The Physical Chemistry of Making Fudge

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There's a lot of physical chemistry involved in making old fashioned fudge. The recipe calls for combining and boiling milk, bitter chocolate or cocoa, and sugar together until the temperature of the syrup reaches 238 degrees F (114^{o} C), pouring the seething mixture into a bowl, cooling to 115 degrees F (46 degrees C), and then beating until the surface shine disappears. If you don't follow the cautions in the recipe -- wash down the sides of the pan with a wet pastry brush or cover the pan for a few minutes early in the cooking process; don't scrape the pan; don't disturb the candy until it's cooled; don't let anything, even a speck of dust, fall into the cooling syrup -- you are very likely to wind up with a coarse, gritty mass instead of creamy fudge.

Sugar dissolves far less readily in cold liquids than in hot. There is no way that two cups of sugar will dissolve in a cup of milk at room temperature. Heating the sugar and milk mixture allows the milk to dissolve more and more sugar, and by the time the mixture is boiling, all the sugar is dissolved. The general principle is that at a particular temperature, a given solvent (in this case, milk) can dissolve only so much of a particular solute (sugar). When the milk has dissolved all the sugar it can hold, and there is still some undissolved sugar left, the mixture is said to be saturated. The higher the temperature, the more concentrated the saturated solution becomes.

Water (and milk) boil at 212 degrees F (100 degrees C) at sea level, but the sugar changes that. In general, a solid dissolved in a liquid makes it harder for the liquid molecules to escape. Consequently, the solution has to be hotter for the liquid molecules to get away at the same rate, and the boiling point rises.

In our fudge, the rise in boiling temperature is an exact function of the amount of sugar in the solution. Consequently, we can use the temperature of the boiling syrup to tell when enough water has boiled away to give the syrup the right ratio of sugar to water. For fudge and similar creamy candies, the syrup should boil at a temperature 26 degrees F (14 degrees C) hotter than the boiling point of plain water.

Some of the initial water in the syrup has now boiled away. Because the sugar couldn't dissolve completely until the mixture was near boiling, the syrup reaches saturation very soon after it starts to cool. If you've done everything right, however, sugar does not come back out of solution. Instead, the syrup continues to cool as a

supersaturated solution. The solid phase -- in this case, sugar -- cannot start to crystallize without something to serve as a pattern, or nucleus. However, if a single sugar crystal is present, the syrup will start to crystallize, the crystals will grow steadily as the syrup continues to cool, and the result will be very grainy fudge.

This is why most fudge recipes require that the sides of the pot be washed down early in the cooking process, either with a wet pastry brush or by putting the lid on the pan for about three minutes to remove any sugar crystals clinging to the container walls. It is also why the recipes specify that the sides and bottom of the pan should not be scraped into the bowl where the candy is to cool. There is too much chance of scraping in a stray sugar crystal.

As the cooling syrup gets more and more supersaturated, its tendency to crystallize becomes even stronger. Even a speck of dust can start the process if all the candy contains is sugar, milk, and chocolate. Using more than one kind of sugar can counter this tendency. Most fudge recipes contain either corn syrup (which contains glucose instead of the sucrose of table sugar) or cream of tartar (which breaks sucrose into glucose and fructose). The different sugars tend to interfere with each other's crystallization and minimize the chance that the candy will crystallize too soon. They must be used in moderation, however -- too much and the fudge will remain a thick syrup forever!

The final stage is stirring the syrup when it is lukewarm to promote crystallization all at once throughout the candy. Disturbing (stirring) a very supersaturated solution causes many crystals to form at once. Because they compete with each other for the dissolved sugar, none can grow very large. The result is the proper creamy texture of fudge and the change in appearance from shiny (supercooled liquid) to dull (a mass of very tiny crystals).