Handbook of Molecular Gastronomy
Scientific Foundations, Educational Practices, and Culinary Applications
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Publication details
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Published online on: 09 Jun 2021

How to cite: - Irem Altan, Patrick Charbonneau, Justine de Valicourt. 09 Jun 2021, Sugars: Soft Caramel and Sucre à la Crème – an Undergraduate Experiment about Sugar Crystallization from: Handbook of Molecular Gastronomy, Scientific Foundations, Educational Practices, and Culinary Applications CRC Press
Accessed on: 11 Oct 2023

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Sugars: Soft Caramel and Sucre à la Crème – an Undergraduate Experiment about Sugar Crystallization

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Introduction
Candy-making entails finely controlling the phase transitions of aqueous solutions of sugar. Both kinetic and thermodynamic aspects of sugar crystallization are indeed at play in the art of confectionery (Hartel, 2013). As part of a course on the chemistry and physics of cooking taught at Duke University, we have illustrated these undergraduate-level concepts by preparing and contrasting soft caramel and sucre à la crème recipes that, remarkably, differ only in their tempering. This laboratory experience allows students to explore the fine dependence of look and mouth feel of candies on the microstructure of sugar. In this chapter, we provide some background on these two candies and detail the physical chemistry involved in controlling their sucrose composition and microstructure.

Historical and Cultural Background
While soft caramel is a fairly generic candy (Larousse, 2009), sucre à la crème is associated with a geographically specific region. Its precise origin remains uncertain, but its deep connection with the French Canadian experience is undebatable: one of its key ingredients, maple sugar, is indeed indigenous to the north east of the American continent. Although recipes for sucre à la crème did not appear in the earliest French-language cookbook written in Montreal (Perrault, 1840; Driver, 2008) – possibly because of a certain contemporary elitism towards the maple sugar used in rural households (Parker, 2006) – by the turn of the 20th century it had become a staple of the genre (Caron, 1883; Ogilvie, 1905; Perrault, 1984; Driver, 2008). The candy even captures the essence of the French Canadian experience for Patriote François-Xavier Prieur, who fondly reminisced of early 19th-century settlers’ huts with “some twists of tobacco, pipes, small bottles containing pepper, cinnamon, nutmeg, sticks of sucre à la crème for the children etc. etc.” (Prieur, 1864; Prieur, 1949).

However, sucre à la crème is not exclusively found in French Canada. Maple cream, as it is also known, has a marked cultural presence in parts of the United States, finding room, for instance, in Frye’s Practical Candy Maker (Frye, 1885), and in the revised edition of The Practical Cook (Sears, 1892). The candy even captured the attention of an anonymous Englishman visiting Vermont in the 1870s (Anonymous, 1873). Whatever the origin of sucre à la crème may be, it long predates that of fudge (Benning, 1990; Larousse 2009), a closely related North American delicacy that only appeared late in the 19th century.

Physical Chemistry of the Confections
Recipes for soft caramel and sucre à la crème can vary, but, from a materials standpoint, both candies are straightforward mixtures of (maple) sugar and dairy fat. The exact source of sugar and fat may change; condensed milk, cream and butter all do the trick, and maple syrup (or cheaper substitutes) nowadays can replace maple sugar (Table 81.1). The deliciousness of the candy relies more on the precise control of material properties than on the refinement of its constituting ingredients.

Specifically, to obtain soft caramel or sucre à la crème, one must properly tune the concentration and microstructure of sugar. The former is set by the terminal boiling point temperature, the second by shearing (or not) the mixture as it is tempered. In order to better understand both processes, we refer to the temperature–concentration sucrose–water binary phase diagram at standard pressure (Figure 81.1). Because maple syrup is a simple aqueous solution of sucrose, 68% by weight, i.e., near the eutectic point, with <1% other sugars and compounds (Ball, 2007), this reference offers a useful framework for interpreting its phase behavior.

A caveat about that phase diagram should, however, be highlighted. The version presented here comes from a critical compilation of various experimental observations (Starzak and Mathlouthi, 2006), but estimates of the boiling point elevation line above around 85% sucrose vary by as much as 5 °C (Hartel, 2011). This regime is subject to a reasonably large uncertainty because it falls in a metastable, out-of-equilibrium range (Brady, 2009), and hence the measurements are preparation-dependent.
TABLE 81.1
Typical Recipes for Soft Caramel and Sucre à la Crème

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>540 g maple syrup</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>240 g heavy cream (35% milk fats)</td>
</tr>
<tr>
<td></td>
<td>45 g butter</td>
</tr>
</tbody>
</table>

Preparation

(i) Mix all the ingredients and bring to a boil until reaching 118 °C. To avoid the formation of sucrose crystals from the splatters, avoid stirring the mixture once boiling is attained and keep the sides of the pot clean.

