitative data on these effects are available in the published literature.
Crystal growth. After the formation of nuclei, molecules start to diffuse and attach to the surface of the crystal (Dirksen and Ring 1991; Mullin 2001). At the same time, molecules of water and any other dissolved molecules diffuse away from the growing surface (Mathlouthi and Genotelle 1998). The molecules of the crystallizing species are thought to migrate along the surface until they find a suitable site to incorporate into the lattice structure. As the crystal grows, the latent heat of crystallization must be removed from the vicinity, either through the liquid phase and/or through the growing crystal.

At the macroscopic level, heat and mass transfer are both important in the crystal growth process. However, heat transfer is relatively fast compared to mass transport phenomena and, consequently, mass transport limitations generally control the crystal growth rate while heat transport seldom has an effect on crystal growth of sugars (Dirksen and Ring 1991). In general, growth of sucrose crystals has been shown to be limited primarily by diffusion of sucrose molecules to the growing surface and diffusion of growth units along the surface to a lattice incorporation site (van Hook 1981). Depending on supersaturation, surface growth is generally driven by self-propagation of spiral dislocations at the surface of the growing surface (Mathlouthi and Genotelle 1998) and/or by the birth-and-spread model, where 2-dimensional nucleation of a stable nucleus on the surface is followed by growth, or spread, of a step as more sugar molecules fill in the layer (Khadour and others 2010). Martins and Rocha (2007) characterized sucrose crystal growth according to a spiral dislocation model, which combined 2-dimensional nucleation and spiral growth. In addition to these surface-controlled mechanisms, desolvation of water molecules from the sugar molecules and counter diffusion of this free water away from the growing surface have also been found to play a major role in determining sucrose crystal growth (Bensouissi and others 2010). The mechanism(s) responsible for sucrose crystal growth remains an active area of research.

Crystal growth continues as long as the solution is supersaturated and molecules have enough mobility to organize into the crystal lattice. As growth continues, the concentration of the remaining liquid phase decreases, or desupersaturates, until phase equilibrium, as defined by the solubility curve on the phase diagram, is reached (Hartel 2001). In Figure 1, this is seen as a decrease in liquid phase concentration as a supersaturated system, initially at saturation concentration initially results in increased growth rate as supersaturation increases. At some point, however, the increased concentration leads to a decrease in the ability of molecules to diffuse and growth rate begins to decrease. When the sweetener concentration is high enough (water content low enough) so that the glass transition temperature of the mixture reaches room temperature, mobility is sufficiently decreased and growth of sugar crystals is shut down completely.

Temperature. Growth rate in concentrated sugar solutions is influenced by changes in temperature in much the same manner as nucleation rate. When a sweetener solution with constant concentration is cooled, there is a temperature where growth rate reaches a maximum, with slower growth at temperatures both above and below that optimal point. Initially, the growth rate increases as the solution is cooled below the solubility point due to the increased supersaturation. However, the increased driving force induced by cooling is offset by the decreased molecular mobility of sweetener molecules.

Molecular mobility/viscosity. As noted for nucleation, mobility is governed primarily by temperature and solution concentration. Diffusivity, or the ability for molecules to move in space, generally correlates inversely with viscosity. Diffusivity decreases (reduced molecular mobility) as concentration increases and temperature decreases (Zhymria 1972).

When molecular mobility is near zero, as in the glassy state, growth is effectively stopped. Any crystals that nucleate prior to formation of the glassy state remain unchanged, without growing, within the metastable glass matrix. Commercial hard candies can potentially contain crystals since a portion of the manufacturing process falls within the crystallization boundary (see Figure 7B). One study estimated that hard candy contains, on average, 2% to 3% crystals (Smidova and others 2004). Any crystals imbedded within the hard candy glass matrix do not grow despite the highly supersaturated condition because of the lack of mobility (Hartel and others 2008).

