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Hysteresis in the phase transition of chocolate

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Abstract

We designed an experiment to reproduce the hysteresis phenomenon of chocolate appearing in the heating and cooling process, and then established a model to relate the solidification degree to the order parameter. Based on the Landau–Devonshire theory, our model gave a description of the hysteresis phenomenon in chocolate, which lays the foundations for the study of the phase transition behavior of chocolate.

Keywords: hysteresis, chocolate, phase transition, Landau–Devonshire theory

(Some figures may appear in colour only in the online journal)

1. Introduction

Current research takes as its motivation the problem of chocolate in IYPT 2014 (International Young Physicists' Tournament). The original task is stated as: 'Chocolate appears to be a solid material at room temperature but melts when heated to around body temperature. When cooled down again, it often stays melted even at room temperature. Investigate the temperature range over which chocolate can exist in both melted and 'solid' states and its dependence on relevant parameters' [1]. As is well known, chocolate is a common foodstuff in daily life, as well as an important industrial material. For example, it is used as the raw material for a recent 3D food printer. The main ingredient in chocolate is cocoa butter; according to the investigation of Lutton [2–4], cocoa butter has six crystalline states with different melting points. The crystalline state is related to the chemical composition of the

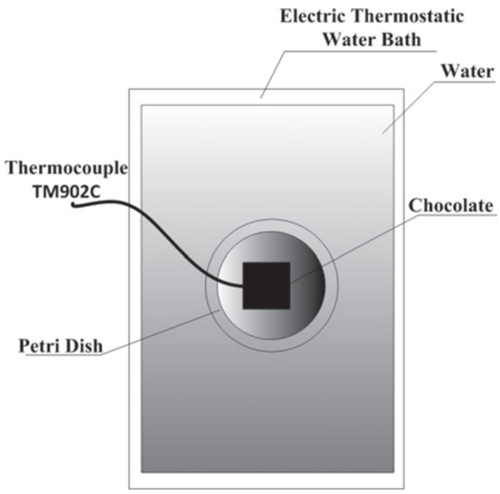

Figure 1. Schematic diagram for the experimental set-up.

cocoa butter [5]. The composition of cocoa butter depends on the country of production and the harvest period [6]. Therefore, the polymorphism of cocoa butter renders chocolate a complex structure.

Chocolate is usually solid at room temperature (20 °C ∼ 25 °C) and melts when the temperature rises to body temperature (36 °C ∼ 37.5 °C); that is, the phase transition occurs during solidification and melting [7]. In the re-cooling process, however, chocolate remains a liquid when the temperature drops to room temperature; that is, exhibits *hysteresis*. In fact, hysteresis behaviors widely exist in the phase transitions for ferromagnetic and ferroelectric systems [8]. While there has been abundant research on hysteresis in ferromagnetic or ferroelectric materials, hysteresis in chocolate remains largely unexplored. In the current research, we selected various chocolate products on the market in order to investigate the properties of their hysteresis. We found that the melting and solidifying degrees of chocolate are connected to the order parameter via a simple and effective model. In particular, hysteresis behavior in chocolate can be explained using the Landau–Devonshire theory.

2. Sample preparation and experiment

We used a medical needle to inject a table tennis ball with water until it is filled, then sealed the ball. The water-filled table tennis ball should weigh 22.5 g. Now the table tennis ball is ready for the measurement of the melting or solidifying degree of chocolate.

The dark chocolate we used is a commercial material manufactured by Leconte Chocolate Corporation. The net weight for each bar is 6.0 g. Put four chocolate bars each in five Petri dishes. Heat them in the electric thermostatic water bath, as shown in figure 1. Stir the chocolate in the five Petri dishes with small wooden sticks every few minutes. When the temperature reaches 40.0 °C, press the ‘maintain’ button. Finally, obtain the melted chocolate laying evenly in the five Petri dishes; the thickness of the chocolate layers in each Petri dish should be approximately 15mm.

