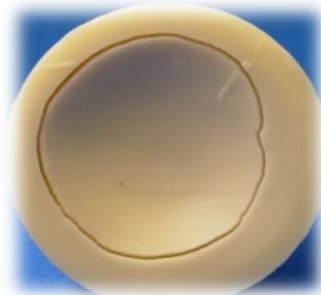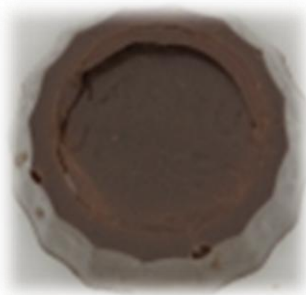# CHALMERS

Modeling of Moisture Migration through Chocolate

Master of Science Thesis [Master Programme: Materials Chemistry and Nanotechnology]

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THESIS FOR THE DEGREE OF MASTER OF SCIENCE

Modeling of Moisture Migration through Chocolate

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Cover:
[Three different pralines showing crack formation due to moisture migration]

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Acknowledgments

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Abstract

Moisture migration in chocolate is an increasing cause for quality deterioration in filled confectionery products. The aim of this study was to develop mathematical models that describe moisture diffusion through dark chocolate. The diffusion coefficient and different diffusion mechanisms were studied, such as Fickian and non-Fickian diffusion. Structural parameters such as swelling kinetics were taken into account.

A total of five models were developed with an increasing complexity and varying boundary conditions. Matlab was used to model where an analytical solution for the problem was available and Comsol Multiphysics was used for numerically solving the problem in lack of an analytical solution. Generally analytical solutions are not available when studying non-linear partial differential equations, which is the case in non-Fickian diffusion. Furthermore, the diffusion coefficient was evaluated using five different equations, three of which were experimental methods and the other two were theoretically derived studying the structure of chocolate. A particular interest was taken in one of the theoretical equations that assumed fast migration through the dispersed phase.

The models were verified by comparing the solutions to experimental data collected during this work as well as data collected by Galler (2011). The results showed that modeling for Fickian diffusion where the transfer only occurred at one surface predicted the data best. Additionally the diffusion coefficient calculated from the equation of interest gave a decent fit for the data collected in this work, while for data collected by Galler (2011) the best fit was given by one of the experimentally derived equations.

The modeling of swelling kinetics gave an indication that this phenomenon might have an impact on moisture migration through chocolate. Including swelling kinetics into the model solved the problem of the solutions not going fast enough towards equilibrium. However, it did not give a very good fit for the data, because the evaluated diffusion coefficient did not take structural changes into account. More needs to be known about the nature of the diffusion coefficient in order to confirm the importance of swelling kinetics.

1. Introduction

Chocolate is a food produced from the cacao tree grown in the tropical regions of America, Asia and Africa. As a food chocolate is unique since it is solid at room temperature and yet it is almost entirely liquid at body temperature. This property is desirable as flavors are released when the chocolate is melting. Chocolate has a sweet taste that is appreciated by the majority of the people, making chocolate one of the most consumed luxury products in Europe with an annual production and turnover of 10.4 million tons and 51 billion euros respectively [1].

The uniqueness comes from the chemical composition and microstructure of the chocolate. Simplified, chocolate consists of sugar and cocoa particles dispersed in a continuous phase of cocoa butter. At 25°C the majority of the cocoa butter is crystalline holding the particles together while at body temperature the cocoa butter is liquid which enables the sugar and cocoa particle to move freely. However the structure is more complicated as cocoa butter can exist in six different crystalline, or polymorphic, forms each displaying different physical properties such as melting point. It is very important for the appearance and the taste of chocolate to obtain one specific fat crystal form (β_V). This is achieved through correct manufacturing and requires multiple processing steps. Hence it is also the cause for substantial production losses in the chocolate confectionery industry.

Apart from the processing, another common problem with chocolate confectioneries is the migration of a component to another domain during storage. In chocolate-coated products the components responsible for quality loss and degradation are usually fat and moisture. Deterioration due to migration of fat or moisture will depend on the filling of the product. Traditional chocolate confectionaries such as pralines usually contain fat based fillings containing highly mobile triacylglycerols which give raise to fat migration through the coating. This can damage the product by different mechanisms of which fat bloom is the most common. Fat bloom is a white/grayish layer of recrystallized fat on the surface of the chocolate and is the major cause of consumer rejection of chocolate products. In addition to the aesthetic damage, fat bloom also changes the sensory quality of the product as flavors are oil soluble and therefore migrate with the fat. Fat blooming is often accompanied with softening of the coating as well as hardening of the filling. However with recent growth in popularity of healthy food, the demand for fruit filled chocolate products have increased. Fruits have higher moisture contents than the surrounding chocolate which promotes moisture migration. Sugar bloom is one of the undesired phenomena caused by moisture migration. Similar to the mechanism of fat bloom, sugar bloom is recrystallized sugar particles that were dissolved by the moisture migrating to the surface. Moisture migration is also responsible for cracking of the coating, drying of the filling as well as mold growth.