Agitation. Agitation of the solution phase in the presence of growing crystals generally enhances the crystal growth rate, particularly in systems like sugars where growth is strongly influenced by mass transfer (Hartel 2001). Increased agitation enhances mass transfer by convection, bringing molecules more quickly to the growing interface. However, once any mass transfer limitation has been completely alleviated, further increases in agitation have little effect on growth (Van Hook 1943).

Formulation factors. Many of the ingredients used in confections influence the rate of molecular incorporation into the crystal lattice. Additives may affect crystal growth either due to a change in the thermodynamic driving force (effect on solubility concentration) or due to specific growth inhibition effects of the individual molecules (Mullin 2001). Growth inhibition from foreign molecules may have 3 causes (Hartel 2001): (1) the foreign molecules may impede diffusion of the sweetener to the crystal surface and thereby slow growth, (2) the foreign molecules may adsorb to the crystal surface (most likely due to hydrogen bonding) and inhibit the ability of molecules to incorporate into the lattice, and (3) the foreign molecules may adsorb so strongly that they actually become incorporated into the lattice itself, thereby preventing addition of new sweetener molecules to the lattice.

To properly study the effects of ingredient additives on crystal growth, it is necessary to account for any changes in solubility induced by the additive. As noted previously, many of the common additives in confections (such as invert sugar and corn syrup) also decrease solubility, causing a change in driving force for crystallization. As shown in Table 3, replacement of sucrose with corn syrup in a formulation changes both the amount of sucrose present and its solubility in the remaining water, thus changing the supersaturation. Unfortunately, not all studies have accounted for this difference.
The inhibition of sucrose crystal growth in the presence of various impurities has been studied widely. For example, Smythe (1967) showed that fructose and glucose inhibit sucrose growth by surface adsorption, whereas raffinose depresses sucrose crystal growth due to its incorporation into the crystal lattice as a tailormade impurity. For this reason, raffinose is much more effective at shutting down sucrose growth than fructose or glucose. More recent studies have further documented the effects of fructose and glucose (and other oligosaccharides) on sucrose crystal growth rate and morphology (Sgualdino and others 1998, 2000; Wang and others 2000; Martins and others 2006; Ouiazzane and others 2008).

Although the majority of impurities retard crystal growth, periodically additives are found that actually enhance crystal growth even after any change in solubility is taken into account. Vasanth Kumar and Rocha (2010) found that an antifoam agent, a coconut oil-based nonionic surfactant used as a processing aid in sugar refining, had growth enhancing capacity at low levels (up to 0.25 g/L H2O). Using a spiral nucleation model of growth, the authors proposed that the surfactant decreased the surface free energy and, thereby, enhanced crystal growth.

**Controlling Phase Transitions**

Table 1 documents the need for each of the different sweetener states in confections. The desired state, whether crystal, glass, or fluid, can only be attained by proper control of formulation factors and processing conditions. Confections where crystals are not desired may be produced either by formulating so there is no residual supersaturation or controlling a supersaturated condition through one or more of various kinetic constraints. In confections where crystals are desired, the number of crystals, size distribution, shape, and sometimes form (hydrate, polymorph, and so on) must be controlled, also through a combination of formulation and processing effects. Of the attributes related to controlling sugar crystallization, the amount of crystalline material (crystal mass fraction) formed, the crystal size distribution, and graining during storage are the most important.

**Crystal mass fraction**

The crystalline content in a confection, or crystal mass fraction (CMF), plays a significant role in product texture and eating quality. CMF varies from a low of zero in completely amorphous candies (gummies and jellies, marshmallow, nougat, and others) to 95% to 98% in candy tablets and powders (Ergun and others 2010), with varying levels between (chewy candies approximately 5% to 10%; fudge approximately 30% to 35%; fondant approximately 45% to 60%).

