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Lipid migration in crystalline fat suspensions: Investigation of possible pathways and mechanisms



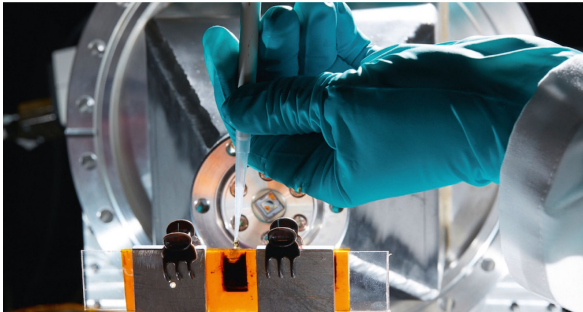
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1

Introduction

Chocolate blooming is one of the major problems in confectionery industry. It is manifested by the formation of white spots or a greyish haze on the chocolate surface due to large fat or sugar crystals. In case of fat crystals one refers to fat blooming and in case of sugar to sugar blooming. The crystals at the surface scatter the incident light and thus appear whitish (Altimiras et al., 2007, Lonchamp and Hartel, 2004, Rousseau and Smith, 2008, Rousseau and Sonwai, 2008). This makes the chocolate unappealing and leads to consumer complaints and subsequently large sales losses for the confectionery industry (Afoakwa et al., 2009a, Aguilera et al., 2004). Formation of sugar bloom is probably a result of recrystallization of dissolved sugar on the chocolate surface. Thereby, moisture dissolves sugar due to for example storage at low temperatures (e.g. fridge) and sugar recrystallizes at the surface. The formation of fat bloom might result from migration of lipids through the chocolate with subsequent recrystallization on the surface (Aguilera et al., 2004, Altimiras et al., 2007, Ghosh et al., 2002, Hartel, 1999). Many research studies aiming to understand blooming of chocolate have been published. Chapter 2 gives an overview of published studies related to chocolate fat blooming and lipid migration in chocolate. But the exact mechanisms are still not fully understood (Aguilera et al., 2004). However, a better understanding of pathways and driving force is a prerequisite to find ways to avoid lipid migration and thus the associated fat bloom formation. There are different possible pathways in chocolate which is composed of particles embedded in a crystalline fat matrix. Thus, migration might take place in the matrix phase, the network of particles or at the interface of particles and matrix. Two main mechanisms are widely discussed in literature: Diffusion as well as convective flow driven by capillary pressure are potential migration mechanisms (Hartel, 1999, Lonchamp and Hartel, 2004). The aim of this thesis is to identify preferred pathways and evaluate possible migration mechanisms. Thereby, the influence of micro- and nanostructure on lipid migration in chocolate is a main focus, because it determines

both, the pathway and the mechanism. By investigation of possible crevices and pores in chocolate, convective flow as a possible mechanism for lipid migration might be excluded or identified as the main transport mechanism. The methods and materials are introduced in Chapter 3.

To identify preferred pathways small angle X-ray scattering tracks migration of oil into porous chocolate powder components in-situ. Small angle X-ray scattering delivers information on a molecular and nanoscale without sample destruction. Besides the evaluation of preferred pathways, structural changes induced by oil migration in chocolate model systems can be investigated. Thereby, synchrotron radiation enables a high spatial and time resolution and is thus a promising technique. Chapter 4 presents and discusses the results of the small angle X-ray study.

Apart from structure features on a molecular and nanoscale, the particle arrangement within chocolate and thus surface area is of high interest for explanation of potential transport pathways. Therefore, further information about the microstructure of chocolate might reveal possible pathways and validate the proposed mechanisms. X-ray tomography is a technique which images the interior structure of a material without sample destruction. The image capture is based on differences in electron density of the different components. The use of synchrotron radiation leads to improved density contrast and consequently enables distinction of particles and imperfections such as cracks, crevices and voids in conventional chocolates. The visualization of chocolate model systems (the fat matrix without particles, pure cocoa butter, and samples with varying particle amount suspended in cocoa butter) supports the understanding of microstructure of chocolate. Finite element method simulations of the solidification process of chocolate gives possible explanations for the origin of cracks and crevices found in chocolate. Chapter 5 is about the structure analysis of chocolate with X-ray tomography.