The migration of different species can often be explained by molecular diffusion. Diffusion occurs as a result of a concentration difference of a species between two points. The direction of the migration is from high to low concentration and is continued until thermodynamic equilibrium is reached. Although diffusion can mathematically be described by Fick's second law, in many cases involving food deviations from this Fickian behavior is observed. The non-Fickian element of diffusion can be attributed to phenomena such as capillary flow, structural changes, eutectics etc. This is particularly the case for chocolate, where plain Fickian diffusion models have failed to predict fat and moisture migration [2]. Thus, more research is required that includes non-Fickian diffusion in filled chocolate products to fully elucidate the phenomenon.

In this work, the moisture migration through chocolate was described by mathematical modeling based on both Fickian and non-Fickian diffusion behavior. Furthermore, in order to calculate diffusion parameters as well as confirm the model, moisture migration mechanisms were studied both through literature and experimental work.

1.1 Aim

The aim of this thesis was to develop a mathematical model that describes moisture diffusion through chocolate and include both Fickian and non-Fickian mechanisms. Different models were developed by using various techniques to determine the diffusion coefficient. Additionally, structure parameters such as swelling were included in the model.

2. Background

2.1 Chocolate

Dark chocolate can be defined as a continuous dispersion of cocoa solids and crystalline sugar suspended in cocoa butter. Solid cocoa particles as well as cocoa butter are both products of cocoa bean processing. In addition, usually a surfactant called lecithin or polyglycerol polyricinoleate(PGPR) is added to provide better stability by increasing the compatibility of the hydrophilic sugar crystals with the hydrophobic cocoa butter [4]. A schematic representation of the chocolate microstructure is shown in Figure 2.1.
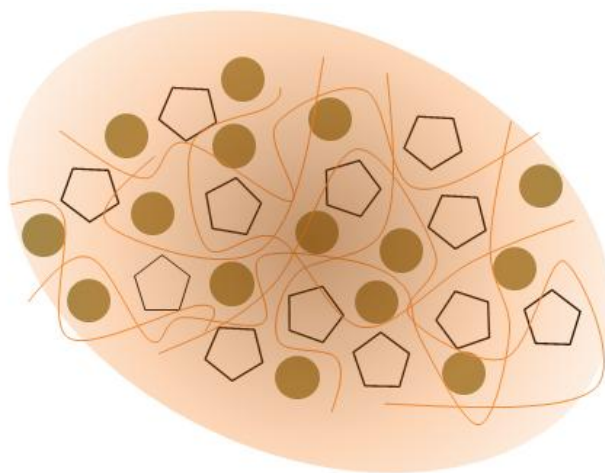
Figure 2.1 Schematic representation of the chocolate microstructure where the brown circles and pentagons represent the cocoa and sugar particles respectively. The orange lines are the solid fat crystals, while everything is surrounded by a continuous cocoa butter phase.

The ratio of the given ingredients is approximately: 50% (w/w) sugar, 29.5% (w/w) cocoa particles, 20% (w/w) cocoa butter and 0.5% (w/w) lecithin. In many countries where chocolate consumption is large this ratio is regulated and is not allowed to vary by much if the product is to be labeled as chocolate [4]. Moreover, other vegetable oils cannot be used instead of cocoa butter.

As for moisture migration the most important ingredient to study is the continuous cocoa butter phase as it has a higher resistance towards water migration compared to the dispersed hydrophilic particles. Hence, the rate of migration will greatly depend on the structure of the fat phase.

2.2 Cocoa Butter

Cocoa butter is the component that determines most of the physical properties of chocolate. It has a very narrow melting range which results in the much desired property that it is solid at room- and liquid at body temperature. In chocolate, cocoa butter at room temperature is a mixture of solid and liquid fat while at body temperature it is completely liquid. The percentage of solid fat content versus temperature was studied by Aguilera et al. (2004) and the significance of solid fat content (SFC) for moisture migration is discussed in later section of this work.

The complexity of cocoa butter lies however in its crystallinity. It can exist in six different crystalline forms denoted with the Greek letter α, β and β´ followed by Roman number I to VI. This polymorphism accounts for different physical properties of chocolate such as melting temperature and profile. Only the β_V polymorph gives the desired properties of the chocolate such as a shiny surface and a distinct snap when broken.