CMF has a complex effect on texture, depending on the type of confection. In nougat, a small amount (approximately 5%) of crystalline sugar is desired to provide a slightly short texture that does not stick to the teeth. Addition of more crystals, up to about 20% to 25%, creates a short texture, so that the nougat breaks cleanly when bit through; the crystals impart the desired texture of grained nougat. However, nougat formulated to contain substantially more crystals (50% to 70% or greater) would have a significantly harder texture, with hardness increasing with CMF. In fondants and creams, there is a direct correlation between CMF and hardness, with lower CMF (more liquid phase) giving softer fondant. Moreover, the use of invertase in certain fondant cream candies causes softening of the fondant primarily through the action of reducing the sucrose crystal content (by inverting sucrose into glucose and fructose). Thus, controlling the amount of crystals present in a confection is important for controlling product texture and quality.

**Predicting crystal mass fraction based on solubility curve.** The phase diagram can be used to calculate CMF, as discussed by Lenz and Hartel (2005) and Ergun and Hartel (2009) assuming that phase equilibrium has been reached. Knowledge of the initial concentration and solubility point for the specific mixtures of sweeteners and other ingredients is necessary for this calculation.

CMF for a simple system made of sucrose and corn syrup, as often found in fondants and creams, can be calculated from a mass balance (Ergun and Hartel 2009):

\[
CMF = \frac{S_T - S_S}{W_T - W_W}
\]

Here, \( S_T \) is total sucrose in the finished product on a 100 g water basis, \( S_S \) is solubility of sucrose at room temperature on a 100 g water basis, \( W_T \) is total solids in the formulation on 100 g water basis, and \( W_W \) is 100 g, the total water content in the finished confection.

To find CMF, several steps are necessary. First, the amount of corn syrup in the liquid phase is calculated from a mass balance on the corn syrup solids (corn syrup solids in equals corn syrup solids out). Next, the sucrose solubility concentration in the liquid phase is determined from the effects of corn syrup solids on sucrose solubility (Table 3). Finally, the mass balance calculation, Eq. (3), is completed to determine CMF.

CMF values for fondant with different ratios of sucrose–corn syrup solids are shown in Table 5 (Ergun and Hartel 2009). Corn syrup solids serve both to replace sucrose in the formulation and to modify the solubility concentration of sucrose in water (Table 3). The net result is that supersaturation decreases as more corn syrup is added to replace sucrose and, as expected, CMF decreases with higher levels of corn syrup solids. At the same time, the concentration of the liquid phase of the fondant increases because all of the corn syrup solids remain dissolved in the aqueous phase. Texturally, reducing CMF by adding corn syrup solids to the formulation causes the fondant to become softer (Lees 1965). In this case, less crystalline mass results in softer product.

Ergun and Hartel (2009) also compared calculated CMF values for 2 types of nougat, grained and ungrained, using the solubility approach. An ungrained chewy nougat formulation (sucrose to corn syrup solids ratio <1) was compared to a grained nougat formulation (sucrose to corn syrup solids ratio >1) in terms of CMF. Even despite a large difference in the ratio of sucrose to corn syrup...
solids, the predicted CMF values were not that different, with the ungrained nougat predicted to have 34.5% crystals and the grained nougat predicted to have 42% crystals. The high predicted CMF makes it clear that the amorphous aqueous phase of the ungrained nougat is still highly supersaturated. It does not nucleate, however, because of the kinetic inhibition of the corn syrup solids and the reduced molecular mobility of the amorphous state. In contrast, the aqueous phase of the grained nougat crystallizes completely because of seed crystals (fondant) added at the end of the process. The seed crystals allow complete crystallization, leading to the short texture expected from a grained confection.

While the mass balance model based on the phase diagram is relatively simple and easy to apply, experimental verification of the calculation has proven difficult, especially in confections with low levels of CMF. In principle, methods of measuring CMF in confections include (1) dilution and filtration to separate crystals from liquid, (2) x-ray analysis, or (3) nuclear magnetic resonance (NMR) (Lenz and Hartel 2005). Unfortunately, the viscous amorphous nature of many confections limits the use of the solvent dispersion method (Lenz and Hartel 2005). The use of x-ray spectroscopy for measuring CMF has been limited, particularly where low levels (<10%) of crystals are present, although Surana and Suryanarayanan (2000) claimed to have used this method to distinguish less than 5% crystallinity in amorphous sucrose. Langrish and Wang (2009) used an x-ray method to track crystallization of either sucrose or lactose from spray-dried powders exposed to humid air. Further technological development of this method is warranted. NMR methods have also been used or claimed to measure CMF in sugar systems. Gallo and others (2003) used a standard pulsed-gradient NMR to quantify the degree of trehalose crystallization from the amorphous phase. Also, solid-state NMR has been suggested as having potential for quantifying CMF in confections, although no published literature work is available documenting this method.