(ii) Soft caramel: pour delicately into a featureless container and cool to room temperature (or below).

(iii) Sucre à la crème: place the pot into a cold water bath to quench the mixture to 55–75 °C, then whisk vigorously. Transfer the mixture into a mold, trace the squares for individual servings and cool down further.

(iii) When it is around room temperature, slice into individual servings. Dipping the knife in warm water can help.

Maple syrup being 68% sucrose, it can be replaced with 370 g of maple sugar, which is nearly pure sucrose (and the ingredient historically used for this recipe), or with 385 g of brown sugar, which is 95% pure sucrose (and is much more affordable).

In this regime, a careful determination of sucrose concentration from the boiling point alone is thus inherently somewhat imprecise. Despite this ambiguity, for the sake of this chapter, Figure 81.1 provides a sufficient experimental guide.

In both soft caramel and sucre à la crème recipes, ingredients are heated up to 18 °C above the boiling point of pure water, i.e., 118 °C under standard pressure conditions. Because the molecular weight of milk triglycerides (Breckenridge, 1967) is about three times that of sucrose (~800 g/mol or more vs. 342 g/mol) and only about a third by weight is used in the recipe (130 g vs. 370 g), the molarity of sucrose is about an order of magnitude larger than that of triglycerides. The contribution of the latter to the boiling point elevation is thus likely to be minimal. For simplicity, we here approximate this colligative property as being fully controlled by the sucrose concentration. This suggests that a sugar concentration of about 85–90% is reached at the target boiling temperature of both preparations.

Once the target sucrose concentration is reached, the mixture is tempered to room temperature or lower. Cooling the mixture sufficiently quickly, within a smooth container and without external shocks, inhibits heterogeneous crystal nucleation. This protocol permits the viscous supercooled fluid to persist without the formation of macroscopic crystals (Figure 81.2). The presence of milk fats and other solutes helps suppress sucrose nucleation. If this soft caramel is then kept at room temperature for a few days, the metastable fluid does eventually crystallize, hence reaching thermodynamic equilibrium. Although further lowering temperature, e.g., below 0 °C, increases the drive for sucrose to crystallize (by growing the difference in chemical potential between the supercooled liquid and the crystal), the caramel is then nonetheless better preserved. The reduction in mass transport at this temperature more than compensates for the reduced barrier to nucleation.

If, in contrast, the mixture is sheared upon cooling, then crystallites quickly form. Because most of these small crystals grow as the mixture is cooled, the degree of shearing and the temperature at which it takes place determine the degree of polycrystallinity, and thus the mouth feel, of the final sucre à la crème (Figure 81.2). Interestingly, it is also possible to obtain a product intermediate between a soft caramel and sucre à la crème by seeding the nucleation process with sucrose crystals (Jeffery, 2001).

The final confections – grained and ungrained, in confectionary speak – differ markedly from one another. The shine of soft caramel reflects its molecularly homogeneous nature, while the matte finish of sucre à la crème captures the intense scattering off its constituting micron-scale crystals (Figure 81.2). The former is chewy, while the latter typically crumbles in the mouth. Despite their obvious similarities, the two products please differently; the authors are split on which one is better.

**Conclusion**

In this chapter, we have briefly reviewed how basic notions of physical chemistry relate to making soft caramel and sucre à la crème.
Sugars: Soft Caramel and Sucre à la Crème

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Acknowledgements

The authors acknowledge the help of Steven Berdnarski, Benoit Charbonneau, Robert Charbonneau, Wouter Ellenbroek, Kathryn Harvey, Julie Parker, Nicole van der Sijs, and Haley Scholz as well as the staff of the Duke University Library and the Bibliothèque et Archives nationales du Québec for getting hold of some of the historical references consulted for this chapter. We also thank Michel Lambert and Jean-Marie Francoeur for stimulating exchanges about the origin of sucre à la crème, and Brigitte Lavoie for providing the material and supplies for the cooking experiments. PC and IA acknowledge support from the National Science Foundation Grant no. NSF DMR-1749374.

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