The impact of microstructure on migration rate is analyzed with macroscopic observation of migration in different chocolate model systems. Thereby, the influence of tempering, which is controlled crystallization, is of high interest. Tempering leads to a more homogeneous and denser structure. In contrast, no tempering is characterized by a higher porosity and possibly inclusions of liquid and thus mobile lipids. A combination of the data from tomography and small angle X-ray scattering can explain the different migration rates found in the macroscopic samples. Based on these findings potential pathways and migration mechanisms can be evaluated. Chapter 6 examines the results from the macroscopic migration experiments. The thesis concludes with Chapter 7, which summarizes the results and proposes a migration model.



2

Theoretical background

The following chapter gives the theoretical background to lipid migration in chocolate. Therefore, first, the material chocolate is introduced in general followed by a more detailed description of the main component cocoa butter. Thereby, the composition, crystallization and the resulting microstructure of cocoa butter are presented. Subsequently, chocolate blooming and mass transport mechanisms are introduced. Finally, published hypothesis of lipid migration in chocolate are described.

2.1 Chocolate

Chocolate, a well-known confectionery product, is characteristic for both its flavor and texture. Thus, chocolate production aims to develop these two attributes to ensure the characteristic chocolate taste experience. Thereby, one of the main properties is that chocolate appears as a solid piece at room temperature but melts during consumption (at body temperature which is about 37 °C). From a material science perspective, chocolate is a suspension with particles surrounded by a semi-liquid crystalline fat matrix, mainly cocoa butter (Figure 2.1). Particles are densely packed with a particle concentration of about 70 wt% (Rousseau and Smith, 2008). The particles are usually sugar, cocoa solids and, in case of milk chocolate, milk powder. To adjust rheological properties an emulsifier which is often lecithin is added to the chocolate recipe (Lonchamp and Hartel, 2004). A mercury porosimetry study revealed that the matrix of chocolate is porous filled with liquid cocoa butter fractions (Loisel et al., 1997). Thus, lipids might migrate to the chocolate surface through the continuous fat phase (Figure 2.1 a), at the interface of the particles and matrix phase (Figure 2.1 b) or through the network of particles (Figure 2.1 c).

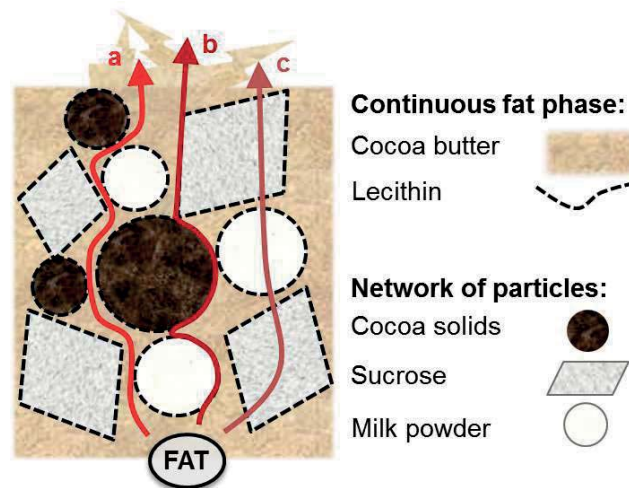


FIGURE 2.1: Chocolate structure: Sucrose, cocoa solids and milk powder particles surrounded by lecithin, an emulsifier, and embedded in a continuous cocoa butter matrix. Possible migration pathways of a lipid molecule within chocolate are a) through the fat matrix, b) at the interface of particles and fat matrix and c) through the network of particles.