**Predicting crystal mass fraction based on empirical ratios.** Over the years, the ratio of sucrose (S) to corn syrup solids (CS) content has been used as a rough indicator of whether graining will occur. Lenz and Hartel (2005) used S/CS to characterize CMF of jelly candies and caramels and found that high ratios (greater than 1 for caramel and 2 for jellies) always led to crystallization, while lower ratios (less than 0.4 for caramel and 0.8 for jellies) always indicated inhibition of graining. However, the ratio, S/CS, was not a sufficiently sensitive indicator to uniquely distinguish sucrose crystallization in the intermediate range of S/CS. Even when water content of the confection was taken into account, no simple application of ingredient ratios was sufficient to uniquely determine whether or not crystallization would occur.

More recently, an empirical approach to determining whether a confection would be expected to grain and, if so, approximately how much graining might be expected, was developed by an experienced candy maker (Noda, private communication). This empirical graining factor, GF, was proposed based on the ratio of concentrations of crystallizing sugar to crystallization inhibitors (or doctors) present in a formulation. By experience, a critical GF was specified previously, which graining was likely to occur. GF can be calculated as:

\[
GF(\%) = \frac{[\text{concentration of crystallizing sugar}]}{[\Sigma \text{concentrations of all sugars}]}(100)
\]  

GF is defined on a dry solids basis, meaning that water content of all components in the formulation must be discounted. Based on practical experience, a GF of about 44% to 45% was the critical GF value that distinguished graining. A formulation with GF 44% was considered to be ungrained while formulations with GF above 45% would be expected to contain crystals.

Ergun and Hartel (2009) compared GF values for nougats with different formulations. A chewy nougat formulation was found to have a GF of 48.5% (more corn syrup than sucrose), while a grained nougat formulation had a GF of 64.1% (more sucrose than corn syrup). Based on texture, the chewy nougat had few if any crystals even though the solubility curve predicted that the aqueous sucrose phase was still highly supersaturated (with an expected 34.5% CMF). The grained nougat, which has the short texture characteristic of a highly crystalline candy, had substantial CMF, based in part due to the addition of powdered sugar as seeds at the end of the batch. The CMF calculated by the phase diagram method predicted a CMF of 42% crystals for this nougat with a 64.1% GF. Clearly, the correlation between CMF calculated by phase diagram and the GF approach do not always agree, thus documenting the kinetic limitations to graining of sugars in such products.

Probably the main limitation of the GF approach, other than it being an empirical description of one part of the phase diagram, is that water content of the finished confection is not factored into the model (Ergun and Hartel 2009). That is, regardless of the finished water content, the predicted GF of a formulation remains the same. As shown in Table 5, the GF value for fondant does not reflect the different water content, reducing its value for predicting CMF. Still, within a category of confections with a narrow range of water content, like nougat, GF has some value as an indicator of whether or not graining will take place. Further research is needed to reconcile the phase diagram approach with these more empirical approaches.

**Crystal size distribution**

In confections where crystals impart textural attributes, typically the smallest possible crystals are desired to impart the smoothest mouthfeel (Jeffery 2001). It is in terms of understanding the size distribution of crystals in a grained confection that the relationship between nucleation and crystal growth is important (Hartel 2001).

In general, to produce the fine crystals desired in confections, several general principles must be followed to control rates of crystal formation and growth (Lees 1965; Hartel 2001):

1. Nucleation must be rapid and intense so that the number of nuclei formed is as large as possible. The large surface area of numerous nuclei means that each crystal undergoes minimal growth once the final phase equilibrium is attained.