2.2.1 Chemical Composition

Cocoa butter mainly consists of different triacylglycerols and a very small amount of minor lipids. Triacylglycerol (TAG) is a naturally occurring ester consisting of three fatty acids on a glycerol backbone. The properties of the TAG will vary depending on the length and saturation of the three fatty acid substitutes. The dominating fatty acids in cocoa butter are oleic acid (O) which is unsaturated, along with saturated stearic (St) and palmitic (P) acid (Figure 2.2). These three fatty acids account for 95% of the total amount of fatty acids in TAGs in cocoa butter. Furthermore, about 80% of the TAGs are monounsaturated with oleic acid in the middle and with stearic and/or palmitic acid in positions 1 and 3. The majority of them in cocoa butter are POP(1-palmitic, 2-oleic, 3-palmitic), POSt(1-palmitic, 2-oleic, 3-stearic) and StOSt(1-stearic, 2-oleic, 1-stearic) type [4]. POSt triacylglycerol is also shown in figure 2.2
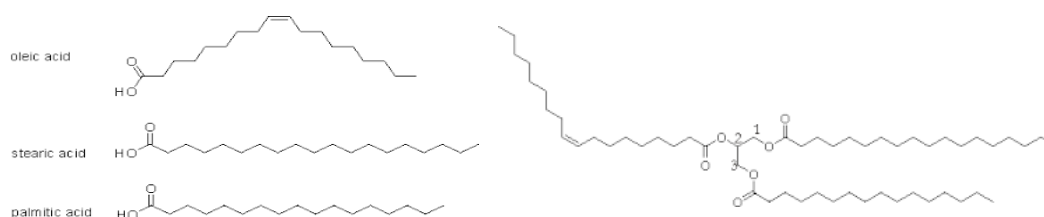
Figure 2.2 a) Structure of the three most occurring fatty acids in cocoa butter. b) Structure of a POSt molecule[4].

The exact composition of the TAGs in cocoa butter is dependent on the origin and refining conditions of the cocoa beans. Malaysian chocolate is typically considered harder than Brazilian due to the presence of more saturated fatty acids. Brazilian chocolate consists of more SOO types of TAGs which decreases the melting point of the chocolate as well as the liquid fat content compared to Malaysian chocolate at same temperature [4].

2.2.2 Polymorphism

As mentioned, cocoa butter can arrange itself in six different crystal packing configurations called polymorphs. There is a difference in packing density of the TAG molecules and hence in thermodynamic stability. Polymorphic transformation occurs forming more stable polymorphs over time due to the difference in the Gibbs free energy. There are two mechanisms from the transformation, either solid-solid or liquid-solid transition of less stable to more stable polymorphs as shown in Figure 2.3.
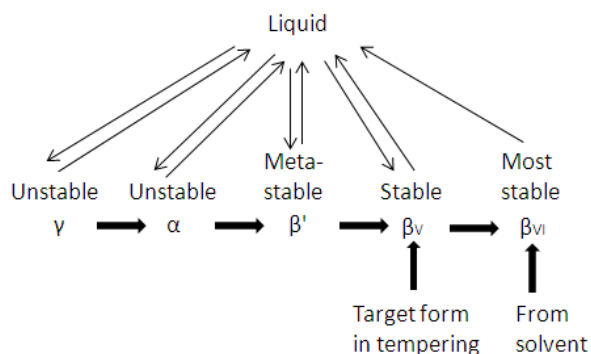
Figure 2.3 Polymorphic transformations in cocoa butter.

The denotations of the polymorphs are derived from a combination of using Roman number from I to VI defined by Willy and Lutton (1966) and the Greek latters γ, α, β', β used in the fat industry. Table 2.1 shows the six different crystal packing systems in order of stability. The melting point is defined rather as a melting range due to the mixture of several different TAGs.

Table 2.1 Melting points and chain packing for cocoa butter polymorphs [5].

Polymorph	Melting point (°C)	Packing
γ	16-18	Double
α	21-22	Double
III	25-26	Double
β'$_{IV}$	27-29	Double
β$_V$	34-35	Triple
β$_{VI}$	36	Triple

There are mainly two ways in which TAGs can arrange themselves in a closed packed system called double and triple chain packing. The double packing system shown on top in figure 2.4 creates a unit of two TAGs with the length on only two fatty acids, having the central fatty acids in the TAGs adjacent to each other. In the triple chain packing system the length of the unit corresponds to three fatty acids where the fatty acid in the middle position of one TAG is adjacent to a fatty acid in one of the outer positions in the next TAG.
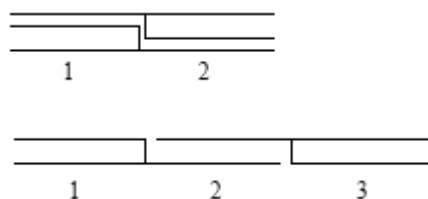
Figure 2.4 Chain packing of TAG molecules in crystal structures showing double packing on the top and triple packing in the bottom [5].