A wide range of chocolate products exists on the market ranging from plain or filled chocolate bars over ice cream additives and pralines with fillings to bakery products. Chocolates can be subdivided into white, milk and dark chocolate. The latter typically contains 20 to 55 wt% of sugar, 45 to 80 wt% of cocoa mass and up to 5 wt% of additional cocoa butter as well as up to 0.5 wt% of lecithin. In contrast, milk chocolate usually consists of less cocoa but 12 to 18 wt% of non-fat milk solids and 3.5 to 6 wt% of milk fat. White chocolate typically lacks any cocoa mass and cocoa powder, but contains up to 50 wt% sugar, a third by weight milk powder and 22 wt% to 30 wt% cocoa butter and some milk fat resulting in a total fat content of 29 wt% to 40 wt%. (Wohlmuth, 2009)

Generally, the first step in chocolate production is to mix the ingredients, which are cocoa mass¹, sugar, fat and optionally milk powder. A size reduction step follows to decrease particle size to less than 40 to 20 μm so that single particles cannot be detected on the tongue and to get a smooth chocolate texture². Typical apparatus for grinding are three- or five-roll refiners. The subsequent step is the so-called conching where the chocolate mass is constantly under agitation at elevated temperatures³. The aim of this step is to develop flavor and texture by removal of undesired acidic and astringent compounds plus to ensure a homogeneous coating of particle surfaces with fat (Beckett, 2009). These are the basic steps for production of chocolate mass, which appears as a viscous suspension. To form a final product with a good snap, gloss and stability, a

¹Cocoa mass is produced from grinding cocoa beans which are fermented, dried, cleaned and roasted followed by separation of shells beforehand (Beckett, 2009)

²The exact size depends on taste and type of chocolate (Beckett, 2009).

³The actual temperature depends on the product (Beckett, 2009).

controlled solidification step is essential. For that purpose, the chocolate mass undergoes tempering, a precrystallization step, and subsequently solidifies under controlled cooling⁴.

The surface of chocolate has a complex topography having an irregular texture with sizes of mostly less than 3 μm and many deep pores with a size of about 3 to 6 μm in diameter and various morphologies (Rousseau, 2006, Rousseau and Smith, 2008, Smith and Dahlman, 2005). The surface of fresh chocolate is relatively smooth and the pores are heterogeneously distributed over the surface. Dahlenborg et al. (2011, 2012) found in addition to pores also protrusion of various sizes from about a micron to about 20 μm which change over storage time into "ridge-like structures" on the surface of white chocolate pralines. The surface structures partly go at least 10 μm into the chocolate and some contained fat and others were empty spaces covered with fat (Dahlenborg et al., 2012). Loisel et al. (1997) confirmed the presence of pores in dark chocolate with mercury porosimetry. They found empty spaces of 1 to 4 %⁵ which are partly filled with liquid fat. Thus, they propose that chocolate structure is a network of cavities with some liquid fat inside. Rousseau and Smith (2008) imaged the cross section of chocolate which has been cut prior to analysis with scanning electron microscopy. They visualized empty pores with a diameter of about 250 microns and channels going more than 100 microns through the entire chocolate sample.

2.2 Cocoa butter

The characteristic properties of chocolate, namely its texture and melting behavior, is strongly influenced by the fat matrix, which is mainly cocoa butter. The structure of cocoa butter influences the physical and crystal properties of cocoa butter such as melting behavior, crystalline form and strength (Aguilera, 2005, Campos et al., 2010, Rønholt et al., 2013, van Malssen et al., 1996). Physical, thermal and mechanical properties then again determine functional and sensory characteristics of the fat mixture and thus consumer experience (Campos et al., 2010, Sato, 1999). The cocoa butter's properties are strongly related to its structure which is determined by the arrangement of molecules. The molecular structure can be subdivided into the shape of the fat molecules (Figure 2.2, Level 2), the packing of the same (Figure 2.2, Level 3) and finally the crystal shapes (Figure 2.2, Level 4) forming crystal grains. The latter interact and finally form a crystal network, which gives cocoa butter the characteristic properties. Narine

⁴Further details on crystallization and tempering can be found in section 2.2.2, page 8 for crystallization in general and page 17 for the tempering process.

