

Soft caramel and sucre à la crème : an undergraduate experiment about sugar crystallization

Irem Altan

Department of Chemistry, Duke University, Durham, North Carolina, United States of America

Patrick Charbonneau

Departments of Chemistry and Physics, Duke University, Durham, North Carolina, United States of America; patrick.charbonneau@duke.edu

Justine de Valicourt

Vestjyllands højskole, Ringkøbing, Denmark

Introduction

Candy-making entails finely controlling the phase transitions of aqueous solutions of sugar. Both kinetic and thermodynamic aspects of its crystallization are 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 (e.g., 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; Perrault, 1984; Ogilvie, 1905; Driver, 2008). The candy even captures the essence of the French Canadian experience for patriot 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 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.

Table 1: Typical recipes for soft caramel and sucre à la crème. Maple syrup being 68% sucrose, it can be replaced with 370g of maple sugar, which is nearly pure sucrose (and the ingredient historically used for this recipe), or with 385g of brown sugar, which is 95% pure sucrose (and is much more affordable).

Ingredients	540g maple syrup 240g heavy cream (35% milk fats) 45g butter
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. (iia) Soft caramel: pour delicately into a featureless container and cool to room temperature (or below). (iib) Sucre à la crème: place the pot into a cold water bath to quench the mixture to 55-75°C, then whisk vigorously. Transverse the mixture into a mold, trace the squares for individual servings and further cool down. (iii) Around room temperature, slice into individual servings. Dipping the knife in warm water can help.

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 1). The deliciousness of the candy relies more on the precise control of material properties than on the refinement of its constituting ingredients.

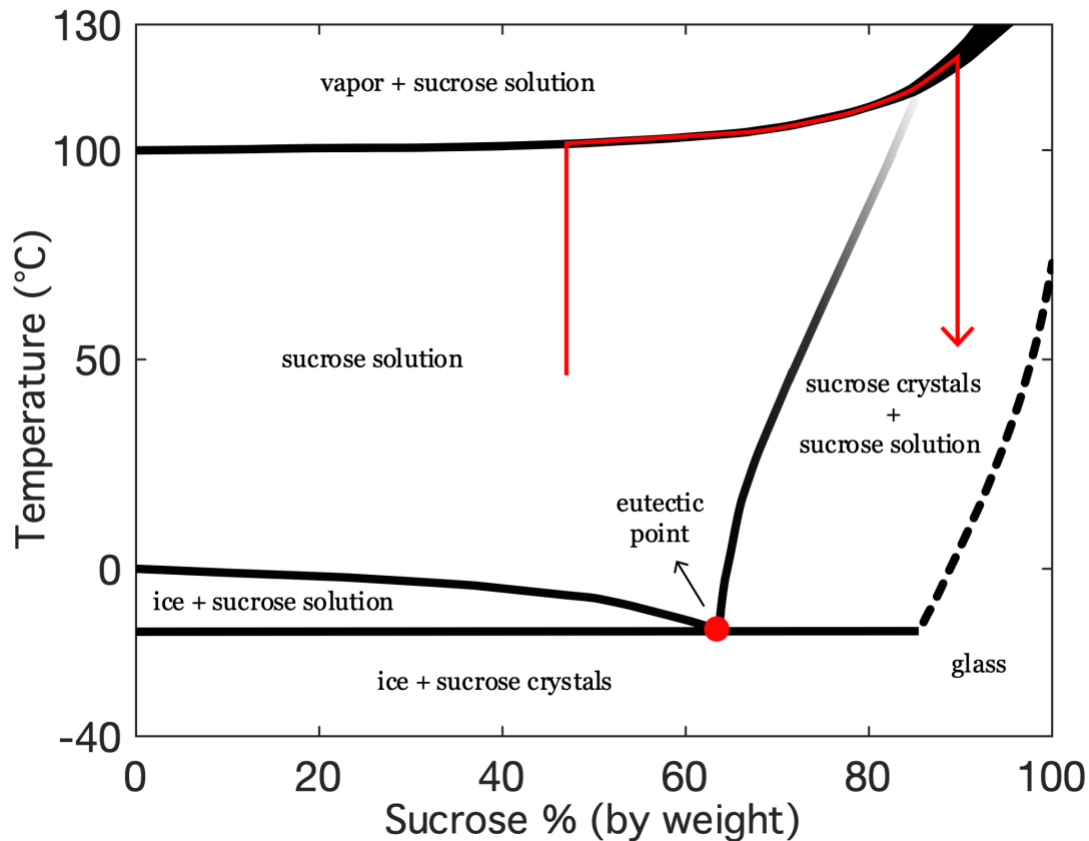


Figure 1. Binary phase diagram for sucrose-water under standard pressure conditions. Vaporization and crystallization lines are drawn from compiled data (Starzak and Mathlouthi, 2006). The broadening of the boiling point elevation line at high sucrose concentration reflects the experimental data scatter in this regime. Note that the glass transition line (Hartel, 1993) should not be viewed as a thermodynamic phase transition, but rather as an out-of-equilibrium marker of dynamical arrest for the (metastable) supercooled solution. The line reported here is for pure sucrose; milk fats shift it to higher temperatures. The red path denotes a typical protocol for preparing soft caramel and sucre à la crème.