The fact that the majority of the TAGs in chocolate are of SOS (saturate fatty acid – oleic acid – saturate fatty acid) type will alter the stability of the packing systems. The oleic acid being unsaturated will have a bend (figure 2.5) and thus change the nature of the packing. In figure 2.4 the packing density is indeed higher in double chain packing. However the in the case of cocoa butter, highest stability is obtained for β$_{VI}$ followed by β$_V$, both having triple packed chains. Figure 2.5 shows how the chains are stacked due the bend in the oleic acid chain and it is apparent that triple chain packing has the highest packing density of the two and therefore a higher stability.
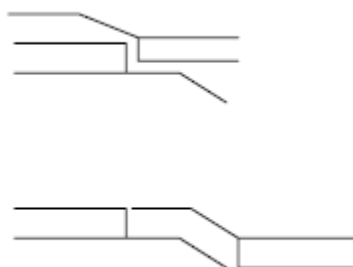
Figure 2.5 Chain packing for cocoa butter. Top: Double chain packing resulting in an unstable structure. Bottom: Triple chain packing resulting in a stable structure [5].

2.3 Crystallization

Cocoa butter crystallization is the phase transition from liquid to solid and involves two steps: nucleation and crystal growth. The nucleation process is governed by thermodynamics and an activation energy barrier has to be overcome in order to form stable nuclei. Higher stability polymorphs require higher activation energy for their formation, which is shown I figure 2.6. This indicates that undesired polymorphs will form readily under given conditions if no pre-crystallization treatment is applied. The subsequent crystal growth means incorporation of liquid TAGs to a crystal lattice which grows from the surface of the nuclei.
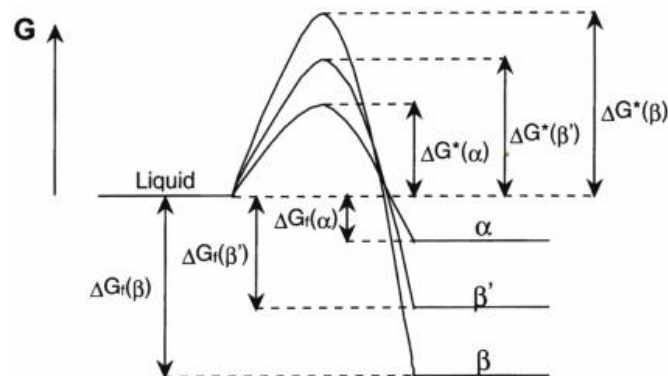
Figure 2.6 Schematic representation of the free energy of fusion and activation energy for different polymorphic ranges of TAGs at given conditions (P,T – where T is below T_{fusion})[6].

There are two types of nucleation: primary and secondary. Primary nucleation occurs in a pure supercooled or supersaturated liquid. Introducing foreign surfaces will reduce the activation energy for primary nuclei formation. The secondary nucleation is subsequently induced by an unknown mechanism [7]. The β crystals will grow on the nucleation site during the solidification of chocolate.

2.4 Pre-crystallization

The goal of pre-crystallization processing is to introduce a sufficient number of nucleation sites for stable fat crystals to grow on. Hence the activation energy for the formation of β-polymorphs has to be lowered. Primary nucleation sites can be introduced to chocolate in two main methods: by externally adding solid cocoa butter crystals as seeds or by a controlled temperature profile solidification in combination with shearing. The pre-crystallization process is often referred to as tempering in the industry and a pre-crystallized chocolate with the desired crystal structure is called well-tempered.

2.4.1 Tempering

The first of the two methods of tempering is called β_{VI}-seeding while the second is traditional tempering using a controlled temperature profile. Both techniques are used in the chocolate industry and are designed to produce well-tempered chocolate i.e. chocolate crystallized in β_V polymorph. In the traditional tempering the chocolate is subjected to three main crystallization stages [8]. The first one is removal of the sensible heat after the chocolate has been melted. This is followed by nucleation and crystal growth through removal of latent heat from the process. Lastly the chocolate is stabilized by melting of unstable polymorphs. In the industry the tempering is done in a three-stage tempering unit shown in figure 2.7. The seeding method is described in detail in 2.4.1.1.
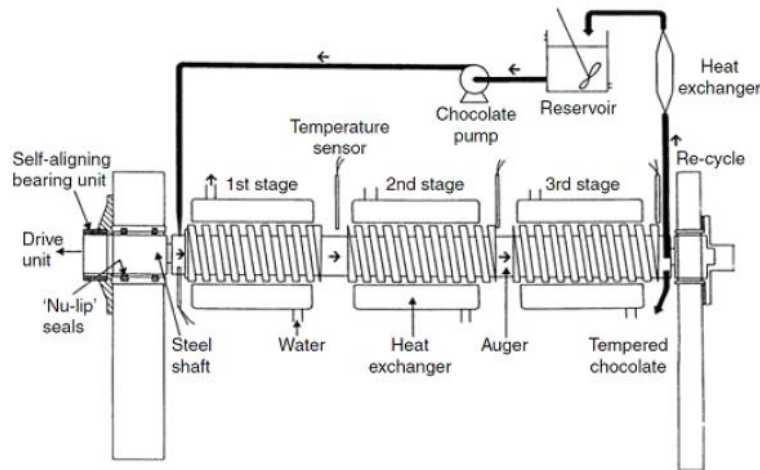
Figure 2.7 Three-stage tempering unit used in the chocolate industry [5].