2. Nucleation must occur within a narrow time span so that all crystals are formed at the same time. This allows all crystals to grow together at the same rate. Crystals formed early in a process spend longer time growing than crystals formed later in the process; the result is a wider spread of crystal sizes with some potentially growing large enough to be detected in the mouth. Further, a supersaturated sugar matrix should be handled with as little agitation or shear as possible until the moment when nucleation is desired, and then intense agitation should be applied to promote the most rapid nucleation.

3. Any potential seed materials must be completely dissolved prior to cooking the sugar batch. Sufficient time at warm temperatures, before boiling commences, is required so that all granulated sugar crystals and any crystals added through addition of reworked candy have completely dissolved. In
sucrose-based confections, boiling a sugar syrup to about 112 °C, where it still has about 15% moisture, causes it to become supersaturated (Ergun and Hartel 2009). That is, during the cooking process, the sugar syrup becomes supersaturated once temperature exceeds about 112 °C. This can be seen in Figure 1 as the point where the boiling point elevation curve intersects the sugar solubility curve. If any crystals are present in the batch at this point or if any seed material is added afterwards, these crystals will not dissolve. Instead, they will begin to grow, at a rate dependent on the supersaturation and molecular mobility.

(4) If seeding is used to initiate crystallization (bypassing nucleation), the seed material must be added at the proper time in the process so that enough seeds survive to grow into product-sized crystals (at phase equilibrium) of the proper size. Specifically, the seeds should be added when the sugar syrup is already supersaturated so they do not dissolve.

For example, controlling crystallization in fondant and fudge processing is critical to obtaining the desired smoothness; numerous small crystals are desired in these products to generate the preferred smooth mouthfeel (Minifie 1999; Jeffery 2001). The general process for making fondant can be seen in Figure 7A (Hartel 2001). In fondant, the syrup is cooked to the appropriate temperature (to attain the desired water content), and then cooled statically to an optimal temperature for nuclei formation, and then agitate intensely with high shear mixing to drive massive nucleation (Minifie 1999). Control of each step is needed to generate the smallest crystals possible for the smoothest fondant (Lees 1965). Should any of points (1) to (3) above not be satisfied, the result will be fondant with coarser texture. The optimal beating temperature for maximum nucleation is generally given as between 40 and 50 °C (Lees 1965; Minifie 1999; Hartel 2001). As noted previously, this temperature provides the best balance between supersaturation driving force, to promote nucleation, and limiting molecular mobility, which inhibits nucleation. At temperatures above and below this optimal point, fewer nuclei are formed (Figure 8), larger crystals are obtained, and the fondant is coarse.

Fondant is often used as the seeding material for the production of fudge and cast creams (Minifie 1999). In the production of cast creams, fondant is added to a thinning syrup (sometimes called bob syrup) along with colors, flavors, and frappé (an egg white to introduce air bubbles). The mixture is heated to blend the fondant smoothly into a homogeneous mass prior to depositing it into a mold of the desired shape. Careful control of the thinning process is necessary to obtain a smooth and uniformly crystallized product. The intent of the thinning syrup is simply to disperse the crystals in fondant without dissolving them; thus, the composition of the thinning syrup should be as close as possible to the composition of the liquid phase of the fondant being used. If improper concentrations of sucrose and corn syrup are used in the thinning syrup, too many fondant crystals will dissolve. Also, if the temperature is raised too high, which might be desirable to enhance fluidity of the mass for easier deposition, an excessive number of crystals will dissolve. Upon cooling of the seeded sugar syrup, the existence of a substantial crystal surface area means that no new nuclei are formed; typically, only growth of existing seed crystals occurs. Even if the initial fondant had very small crystals, these will grow to some extent during the cast cream process and excessive warming results in larger crystals, or coarser creams.