Take out the chocolate samples and monitor the temperature inside the samples in real time with thermocouples. When the temperatures decrease to room temperature (23 °C ∼ 25 °C), refrigerate the samples (about 2 °C). When the temperature falls below

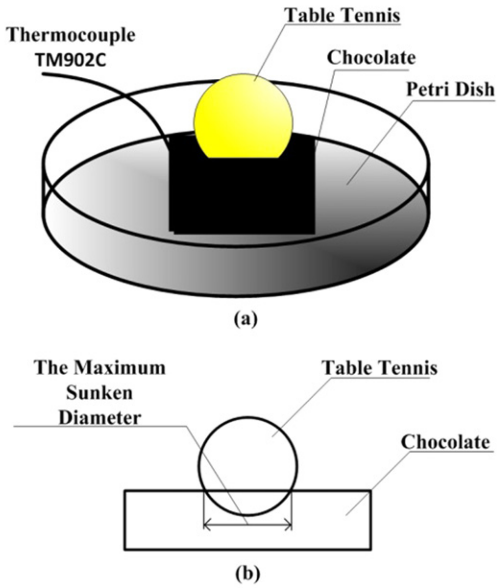

Figure 2. Schematic diagram for the experimental process.

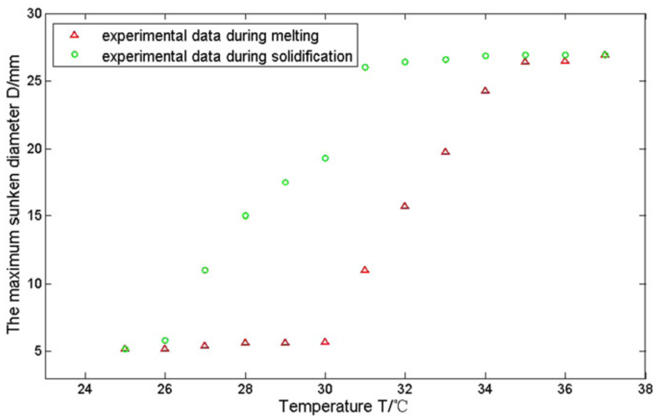

Figure 3. Experimental data for the maximum sunken diameters versus temperature.

10 °C, the chocolate samples are considered to have solidified completely. The temperature of a water bath is set at 24.0 °C; when this temperature is reached, take the chocolate samples out from the refrigerator. When the temperature returns to 23 °C, place the five chocolate samples in the electric thermostatic water bath. Ensure that they float on the surface of the water away from the wall of the tank.

Now set the temperature of the water bath to 25.0 °C. When the temperature remains at 25.0 °C for approximately 10 s, take one of the samples out. Lay the table tennis ball gently on the chocolate sample, as shown in figure 2(a). When the temperature on the thermocouple flashes from 25 °C to 24 °C three times, slowly lift the table tennis ball vertically away. Measure the maximum diameter of the chocolate area on the table tennis ball, which is also

Table 1. The maximum sunken diameters of the chocolate during heating and cooling processes.

Temperature $T\,°\mathrm{C}^{-1}$	The maximum sunken diameter $D\,\mathrm{mm}^{-1}$ (heating)	The maximum sunken diameter $D\,\mathrm{mm}^{-1}$ (cooling)
25.0	5.20	5.20
26.0	5.20	5.80
27.0	5.40	11.00
28.0	5.60	11.00
29.0	5.60	17.50
30.0	5.65	19.30
31.0	11.00	26.00
32.0	15.65	26.40
33.0	19.75	26.55
34.0	24.25	26.85
35.0	26.40	26.90
36.0	26.45	26.90
37.0	26.90	26.90

the maximum sunken diameter in the chocolate sample. Use a piece of wood to flatten the chocolate sample in the Petri dish until the sample cannot be pressed any more, and then place it back into the water bath. Clean the chocolate on the table tennis ball and repeat the entire procedure for the other four samples.

Use the same method to measure the maximum sunken diameters from 26 °C to 37 °C in 1 °C steps and the maximum sunken diameters from 37 °C to 25 °C in −1 °C steps. The average results for the five groups of samples are listed in table 1 and shown in figure 3.

3. Theoretical analysis

From the results of the experiment, hysteresis is clearly exhibited in the melting and solidification of chocolate. Hysteresis behavior in phase transitions can usually be phenomenalogically described with the Landau–Devonshire theory [9].