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 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. 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 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 minimal. For simplicity, we thus 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 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 shortly after crossing the crystal solubility line, 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 mouthfeel, of the final *sucre à la crème* (Figure 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 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.



Figure 2: (left) Soft caramel has a smooth and shiny appearance; (center) sucre à la crème contains microcrystals that heavily scatter light, giving the confection a matte appearance; (right) a lightly sheared mixture seeds few sucrose nuclei, which grow to be macroscopically coarse.

Conclusion

In this chapter, we have briefly reviewed how basic notions of physical chemistry relate to making soft caramel and sucre à la crème. Coupling the colligative properties of aqueous sucrose solutions with shear-induced crystallization results in a characteristic micro-crystalline candy with broad appeal. These concepts, being fairly elementary, are well within reach of first-year college students with a high-school science background. Interestingly, this simplicity is also reflected in that other culinary cultures transform similar ingredients by similar approaches. Because no obvious historical link relates sucre à la crème with the Scots tablet (Pagrach-Chandra, 2013; McNeill, 2010) or the Dutch borstplaat (Pagrach-Chandra, 2013; Berkum, 1900), among others, their parallel emergence is likely. The appreciation for sugary confections is almost as universal as the underlying physical chemistry.

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References

- Anonymous. 1873. An Englishman in Vermont, *Macmillan's Magazine*, 28, 171-180.
- Ball DW. 2007. The Chemical Composition of Maple Syrup, *J. Chem. Ed.*, 84, 1647-1650.
- Benning LE. 1998. *Oh, Fudgel: A Celebration of America's Favorite Candy*, New York, Henry Holt and Company.
- Berkum Nv. 1900. *De Hollandsche tafel in Indië*, Noorduyen.
- Brady JB. 2009. Magma in a beaker: analog experiments with water and various salts or sugar for teaching igneous petrology, *Can. Mineral.*, 47(2):457-71.
- Breckenridge WC, Kuksis A. 1967. *J. Lipid Res.*, 8(5), 473-478.
- Caron M. 1883. Directions diverses données en 1878 par la Révérende mère Caron alors supérieure générale des soeurs de charité de la Providence pour aider ses soeurs à former de bonnes cuisinières, 2nd Edition, Montréal.
- Driver E. 2008. *Culinary Landmarks: A Bibliography of Canadian Cookbooks, 1825-1949*, Toronto, University of Toronto Press.
- Frye GV. 1885. *Frye's practical candy maker*, Chicago, Press of E. J. Decker.
- Hartel RW. 1993. Controlling Sugar Crystallization in Food Products, *Food Tech.*, 47(11):99-107.
- Hartel RW, Ergun R, Vogel S. 2011. Phase/State Transitions of Confectionery Sweeteners: Thermodynamic and Kinetic Aspects, *Compr. Rev. Food Sci. Food Saf.*, 10:17-32.
- Hartel RW. 2013. Advances in Food Crystallization, *Annu. Rev. Food Sci. Technol.*, 4:277-292.
- Jeffery MS. 2001. Grained and Ungrained Confections, *Manufact. Conf.*, 73(11), 97-110.
- Larousse. 2009. *Larousse Gastronomique: The World's Greatest Culinary Encyclopedia*, Clarkson Potters Publishers, New York.
- McNeill FM. 2010. *The Scots Kitchen: Its Traditions and Lore*. Edinburgh, Birlinn Limited.
- Ogilvie. 1905. *Ogilvie's book for a cook : a selection of recipes and other things adapted to the needs of the average housekeeper, some entirely new, and all have been thoroughly tested*, Montreal, Ogilvie.
- Pagrach-Chandra G. 2013. *Sugar & Spice: Sweets and Treats from around the World*, Northampton, Interlink Books.
- Parker J. 2006. «La Cuisinière Canadienne. Contenant tout ce qu'il est nécessaire de savoir dans un ménage...» : Témoin de l'émergence d'une cuisine nationale au carrefour des cultures au XIXe siècle. MA Thesis in History, UQAM. <https://histoire.uqam.ca/wp-content/uploads/sites/21/2017/03/Julie-Parker.pdf>.
- Perrault L. 1840. *La Cuisinière canadienne, contenant tout ce qu'il est nécessaire de savoir dans un ménage [...]*, Montréal, Louis Perrault.
- Perrault L. 1984. *La Cuisinière Canadienne*, Montréal, Edi-Courtage.
- Prieur FX. 1864. Notes d'un condamné politique de 1838, *Soirées Canadiennes*, 4, 167-407.
- Prieur FX. 1949. Notes of a convict of 1838, Translated by George Mackaness, *Australian historical monographs No. 18*.
- Sears DS. 1892. *The Practical Cook : A Collection of Tested Recipes, Revised Edition*, Omaha, Young Men's Journal Co.
- Starzak M, Mathlouthi M. 2006. Temperature dependence of water activity in aqueous solutions of sucrose, *Food Chem.*, 96: 346-370.