Controlling crystallization during production of the sugar shell of panned candies has been widely studied, particularly for hard panned candies (Shastry and Hartel 1997; Ben–Yoseph and others 2000; Ben–Yoseph and Hartel 2006). The sugar shell of hard-panned candies is comprised of numerous small crystals, typically thought to be somewhat fused together to produce a hard, brittle texture. The sugar shell is created by first spreading a thin layer of highly supersaturated sugar syrup, the engrossing syrup, over the centers in a rotating pan and then allowing sufficient time for crystallization to occur while drying the water out of the shell. To obtain the proper shell texture requires control of a large number of variables that influence crystallization, including composition of the syrup as it is applied, temperatures of both engrossing syrup and centers, rate of drying air, tumbling speed of centers in the pan, and frequency of application of engrossing syrup. Conditions that produce the greatest rate of crystallization are required; unfortunately, the optimal conditions depend on the particulars of the candy being produced so that no specific guidelines are available. One aspect of considerable concern is to avoid any doctoring agents or crystallization inhibitors that might slow down the phase transition. Thus, for example, a sucrose engrossing syrup must be free from corn syrup and a sorbitol engrossing syrup must be free from the impurity mannitol. These impurities are widely known to inhibit crystallization of other sugars.

Crystallization during storage

Ungrained confections are formulated and processed so as to prevent grainning. However, as noted earlier, many ungrained candies are actually supersaturated with respect to the sweeteners, but do not grain over time due to kinetic constraints.

Cotton candy is a metastable confectionery in the glassy state. The glass is formed by melting colored and flavored sucrose crystals in a spinning head with small holes on the outside of the disk. Once liquefied, the molten sugar flows through the holes to form thin strands of liquid sugar, which cool quickly to ambient temperature to a glassy candy floss. Since cotton candy has no corn syrup in its formulation to act as crystallization inhibitor, prevention of crystallization is due entirely to the limited molecular mobility in the glassy state. In addition, due to the high surface area of the candy floss, it is prone to moisture uptake, collapse, and recrystallization during storage (Labuza and Labuza 2004). Cotton candy remained stable for over 2 y when held at 11% RH, but crystallized within 3 d when held at 33% RH. In this range of RH, the cotton candy had picked up sufficient moisture that its $T_g$ had been reduced to below the storage temperature (22 °C). As long as the $T_g$ of the cotton candy remained above storage temperature, the candy retained its glassy nature. When $T_g$ dropped below room temperature due to excessive pick-up of moisture, the candy grained. The rate of graining was dependent on the difference between the $T_g$ of the candy and the room temperature. Graining occurred more rapidly during storage at higher RH because enhanced moisture uptake caused a greater reduction in $T_g$, which ultimately allowed the sucrose molecules sufficient mobility to organize into a crystal lattice.

Hard candies are also a metastable sugar glass, prone to crystallize if conditions change. Graining during storage can occur in hard candies for 2 reasons (Kitt 1993). First, if crystals are already present within the glassy matrix (formed during manufacturing), all that is required for these crystals to start to grow is that the temperature increases above $T_g$ to enhance molecular mobility. Once the sugar molecules have sufficient mobility, they can join the crystal lattice and the existing crystals grow. This form of graining is called internal graining. Alternatively, a hard candy can begin to grain when sufficient moisture is adsorbed to the surface to increase
molecular mobility to the point where nucleation can occur (Liang and others 2007; Hartel and others 2008). As moisture penetrates into the candy piece, a syrup layer forms at the surface with a reduced $T_g$ due to the higher water content. The mobility of sugar molecules in this layer is sufficiently high to promote graining. Continued graining occurs as the layer slowly proceeds into the center of the confection. In both cases, internal and external graining, flavor molecules more readily diffuse out of the candy causing a decrease in flavor. Also, the rearrangement of color molecules causes a change in appearance and texture of the candy as graining proceeds.

