2014 Problem 17 : Chocolate hysteresis

When cooled down again, chocolate often stays melted even at room temperature

Rebecca Frank
AHS School Vienna
Austria
rebeccafrank5398@gmail.com

Abstract

When making chocolate, the chocolatier has to watch out for the crystal formation in the chocolate butter because only the most stable and highest quality crystal gives the "melt-on-the-tongue taste". In the following text the melting and crystallisation of chocolate is explained as well as which parameters are needed to achieve the greatest effect in the hysteresis (the state at which the chocolate can be a liquid or a solid.) Several experiments using various chocolates have shown that different types of crystals, less stable and more stable crystals, depend on the solidification of the chocolate as well as the cooling process and the quantity of the chocolate butter and powder. In these experiments, various parameters have been changed to find out: what exactly is important in the chocolate to give it its taste and what is the temperature range of its hysteresis.

Introduction

It is a common phenomenon that when you leave chocolate in a car on a hot summer's day, it melts. To get it back into its initial state, you have to cool the bar of chocolate, often by putting it into the fridge. Exactly this phenomenon was investigated in the project 'Chocolate Hysteresis'. For this, various experiments were performed to investigate the important parameters and temperature ranges of the hysteresis.

Chocolate is made up of a lot of different components. The main ingredients are cocoa butter which stores the heat when chocolate is warmed and cocoa powder which gives the chocolate its magnificent taste. Chocolate is not simply a mixture of some ingredients. The chocolatier who makes the chocolate has to mix it for over 12 hours! This is because of the crystallisation in the cocoa butter. The longer you mix the chocolate (in a warm environment), the better the taste and consistency will be which is an important component for high quality chocolate is.

In chemistry, crystallisation is a daily phenomenon which is linked to the various polymorphs (structures) of the substances. But in physics, we are more interested in the energy compound of this phenomenon and the state of our material.

Mr Shukoff was one of the first to observe the melting and solidification curves of various substances, including chocolate. He is known for the Shukoff-flask which he used for cooling chocolate. Not only is he known for the flask, but he is also known for the Shukoff-curve which he observed whilst cooling his chocolate. The Shukoff-curve is the jump in temperature when chocolate is cooled back down again. The jump occurs because latent heat is set free. This latent heat is important for crystals to form and become more stable, because the crystallisation process requires a lot of energy which is then given off as heat.

Not a lot of work has been done on the hysteresis itself. Various papers have been published on the water component in chocolate [5] or the quality of chocolate butter [1]. Chocolate hysteresis has not been deeply investigated yet and therefore it is an important subject which needs to be analysed further.

Basic knowledge

Chocolate hysteresis is not like rubber hysteresis where you pull a rubber band and it does not jump back to its original length. Chocolate hysteresis is a state where, chocolate can be in a liquid as well as a solid state. As figure 1 shows the melting and solidification of chocolate, the area in between the two curves is the hysteresis.

For example, a chocolate bar at room temperature (approx. 23°C), when heated will still be liquid at room temperature. This is chocolate hysteresis which is dependent on time and how the chocolate is cooled.

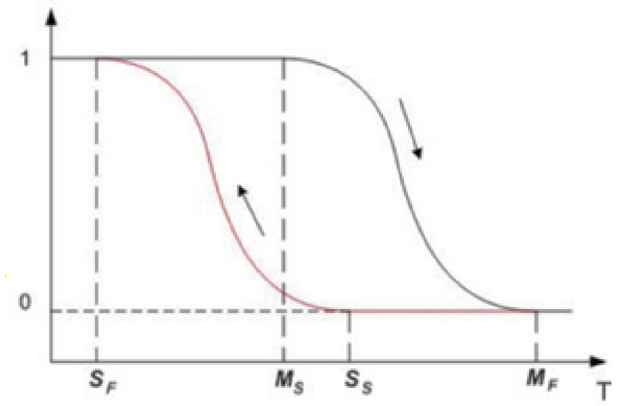

Figure 1: Chocolate Hysteresis: when heating and cooling chocolate again, a range in which it is liquid and solid is formed. This is called hysteresis.

Cocoa butter as is known is made of little crystals. In total we differ between 6 different crystals (as shown in figure 2) [1] of which there are different forms of stability. The more stable crystals give the chocolate a better taste and therefore much higher quality.

Form	Stability	Melting Point °C	Basic Polymorph
I	unstable	17	γ/sub-α
II	meta-stable	23	A
III	meta-stable	25	β'
IV	meta-stable	28	β'
V	stable	33	β
VI	most stable	36	β

Figure 2: Table of various crystals in cocoa butter. Unstable crystals melt at a lower temperature than stable crystals which normally melt at body temperature and give the "melt-on-the-tongue taste".