⁵The exact porosity was dependent on the solidification process of the chocolate mass and fat content. For well-tempered chocolate with 31.9 % cocoa butter they measured a porosity of 1 %, whereas it increased to 2 % at fat content of only 29.5 % and to 4 % for over-tempered samples.

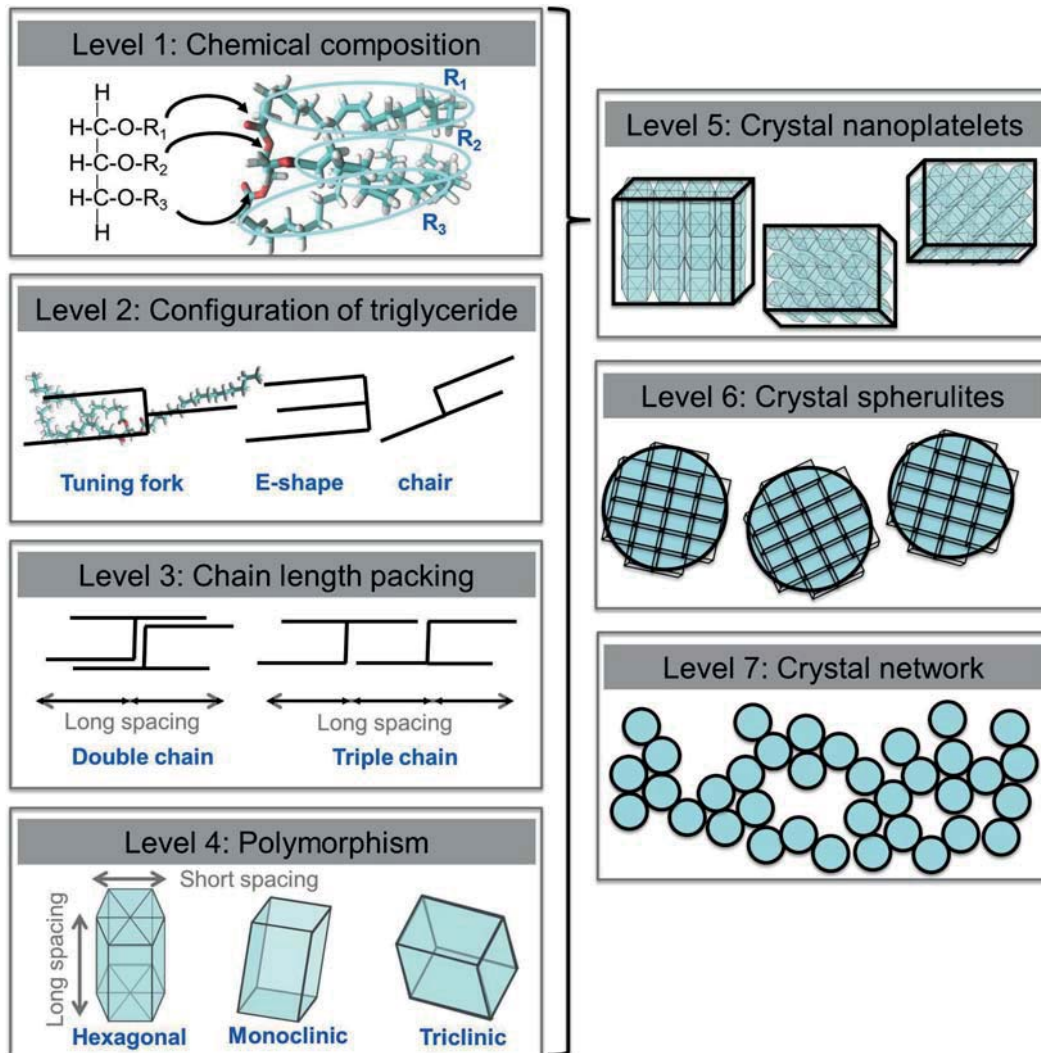


FIGURE 2.2: Different levels of structure of cocoa butter.

and Marangoni (1999b) describe the cocoa butter fat network structure as that of colloidal gels (Figure 2.2, Level 5 to 7). The shape, packing and crystal structure depend on the composition (Figure 2.2, Level 1) alongside with the process conditions (mainly temperature and agitation during solidification) (e.g. Lutton, 1950, Rønholt et al., 2013, Sato, 1999). The different levels forming the cocoa butter structure are discussed in more detail in the following.