There are many advantages of having a well-tempered chocolate apart from the shiny surface and snap. They include: easier demolding, increased shelf life, better heat resistance and shortest cooling time and superior heat transfer properties making it the most energy efficient polymorph to work with [9].

2.4.1.1 β_{VI}-Seeding

This method of tempering was originally designed by Zeng during his doctoral thesis at ETH Zurich (2000). The method was based on addition of solid cocoa butter in the β_{VI} polymorph that serves as nucleation sites for the crystallization of β_V chocolate. The β_{VI} polymorph is added to the melted chocolate mass at a temperature of 33-34°C which is just below the melting point for β_{VI} crystals and matches the melting point of the β_V polymorph. This guarantees that lower melting polymorphs will not be formed while keeping the temperature constant. Furthermore, β_{VI} crystals will itself not form because they do not crystalize from liquid chocolate as seen in figure 2.3. This results in a desired β_V polymorph crystallized chocolate.

The advantage of β_{VI} seeding over traditional tempering is that the method is simple and far more energy efficient in comparison to chocolate being continuously ran in a temperature profile program. It is however important that the amount of seeds used actually produces a sufficient number of nucleation sites and that they are homogenously distributed over the chocolate in order for β_V crystals to form during the solidification process.

The structure of β_{VI}-seeded chocolate was studied by Svanberg et al. (2011) using confocal laser scanning microscopy (CLSM). The study showed that seeded chocolate had a homogenous distribution of fast growing crystals compared to the heterogeneous non-seeded crystallization. Figure 2.8 shows the result of the study comparing seeded and non-seeded chocolate.

Figure 2.8 "CLSM of seeded and non-seeded cocoa butter. The phases can be distinguished by Fluorescent labeled non-polar fatty acid analogue BODIPY FL C16 which show highest affinity to the liquid fat fraction. Therefore solid particles appear black, liquid fat bright yellow and fat crystals in darker orange." [10]

2.4.2   Temper Degree

Using the right conditions during the pre-crystallization process will result in a well-tempered chocolate. However a chocolate can also be under- or over-tempered if the pre-crystallization is not optimal. Moreover if there is complete lack of pre-crystallization the resulting chocolate will be untempered and display significant difference in physical properties.

The degree of tempering of the chocolate can be measured using a temper meter. Before solidification a small portion of the chocolate is put in a sealed cooler with a thermometer measuring the temperature in the center of the chocolate. The chocolate is cooled down to 8-10°C and temperature variation inside the sample is recorded over time. This generates a so called tempering curve, i.e. temperature versus cooling time, which is then used to determine the temper degree. The shape of the curve will be unique to different degree of temper due to the different magnitude of the latent heat being released during the cocoa butter crystallization. The latent heat will reverse the cooling/temperature drop resulting in temper curves similar to what is shown in figure 2.9. The cooling rate increases again once the bulk chocolate has solidified.
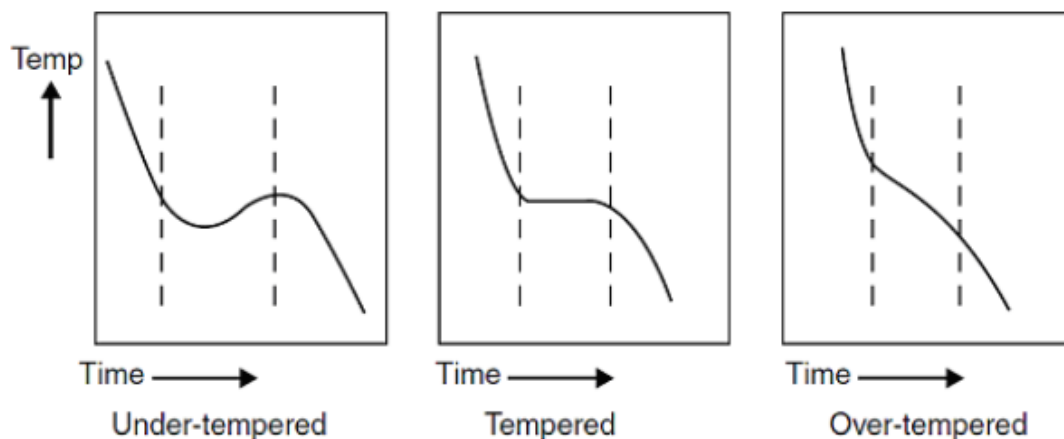
Figure 2.9 Temper curves for the three common cases of pre-crystallized chocolate [5].

The temper degree can be roughly estimated from the shape of the temper curves. As shown well-tempered chocolate shows a plateau in the temper curve as the latent heat of crystallization is equal to the rate of cooling. In the case of under-tempered chocolate not enough stable seeds had been added. Consequently the crystallization starts at lower temperature and is rather rapidly releasing a high amount of latent heat. On the other hand, over-tempered chocolate contains too much seed which makes that crystallization start at a higher temperature. Also this crystallization is slower and less latent heat is released. Under-tempered chocolate will contain unstable polymorphs which also form under the process of solidification. This results in a chocolate with underwhelming physical properties. Over-tempered chocolate will have a high viscosity making the production less energy efficient and causing problems during the molding. The temper degree is given in units of temper index (TI) and a TI value of 5 is an indication that the chocolate is well-tempered. Any value above 5 shows an over-tempered while below 5 denotes under-tempered chocolate.