Levenson and Hartel (2005) studied the onset of nucleation of sucrose from sugar glasses held at elevated temperatures. The induction time for onset of graining decreased exponentially as storage temperature increased. The increase in temperature above $T_s$ enhanced molecular mobility and allowed the sucrose molecules to come together into a crystal lattice. The induction time for nucleation was directly related to the difference between storage temperature and the $T_g$ of the initial glass. Thus, nucleation from the glassy state is governed by the glassy state ($T_g$) and not by the supersaturation driving force (concentration difference to solubility).

In many confections, the addition of corn syrup or other doctoring agents has been shown to help inhibit graining even when molecular mobility is sufficient for crystallization to occur (sufficiently low $T_g$). The ability of corn syrup solids to inhibit nucleation of sucrose is widely accepted in practice although little experimental data documenting this fact are available in the literature. Shastry (1991) showed that 20% corn syrup solids reduced induction time for sucrose by a factor of 2 to 3 when compared at the same low supersaturation. Once supersaturation ratio ($C/C_s$) was above about 1.3, even 20% corn syrup had no effect on induction time for nucleation—all systems nucleated rapidly. Gabarra and Hartel (1998) showed that corn syrup fractions with varying degrees of polymerization inhibited crystallization of sugar glasses beyond their effects on $T_g$. Labuza and Labuza (2004) showed that addition of raffinose in cotton candy delayed the onset of graining. Although raffinose and corn syrup solids raise $T_g$ of the candy, the effects on nucleation are greater than can be explained by the effect on $T_g$. Thus, doctoring agents have an additional effect on graining separate from their effect on $T_g$. This effect is most likely related to the ability of the molecules of the doctoring agent to interact or associate chemically (such as via hydrogen bonds) with sucrose to prevent lattice incorporation.

Lenz and Hartel (2005) used an empirical approach to account for inhibitors in a study on graining during storage of jelly candies and caramel. In both cases, the induction time for graining decreased as the ratio of sucrose (S) to corn syrup (CS) decreased since the system became more supersaturated. However, the ratio S/CS was not uniquely sufficient by itself to characterize whether the confection would grain or not. A range of S/CS was observed where nucleation would potentially occur, but did not always take place. The water content (or the ratio of sucrose to water) could explain the differences in nucleation of caramel, but did not explain this behavior in jelly candies. To best prevent graining in these ungrained confections, it is best to formulate in the region where nucleation was always inhibited.

Confectioners also claim that lower-DE corn syrups have more of an inhibition effect on sucrose graining. However, data in the literature on controlled systems do not confirm that claim. Levenson and Hartel (2005) found no differences in induction time for glasses made with 36, 42, or 63 DE corn syrups. Perhaps, the wide scatter in the nucleation data overshadowed any statistical differences in induction time for the different systems.

Conclusions

Numerous factors go into controlling the phase/state transitions of sweeteners in confections. Understanding the factors that affect whether sweeteners form crystals or the glassy state is critical to the texture and quality of many foods and confections. In principle, crystallization is driven by a supersaturation driving force but inhibited by various resistances or constraints.

The phase/state diagram for a sweetener or combination of sweeteners delineates regions of temperature and concentration (inversely, water content) where crystallization may occur and where the glassy state may be expected. This is seen as the deviation in concentration above the saturation concentration, as expressed by a supersaturation driving force. Choice of operating conditions to produce confections with the desired state of sweetener should be guided by the phase/state diagram.

However, the phase diagram is only a guide since it assumes an equilibrium state is achieved, something not often found in most foods and confections. There are kinetic constraints on crystallization that often govern whether or not crystals form. For crystallization to take place, the sweetener molecules must have sufficient mobility (both translational and rotational) to orient into a stable crystal lattice. If molecular mobility is restricted, for example by low water content (high viscosity), crystallization does not occur despite the large driving force for crystallization. Crystallization may also be inhibited through addition of doctoring agents such as corn syrup and invert sugar. The physicochemical interactions between these doctoring agents and sugar molecules effectively prevent crystal lattice formation.

To improve the confectioner’s ability to control crystallization, further advances are needed to rationalize the contributions of supersaturation driving force and kinetic constraints on crystal formation and growth.

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