More stable crystals, such as the beta crystals that are more resistant to higher temperatures, are the high quality crystals chocolatiers try to achieve for their chocolate. This is very time consuming and is done by repeating the melting and cooling process. Figure 3 shows the logarithmic time of the melting and cooling process.

Every chocolate starts with an unstable crystal and during the period of cooling and heating, these crystals become stronger and more stable. The Shukoff-curve made it easier to observe the phase change in crystals which give out latent heat when changing their phase. So this phase change becomes more visible when observing the crystal formation. There is only a small boarder of liquid where you can get high quality crystals.

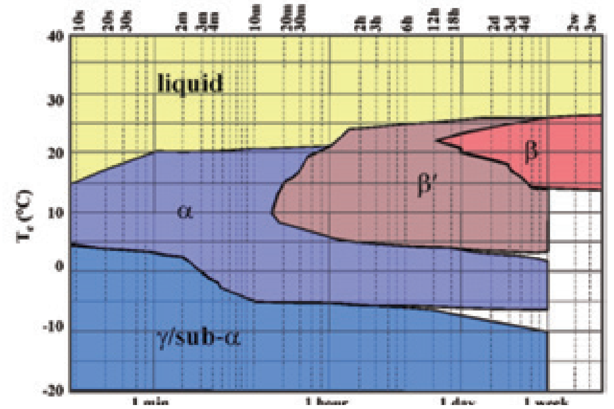

Figure 3: Time-temperature graph which shows that stable crystals (beta crystals) only evolve in certain conditions such as a long time-range and a small temperature range.

Methods And Materials

Much store bought chocolate contains artificial flavouring, but chocolate can also be chocolate without anything artificial. Chocolate originated from the Mayas who made chocolate as a gift for their gods to heal their people. These chocolates consisted of crushed cocoa beans, the cocoa powder and different kinds of fats. Nowadays this is the cocoa butter.[3]

For the following experiments, various parameters were changed to get results on the hysteresis.

Experiment 1: How Important Is Cocoa Powder?

At first, chocolate was mixed to investigate a "clean" chocolate without any additives and to change the amount of cocoa powder. It was distinguished between 20% and 40% cocoa powder. These test tubes, as shown in figure 4, were filled with the chocolate either the 20% or the 40% cocoa powdered chocolate and then were compared to oil in an isothermal bath in which the temperature could be regulated manually.

Figure 4: Isotherm with one sample and one against sample.

After heating both chocolates to about 80°C to dissolve all crystals, the chocolates were placed into the isothermal which was cooled down to 18°C. At about 19, 4°C, the 20% chocolate set latent heat free and therefore it was clear that the solidification had begun. Comparing the 20% cocoa powder chocolate to the 40%, it was clear that the 40% chocolate solidifies at a similar temperature, though more latent heat was released in the 40% chocolate.

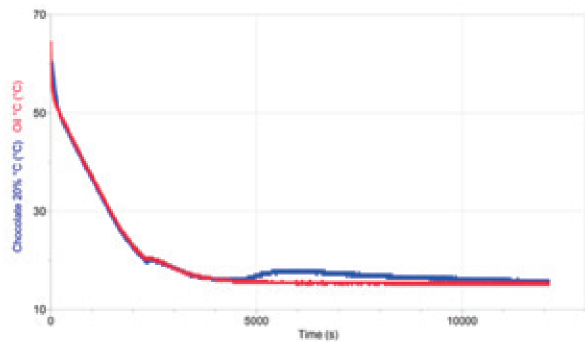

Figure 5: x-Axis: Time; y-Axis: Red line: Oil (against test) Blue line: Chocolate 20%. One phase change at which more Gibbs free energy is needed than with the 40% cocoa-powdered chocolate.

Having the cocoa powder which makes the seeds in the chocolate inhomogeneous, means that less Gibbs free energy is needed and therefore there is higher latent heat that is set free.

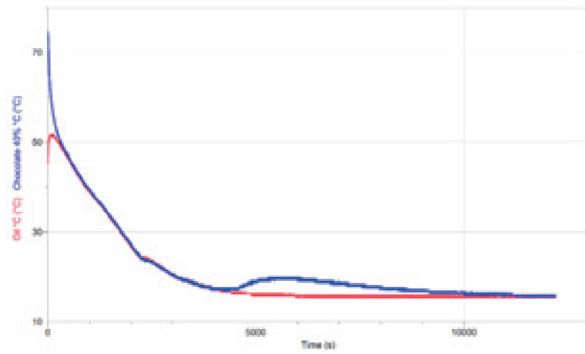

Figure 6: x Axis: Time; y-Axis: Red line: Oil (against test), blue line: Chocolate 40%. Having more cocoa powder, more seeds in the chocolate, means that less Gibbs free energy is needed and therefore more latent heat is been given off.