2.5 Diffusion in Food

2.5.1 Theoretical Aspects of Diffusion

Diffusion is a transport process in which matter is moved from one part of a system to another as a result of random molecular motion [11]. The driving force of diffusion is a concentration gradient of a species between two points in a system. Molecular or ordinary diffusion should not be confused with pressure, thermal or forced diffusion where the process is not governed by concentration differences, but by other means [12]. Although the motion of single molecules can be described as completely random, the overall transfer will be directed from points of higher concentration towards lower concentration. This phenomenon will continue until thermodynamic equilibrium is reached.

In many cases it is interesting to study diffusion of matter in different physical states, for example the diffusion of gas through solids. This can certainly be the case when it comes to diffusion through food, and especially for moisture migration through chocolate. In that case the migrating molecules (the gas) first have to dissolve at the interface before they diffuse though the solid material. The solubility of the penetrant then becomes an important factor in the diffusion process. Solubility can be described as the thermodynamic compatibility between the gas and the solid and is often defined as the maximum volume of a species dissolved in a unit volume of solid material at equilibrium [13]. The interaction of the involved species at the phase boundary is usually given by a sorption/desorption isotherm and will be discussed further in section 2.5.2.1.

Other important factors arise when the gas is already dissolved and starts to diffuse. These factors include chemical composition and structure of the solid material. Foods often have complicated

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chemical compositions and structure which makes the complete understanding of the diffusion phenomenon difficult. Additionally foods can undergo structural changes as a direct result of the moisture migration. These structural changes will in turn affect the moisture migration.

2.5.1.1 Mathematical Analysis

In 1855 the German biophysicist Adolf Fick realized that diffusion of matter is analogous to diffusion of heat. Heat conduction, also being caused by random molecular motion, already had a mathematical formulation and solution purposed by Fourier in 1822 [11]. Fick used these findings by Fourier to create a mathematical description of the diffusion phenomenon.

 When the concentration profile, $\frac{\partial c}{\partial x}$, is constant with respect to time, the diffusion process is said to be in steady-state. For the simplest case of one-dimensional, single component diffusion in steady-state over a material of thickness x, the process can be described by Fick's first law [13]:

$$J = -D \frac{\partial c}{\partial x} \qquad (1)$$

where J is the molar flux or the rate of flow per unit area of the diffusing molecules often given in mol cm^{-2} s^{-1} and D is the diffusion coefficient in cm^2 s^{-1}. The diffusion coefficient is a constant that relates to the lack of resistance to mass transfer in any given set of materials i.e. higher diffusion coefficients indicate that the resistance to mass transfer is lower. However when studying the moisture migration through chocolate it is more interesting to look at non-steady state diffusion, where the concentration profile is changing over time. In that case the diffusion equation is given by Fick's second law:

$$\frac{\partial J}{\partial x} = -\frac{\partial c}{\partial t} \qquad (2)$$

The flux term can be eliminated by substituting equation (1) into (2), thus resulting with the most used formulation of Fick's second law given by:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \qquad (3)$$

This equation is often simplified to equation (4) by assuming that the diffusion coefficient is concentration independent.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (4)$$

Simplification and assumption are necessary when solving and modeling the non-steady state diffusion equation. Have in mind though, that the diffusion coefficient generally is dependent on concentration. The simplifications are usually made to allow for easier analytical solutions of the partial differential equations as well as decreasing the computation time of models.

2.5.1.2 Diffusion Coefficient

In order to solve the non-steady state diffusion equation, the diffusion coefficient needs to be known. The diffusion coefficient is the reciprocal of the resistance to the mass transfer and is unique to any set of two materials. This kind of coefficient is called the mutual diffusion coefficient, also known as the efficient diffusion coefficient (D_{eff}). In contrast to D_{eff}, the self-diffusion coefficient measures the rate of diffusion of a component into another component of uniform chemical composition [13]. Only the effective diffusion coefficient is important for studying diffusion of moisture through chocolate.

For liquids the coefficient is generally predicted using Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta r} \qquad (5)$$

where k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the medium through which diffusion is occurring and r is the radius of the penetrant molecules. Although this equation is often used as a reference when calculating the diffusion coefficient it is only accurate in 20% of the cases [13].