2.2.1 Chemical composition

Cocoa butter is a fat mixture comprised of mostly triglycerides (triacylglycerols), which are esters of glycerol and fatty acids (Figure 2.2, Level 1) with a few other minor components (Himawan et al., 2006, Lipp and Anklam, 1998). The chemical composition

of cocoa butter is dependent on the origin, the harvest time and plant (see for example Figure 2.3). About 80 % of the cocoa butter are triglycerides with an unsaturated fatty acid in between two saturated fatty acids. More than 95 % of the fatty acids are oleic (O), stearic (S) or palmitic (P) (Beckett, 2000, Metin and Hartel, 2005). Oleic acid is composed of 18 carbon atoms with 1 unsaturated bond (C18:1 with an unsaturated bond at C9), stearic acid has 18 carbon atoms as well but no unsaturated bond (C18:0), same as palmitic acid which has 16 carbon atoms without any unsaturated bond (C16:0) (Campos et al., 2010). The saturated fatty acid chains are linear and have a kink at positions with double bonds (Himawan et al., 2006). Cocoa butter in chocolate contains palmitic, stearic and oleic acids in nearly equivalent amounts (Rothkopf and Danzl, 2015). The main triglycerides in cocoa butter are palmitic-oleic-palmitic (POP), stearic-oleic-stearic (StOSt) and palmitic-oleic-stearic (POST) triglyceride. These three triglycerides make up about three quarter of components in cocoa butter (Figure 2.3) (Lovegren et al., 1976, Torbica et al., 2006, van Malssen et al., 1996). Their melting

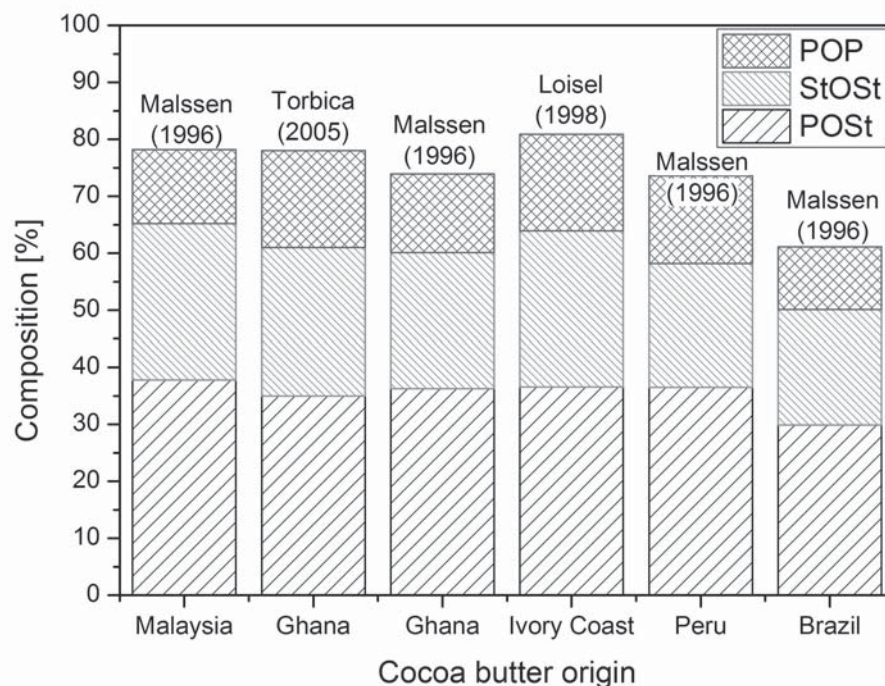


FIGURE 2.3: POP, POST and StOSt amount in cocoa butter from different origins published in Torbica et al. (2006), Lovegren et al. (1976), van Malssen et al. (1996).