These results show that cocoa powder does not play a big role in the solidification of chocolate but also that the heat storage is in the cocoa butter and therefore only cocoa butter is used in the following experiments to see the melting more clearly.

Experiment 2: Which crystals evolve in our cocoa butter?

With this experiment which is shown in figure 7 the question which should be solved was: which crystals form in the cocoa butter (in all experiments the same cocoa butter was used). The cocoa butter was heated, to melt and annihilate all crystals, and was then cooled down in an ice bath to 3°C. Once the cocoa butter was solid, it was kept in the ice bath for another three hours. After the three hours, the cocoa butter was put into a thermal bath which was heated to 23°C – the temperature at which the unstable crystals dissolve. By this time the cocoa butter had melted half way but a part did not melt which showed that the more stable crystal (the beta-prime crystal) (see figure 2) had evolved. Eventually when the thermal bath was heated to 27°C, the whole cocoa butter had melted.

Figure 7: Cooling bath to shock cool the cocoa butter and to analyse how many phase changes may occur when shock cooling.

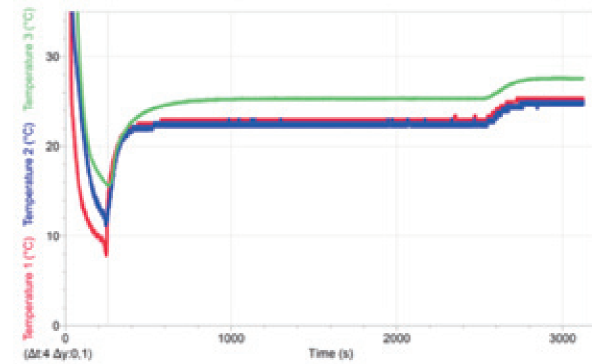

Figure 8: x-Axis: Time, y-Axis: Red line: temperature of first probe; blue line: temperature of second probe; green line: temperature of third probe. Heating cocoa butter in an isotherm, part of the cocoa butter melted and therefore it got heated even more to melt the other half → points towards the fact of having two different types of crystals.

With this experiment it was observed that two crystals evolved in the cocoa butter and therefore only these two crystals were taken into consideration in the following experiments.

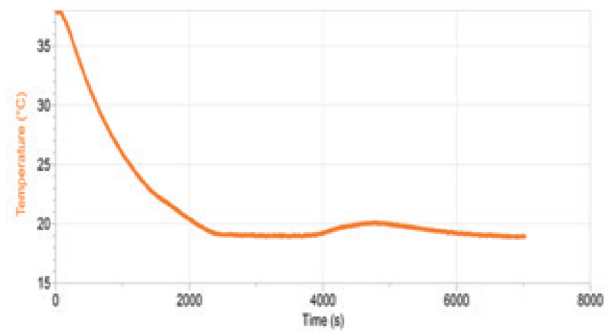

Figure 9: x-Axis: Time, y-Axis: Temperature of probe. Latent heat was freed twice – 2 phase changes occurred.

Experiment 3: Shock cooling

With this experiment it was shown that not only the setup was the best possible setup, but also that the theory does not always have to be correct. Comparing the used setup with a DSC (Differential Scanning Calorimeter) (see figure 10), it was discovered that the used setup does not give any different results but is easier to use.

In this experiment chocolate was compared to cocoa butter. Both samples were heated up to approx. 60°C and then shock cooled at 18°C. Theory states for cocoa butter when shock cooling chocolate or cocoa butter, only the unstable phase of the crystal is formed. This was shown to be wrong in experiment 2 (see figure 9).

Seeing that the first and second experiments could be examined in such a comparison, the next step was to see if the used setup works as well as a DSC.

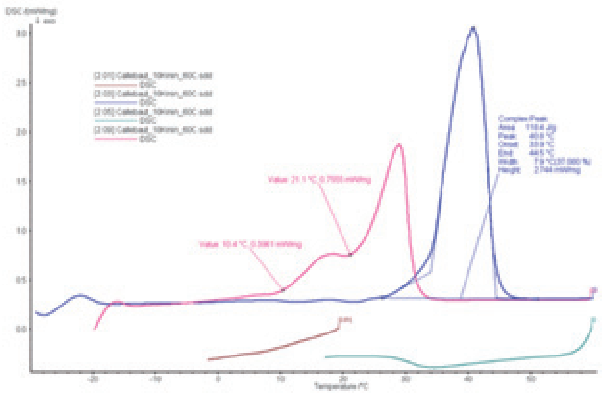

Figure 10: x-Axis: Temperature, x-Axis: Temperature difference between probe and pressured against probe. Comparing chocolate to cocoa butter the chocolate sets more latent heat free and crystallises faster as shown in experiment.