However, there are many other known estimates of the diffusion coefficient that are more attuned to the experimental setup used for this work. Thus, methods for calculating the diffusion coefficient in moisture uptake experiments are of most importance. A technique for estimating D_{eff} in such an experiment was developed by Shen and Springer (1981). They purposed a mathematical expression of D_{eff}:

$$D_{eff} = \pi \left(\frac{l}{4M_m}\right)^2 \left(\frac{M_2 - M_1}{\overline{t_2} - \overline{t_1}}\right)^2 \qquad (6)$$

where M_2 and M_1 are moisture contents at times t_2 and t_1 respectively and M_m is moisture content at t_∞ and represents the moisture content when steady state is reached [14]. L is the thickness of the sample which also corresponds to the length of the diffusion. The diffusion coefficient is consequently calculated from the gradient of the M(t) versus $\overline{t}$ curve.

In their study about chocolate migration from 1988, Biquet and Labuza also calculated the diffusion coefficient from the slope of lnΓ versus time as shown below:

$$\ln \frac{M - M_m}{M_i - M_m} = \ln \Gamma = \frac{-\pi^2 D_{eff}}{l^2} \cdot t + \ln \frac{8}{\pi^2} \qquad (7)$$

where M_i is the initial moisture concentration and the other terms being denoted the same as in equation (6) [15]. In this formulation Biquet and Labuza (1988) assumed that the chocolates where infinite slabs as the diameter was significantly larger (almost 100 times) than the thickness of the samples. From there it can be assumed that there is no diffusion in the radial direction as well as moisture uptake taking place at only one side. According to J. Crank (1975) for this kind of system the solution to Fick's second law converges rapidly for large values of time which yields equation (7).

A similar approach was made by Vieth (1991) when he described the effective diffusion coefficient in moisture uptake experiment by the following relation:

$$D_{eff} = \frac{l^2}{6t_{lag}} \qquad (8)$$

where t_{lag} can be described as the time it takes to reach the steady state and can be calculated by plotting the weight loss/gain versus time after steady state is reached.

In addition to these calculation techniques, the diffusion coefficient can be experimentally determined by few methods, including diaphragm cell method, the rotating disk, NMR (nuclear magnetic resonance) spin echo, interferometer methods (Gouy interferometer) [13][17]. The data obtained from NMR experiments should be handled with care as the coefficient measured is the self-diffusion coefficient and not the effective one [2]. Works of Schmidt and Lai, Schmidt et al, as well as McCarthy et al show that the MRI (magnetic resonance imaging) is the most promising technique for studying moisture diffusion in foods [2].

2.5.1.3 Structural Effects

Moreover, diffusion coefficients are highly dependable on the structure of the material through which diffusion is occurring. The structure is even more important when dealing with impermeable solids where diffusion can only take place within fluid-filled pores. In that case the diffusivity is given by:

$$D_{eff} = D\frac{\varepsilon}{\tau} \qquad\qquad (9)$$

where D is the diffusion coefficient within the pores, ε is the porosity (void fraction) and τ is the tortuosity of the pores i.e. deviation from linear diffusion path. The porosity generally varies between 0.3 and 0.8 while tortuosity between 2 and 6, thus giving a D_{eff} 6 to 15 times larger than D [17].

This equation can be modified for different geometries and pore sizes, however chocolate and many other foods have other important structural properties that affect the diffusion. The continuous cocoa butter phase is hydrophobic and can be considered impermeable for moisture in comparison to the sugar and cocoa particles. Sugar is highly hydrophilic and also cocoa particles contain some hydrophilic components in their porous structure. Thus, it will allow the moisture to diffuse through the particles as well as along the surface of the sugar. Aguilera and Stanley studied this effect where simple spherical particles were assumed to be dispersed in a continuous phase making a two-phase composite material. They found an expression for determining the effective diffusion coefficient:

$$\frac{D_{eff}-D_c}{D_{eff}-2D_c} = \phi \ \frac{D_d-D_c}{D_d+2D_c} \qquad\qquad (10)$$

in which D_c and D_d are the diffusion coefficients of the continuous phase and the particles respectively and ϕ is the volume fraction of particles in the system. This equation was originally derived from using equation (11) provided by Cussler (1997) also assuming spherical geometry in a two-phase composite:

$$\frac{D\prime}{D_c} = \frac{\frac{2}{D_d}+\frac{1}{D_c}-2\phi\ \frac{1}{D_d}-\frac{1}{D_c}}{\frac{1}{D_d}+1+D_c+\phi\ \frac{1}{D_d}-\frac{1}{D_c}} \qquad\qquad (11)$$

where D' is the effective diffusion coefficient for such a system. This equation can be simplified for two extreme cases, namely when the diffusion through the dispersed phase is very slow in comparison to the diffusion through the continuous phase i.e. D_d 0. Hence equation (11) reduces to:

$$\frac{D\prime}{D_c} = \frac{2(1-\phi)}{2+\phi} \qquad\qquad (12)$$

The other extreme is when the diffusion through the disperse phase is very fast i.e. D_d ∞ and equation (11) becomes:

$$\frac{D\prime}{D_c} = \frac{1+2\phi}{1-\phi} \qquad\qquad (13)$$

As for chocolate it is expected that equation (13) will describe the effective diffusion coefficient more accurately, as the diffusion of moisture is faster through the hydrophilic sugar and cocoa particles in comparison to the hydrophobic cocoa butter matrix. Predicting the diffusion coefficient is essential for modeling and understanding of the mechanisms of moisture migration through foods.