range is at about room temperature. Only about 1 % to 2 % of cocoa butter is all saturated fatty acids and thus melts at higher temperatures (Beckett, 2000). Besides the main triglycerides, 5 % to 20 % of cocoa butter fats have a saturated and two unsaturated oleic acids like stearic-dioleic (StOO) and palmitic-dioleic (POO), which are liquid at room temperature (Beckett, 2000). In addition, fats like cocoa butter contain

di- and monoglycerides as well as phosphoric acids as other minor components (Beckett, 2000, Metin and Hartel, 2005).

2.2.2 Crystallization and structure

Cocoa butter solidifies in a crystalline form which gives the fat mixture the typical structure (e.g. Metin and Hartel, 2005, Sato, 2001). The crystallization process determines for example the mechanical (such as hardness) and visual (e.g. gloss, color, surface appearance) properties of cocoa butter induced by a variation in microstructure (surface as well as internal network structure) (Afoakwa et al., 2008a). Thus, the following aspects are shortly introduced: First, kinetics of cocoa butter crystallization are presented. Secondly, the packing of triglyceride molecules and formation of fat networks are discussed. Thirdly, the solid fat content, which is an important property of cocoa butter, is reviewed. The exact temperature profile of the solid fat content depends on a variety of conditions, such as chemical composition of cocoa butter, history and time effects and cooling conditions. And finally, the influence of minor components on crystallization is shortly presented in this section.

2.2.2.1 Kinetics of cocoa butter crystallization

Cocoa butter is liquid at temperatures above approximately 40 °C (Figure 2.5). At lower temperatures fats are in an ordered structure even in its liquid phase. This also leads to a memory effect according to Hernqvist (1990), Metin and Hartel (2005). So, fats might solidify in the same crystalline structure when re-cooled after melting at a lower temperature. Loisel et al. (1998) found with differential scanning calorimetry (DSC) and X-ray diffraction (XRD) a liquid-crystal organization with crystalline parts and less organized structure resulting in diffuse scattering. van Malssen et al. (1996) explained the memory effect with high stability of StOSt crystallites, being according to them the most important triglycerides for the memory effect, with melting temperatures of more than 40 °C (Sato et al., 1989).

The crystallization process starts with nucleation which is the formation of small crystals in the solution which subsequently grow (Metin and Hartel, 2005). Nuclei form due to accumulation and aggregation of molecules in the liquid phase (so called homogeneous nucleation). Nucleation can be facilitated by external nuclei such as foreign particles or walls (so called heterogeneous nucleation). Its rate depends on temperature profile and saturation but also on the polymorphic crystal form and determines number and size of crystals (Metin and Hartel, 2005).

Once nuclei are present the crystals grow by further aggregation of triglyceride molecules from the liquid phase. Molecules from the liquid phase diffuse and attach to the surface of the crystals to grow. According to the review by Metin and Hartel (2005) the attachment is more likely for similar molecules. Crystal growth ends when there is no more driving force for crystallization which it is at phase equilibrium of the system (Metin and Hartel, 2005). Adam-Berret et al. (2011) first observed melting of small crystals which subsequently recrystallize on larger ones due to Ostwald ripening. The higher the solid fat content, and thus the less liquid fat, the more pronounced was the effect of melting and recrystallization of small crystals.

A possible way to model crystallization kinetics is the Avrami equation (Avrami, 1939, 1940, 1941), which has been applied to cocoa butter crystallization by e.g. Le Reverend et al. (2009), Metin and Hartel (2005). Ziegleder (1990) analyzed crystallization with differential scanning calorimetry (DSC). According to him it is possible to linearize the DSC measurement curves with the Avrami equation:

$$1 - \frac{\alpha}{\alpha_{max}} = e^{-k_A \cdot t^n} \quad (2.1)$$

with the time t , α which is the crystallized part and α_{max} which is the maximum crystallized part. k_A is the rate constant and n a dimensionless constant. The Avrami equation describes the growth of crystalline spherulites in polymers and gives physically relevant parameters such as a rate constant and spatial orientation. The influence of the origin, degree of ripeness, quality condition and temperature on the crystallization time of cocoa butter was investigated by Ziegleder (1990). The crystallization process is dependent on the origin, degree of ripeness and quality condition. Ziegleder (1990) used isothermal conditions in the DSC to get access to the fat crystallization. $\lg(-\ln(1 - \frac{\alpha}{\alpha_{max}}))$ can be plotted against $\lg(t)$ which can be applied to the DSC data to determine the Avrami constants of Equation 2.1. Ziegleder (1990) found out that the crystallization time t showed a large range for cocoa butters with different origins. He explains the variations with the different compositions of fatty acids and triglycerides (Figure 2.3, Level 1). In general, diglyceride (such as present in cocoa with mold infestation) inhibit crystallization⁶. The tested cocoa butter from Malaysia was fastest compared to Nigeria and Bahia (which was slowest). Cocoa butter from southeast Asia is very hard (thus has a high melting temperature) because of many symmetrical and saturated triglycerides. This makes the development of a crystal easier and increases the rate of seed growth. There is a strong temperature dependence on the crystallization time. Whereby, the warmer the temperature, the slower the crystallization because of the exothermic nature of the

⁶Additional information on the influence of addition of other components such as minor components on crystallization are summarized in Section 2.2.2.6 on page 18.

crystallization process at temperature higher than 20 °C. At lower temperatures, seeding rate and growth are slowed down due to increasing viscosity. The seeding rate in the fat increases exponentially with linearly decreasing temperature (at temperatures larger than 20 °C). Furthermore, Ziegleder (1990) observed that there is a very small exothermic peak at the beginning of the isothermal phase probably due to the ingredients but this is not fully understood yet. Ziegleder (1990) describe the crystallization based on the Avrami equation as being a spherical process because the Avrami constant was $n = 4.4$ and a value of $n = 4$ is typical for three dimensional growth⁷. The deviation can be explained with non-homogeneous crystallization (Ziegleder, 1990).

The 3-dimensional network forms due to nucleation of triglycerides and subsequent growth as discussed in the part about structure of crystalline network (Section 2.2.2.3 on page 14). Thereby, particles inside the fat matrix influence the spatial distribution of fat crystal nuclei and crystallization pathway according to Rousseau and Sonwai (2008). They further explain that particles might act as sites for heterogeneous nucleation and possibly enhance growth by better heat and mass transfer⁸.

Further information about solidification, phase transformation behavior and thermodynamic as well as kinetic aspects of fat crystallization can be found for example in Himawan et al. (2006), Metin and Hartel (2005), Sato (1999, 2001).

2.2.2.2 Packing of molecules in crystalline structure

The triglyceride molecules can pack into different geometrical crystal arrangements, denoted as polymorphic forms, which impacts fat properties such as melting profile (Himawan et al., 2006). Thus, from a crystallographic point of view, cocoa butter presents six known polymorphic forms, which are denoted either using Roman numerals (I-VI) or using the crystallographic nomenclature (γ , α , β'_2 , β'_1 , β_2 , β_1) according to Lonchamp and Hartel (2004), Rousseau and Smith (2008), Wille and Lutton (1966). Both nomenclatures are evenly used in the literature and are interchangeable. In this thesis, the Roman numerals will be used to denote the cocoa butter polymorphic forms. van Malssen et al. (1996) instead claimed that only four distinct polymorphic forms exists with the other two being sub phases. They support their hypothesis with similar scattering patterns for the sub-phases and explain the differences in melting temperatures with a strong influence of composition. According to them, the different polymorphic forms are aggregations of individual crystallites with a distinct melting point each, which

⁷Further information on the application of the Avrami equation onto lipid systems can be found in Narine et al. (2006).

⁸The section about the influence of addition of other components such as minor components on crystallization is presented in Section 2.2.2.6 on page 18 and gives more examples on how other components such as minor ones or addition of particles influence the crystallization process.