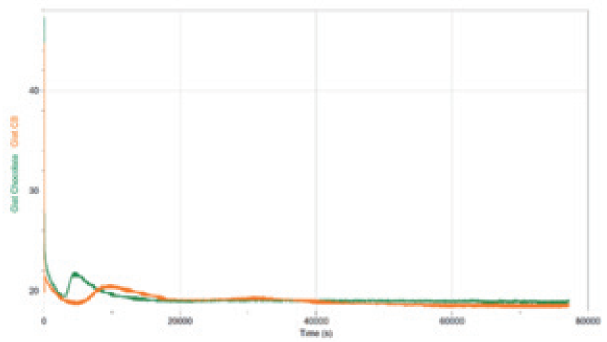

Figure 11:x-Axis: Time, y-Axis: green line: temperature of chocolate, yellow line: temperature of cocoa butter. DSC results – show latent heat was set free but not very clear at what temperature therefore initial setup is better for this type of experiment.

Both experiments from the setup and from the DSC showed one phase change when shock cooling cocoa butter. It is known though that the cocoa butter which was used can have two phase changes. This did not appear because the length of the cooling was not long enough.

Experiment 4: Illumination and phase changes

In this experiment the definite phase changes were documented by shining a laser through the melted cocoa butter (see figure 12). The amount of phase changes is identified by how often the cocoa butter crystallises. With a light sensitive device, the laser was caught and the light intensity was measured. First heating the cocoa butter and then putting it into a thermal bath in the main setup, showed at what point the chocolate began to crystallise.

Once the cocoa butter was crystallised (in one experiment after one phase change and the other experiment after two phase changes), the cocoa butter was heated up again. Comparing the first and the second phase changes, it was observed that cocoa butter melts at a different temperature when undergoing one phase change than when undergoing two phase changes.

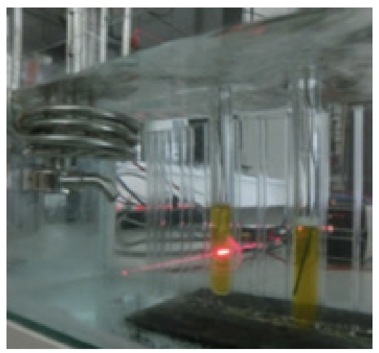

Figure 12: Red laser shining through melted cocoa butter into a light sensitive device measuring the lux of the laser.

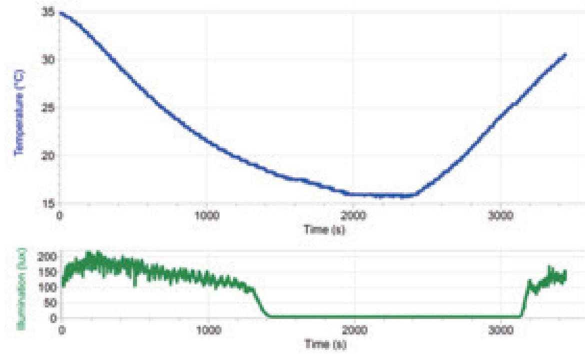

Figure 13: both x-Axis: Time, y-Axis: blue line: temperature of probe; green line: light intensity of light sensitive device. Illumination data shows when the cocoa butter has crystallised, temperature data does not show this precisely. When heating the cocoa butter again it stayed crystallised at a higher temperature than initially.

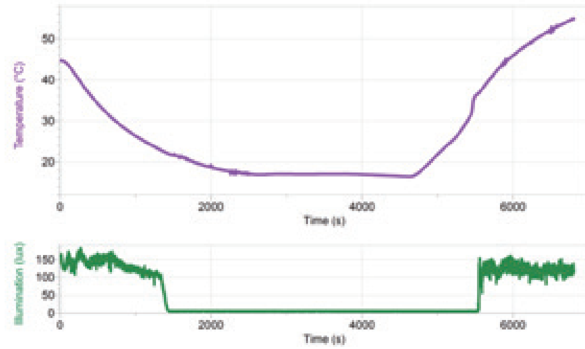

Figure 14: Both x-Axis: Time; y-Axis: pink line: Temperature of probe; green line: light intensity of light sensitive device. Waiting for two phase changes cocoa butter only melts at an even higher temperature than when after one phase change.