According to the Landau–Devonshire theory, the free energy of the system can be expressed as:

$$\phi_h = \phi_0 + a\left(T - T_c\right)\eta^2 + B\eta^4 + D\eta^6 - Vh\eta \tag{1}$$

where η is the order parameter, T the temperature, ϕ_0 the initial free energy, T_c the characteristic temperature. Meanwhile a, B, D, V and h are the parameters irrespective of temperature. The stabilization condition for the free energy is given by:

$$Vh = 2a\left(T - T_\mathrm{c}\right)\eta + 4B\eta^3 + 6D\eta^5. \tag{2}$$

For convenience, equation (2) can be written in the following form:

$$T = \frac{\alpha}{\eta} - \beta\eta^2 - \gamma\eta^4 + T_\mathrm{c} \tag{3}$$

where $\alpha = \frac{Vh}{2a}$, $\beta = \frac{2B}{a}$, and $\gamma = \frac{3D}{a}$. These parameters are closely related to the system, and have a significant impact on the free energy.

The solidification degree reflects the order degree of the chocolate, i.e., there should be a positive correlation between the order parameter of the system and the solidification degree of

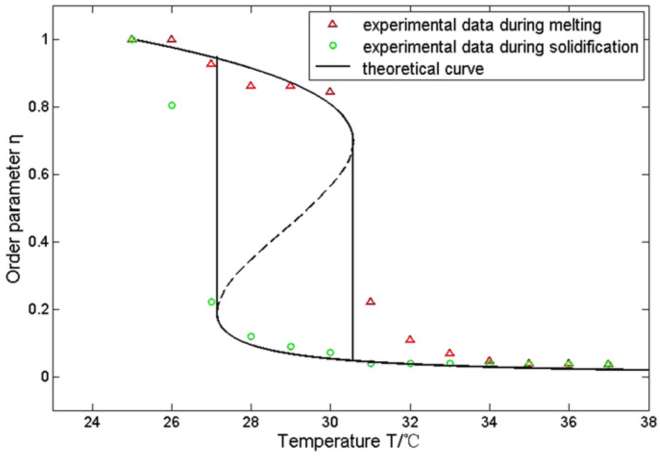

Figure 4. The theoretical curve and experimental data.

the chocolate. Based on this experiment, the larger the maximum sunken area, the smaller the solidification degree, i.e., the lower the internal order degree of the chocolate. Therefore, there should be a negative correlation between the solidification degree and the maximum sunken area. In other words, the order parameter of the system is negatively correlated with the maximum sunken diameter.

We propose a simple inverse-square relation to model this negative correlation:

$$\eta = k\frac{1}{D^2} \tag{4}$$

where D indicates the maximum sunken diameter from the experiment and k is the proportional coefficient. When the maximum sunken diameter D reaches its minimum value, the degree of ordering of the chocolate is the highest, i.e., η is largest. Introducing the normalized processing, the coefficient k can be determined while η is set to 1 and D reaches its minimum value as follows:

$$k = D_{\min}^2 = 27.04\ \text{mm}^2.$$

Therefore using equation (4), all the experimental data for maximum sunken diameter versus temperature can be converted into data for the order parameter of the system versus temperature, as shown in figure 4. Then the normalized experimental data enable us to determine the four parameters (α, β, γ, T_c) in equation (3), so that the theoretical curve based on the Landau–Devonshire theory is obtained. We found that the experimental data fit the theoretical curve well, and the parameters of the theoretical curve can be determined as follows:

$$\alpha = 0.27\ ^\circ\text{C},\ \ \beta = -20.90\ ^\circ\text{C},\ \ \gamma = 21.04\ ^\circ\text{C},$$
$$T_c = 25.00\ ^\circ\text{C}.$$

Furthermore, we determined the phase transition temperatures: for melting while increasing temperature and solidification while decreasing temperature, they were 30.57 °C and 27.14 °C, respectively. These results demonstrate that the Landau–Devonshire theory can give a phenomenological interpretation for the hysteresis of chocolate, revealing the change of the internal order degree in the process of heating and cooling.

4. Conclusions

This paper presented a reproducible experiment to demonstrate the hysteresis phenomenon of chocolate in melting and solidification. By building a reasonable model relating the solidification degree to the order parameter, we report a phenomenological explanation using the Landau–Devonshire theory. The critical temperatures, as well as related parameters, are also determined. This work, by synthesizing experimental research with theoretical analysis, not only advances our understanding of hysteresis in an important industrial material, but also provides an empirical framework to advance undergraduates' knowledge in experimental practice, mathematical analysis and physical modeling.

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