All four experiments lead to the one question: what are the relevant parameters and the temperature range of the chocolate hysteresis?

Results and Discussion

The temperature ranges vary from cocoa butter but using a pure cocoa butter from Africa will lead to similar results. The various phase changes of the crystals in the cocoa butter are also very important.

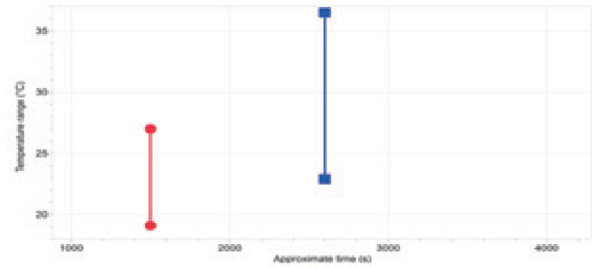

Figure 15: x-Axis: approximate time; y-Axis: Temperature range of hysteresis. Temperature range of hysteresis when waiting for one phase change or waiting for two phase changes.

1st phase change: 19,1°C – 27°C

2nd phase change: 22,9°C – 36,5°C

Throughout these experiments, the following factors were considered as very influencing:

Cocoa butter, how it is cooled, how long it is cooled; cocoa powder which does not change the temperature range but accelerates the process and influences the amount of latent heat released.

Conclusion

Further studies are required. Not only should a DSC be done with various chocolates to compare the used setup, but also the crystals of the cocoa butter should be looked at under an electron-microscope.

Each of the completed experiments viewed a different part of the melting or cooling process and together, this can lead to very precise results.

These results hopefully encourage others to observe chocolate hysteresis and come up with more ideas than the Austrian team has to date. Due to chocolate hysteresis being such a broad topic, there are a lot of things still to be observed and therefore it is even more important for further studies.

Acknowledgment

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References

[1] Kattenberg, H., Qualität der Schokolade hängt von der Kakaobutter ab, www.sweetcom.de/archiv/pdf/2001/pdf010301.pdf

[2] Systech-Analytics, Shuhkoff Cooling Curve, www.systech-analytics.com/fileadmin/documents/chocolat/Exotherm_8000_Brochure_english.pdf.

[3] Rowat, A., et. Alii, „The Science of Chocolate: Interactive Activities on Phase Transitions, Emulsification, and Nucleation", Journal of Chemical Education, Vol. 88, No.1 [2011], p.29-33.

[4] Sato, M., et. Alii, "Crystrallization, transformation and microstructures of polymorphic fats in colloidal dispersion states", Current Opinion in Colloid and Interface Science, [2011], p.384-390.

[5] Wille, R., & Lutton, S., Polymorphism of Cocoa butter, The Journal of the American Oil Chemists' Society, Vol.43, [1966], p.491-496.

2014 Problem 8 : Freezing Droplet

The shape of the water droplet may become cone-like with a sharp top

Iman Mojtahed
Mofid 1 High School

Amir Reza Soheili
Science & Technology University

Reported in PYPT 2014, Ariaian Young Innovative Minds Institute, AYIMI
Tehran, Iran
P.O.Box: 17185-614
info@ayimi.org

Place a water droplet on a plate cooled down to around -20 °C. As it freezes, the shape of the droplet may become cone-like with a sharp top.Investigate this effect.

Abstract

When a water drop is placed on a very cold surface, it freezes and is changed to a pointy tip drop. This phenomenon is not limited to water drop, and with every liquid that meets some specifications we can observe this happening.

The main reasons for this phenomenon are vertical expansion of drop and overcoming of surface tension of drop on its weight. If these two conditions exist for each fluid, its drop will expand vertically. Thus the bottom section of drop will expand vertically and the remaining portion of drop (which is above the frozen part) will move upward without any change. This happening will continue until we reach to the top of drop. At this point, the entire lower surface has been frozen, so the last point will move upward, without any transformation, and produce a sharp point (a pointy tip) which is called singular shape.

In this article, I am going to prove this theory and analyze pointy ice-drops phenomenon using some experiments.

Observations

The first step to solve any problem is observation. So according to the question, we should prepare necessary conditions for freezing the drop and appearing singular point. The first condition of the problem is temperature. There are many ways to receive -20°C, like using liquid nitrogen or liquid hydrogen; but the simplest way is using freezer. To do that, we should fill a plate with salty water and place it in a freezer with temperature control. The reason to use salty water is its lower melting point in comparison with other accessible liquids. Because of its low melting point, it can keep temperature constant for