2.5.1.4 Diffusion Mechanism

When describing diffusion mechanisms in foods we often have to reference polymer behavior in order to obtain a better understanding of the process. Terms like *swelling* and *relaxation* are important to mention when studying diffusion. Swelling is the increase in volume caused by the adsorption of the diffusing molecules within the polymer while relaxation is a measure of stress relieve in a polymer under constant strain and is a direct result of the viscoelasticity of polymers. The diffusion mechanism is decided by the microstructure and thermodynamics of the involved species. However relaxation is a process that will change the microstructure, hence affect the diffusion itself. According to Alfrey, Gurnee and Lloyd (1966) diffusion can be classified in three different categories with respect to the rates of diffusion and relaxation.

The first case, naturally called Case I or Fickian diffusion occurs when the rate of diffusion is much slower than that of relaxation. Sorption equilibrium is reached fast leading to time-independent boundary conditions. From this follows also that swelling of particles is not affecting the diffusion. Case II (SuperCase II), is the other extreme in which diffusion is very rapid compared with the relaxation processes. Sorption is in this case affected by swelling kinetics. The third and last case is called Non-Fickian or anomalous diffusion which occurs when the diffusion and relaxation rates are in the same order of magnitude. Generally, glassy polymers tend to exhibit Non-Fickian behavior while rubbery polymers show Fickian behavior.

Case I and II are simple mechanisms in a way that both are governed by a single parameter. In Case I it is the diffusion parameter that describes the rate of diffusion while in Case II it is the sorption rates. Non-Fickian diffusion lies in between Case I and II and generally needs two or more parameters to describe the diffusion and relaxation affecting it.

Non-Fickian diffusion generally occurs when the mass transfer is accompanied by a simultaneous phase change from an amorphous to a crystalline state (also from solid to liquid state) or/and by slow relaxation of polymer chains compared with the migration of the diffusing species. Moreover there are different types of anomalies requiring different models in order to explain the diffusion. A summary of the characteristics of the different anomalies are shown in Figure 2.10.
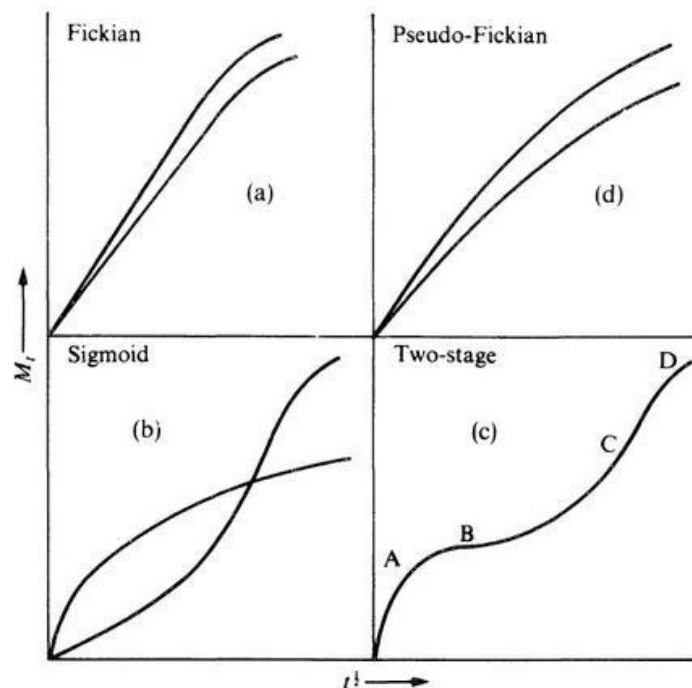

Figure 2.10 Diffusion behaviors of different anomalies [18].

The figure is representing the sorption behavior of different polymers, where one of the curves is the adsorption and the other is the desorption curve. Non-Fickian behavior is shown in cases (b) and (c), where (b) describes a sigmoidal shaped curve and (c) describes two-stage sorption. Characteristically food has shown sigmoidal sorption behavior in many cases [11]. In moisture migration through chocolate one might expect physical changes such as swelling and/or phase transition within the crystalline state of both sugar and cocoa butter resulting in non-Fickian diffusion [2]. This was confirmed by Biquet and Labuza (1988) who constructed a sigmoidal sorption isotherm. Nevertheless, both Fickian and non-Fickian diffusion behavior of chocolate will be investigated in this project.

2.5.2 Moisture Migration through Chocolate

As discussed in chapter 2.5.1, diffusion if driven by concentration differences across two points in a system. When studying moisture migration the diffusion is not necessarily directed from higher to lower water content but rather higher to lower water activity (a_w) [19]. The water activity gradient is the driving force for moisture migration and is related to chemical potential by equation (14) which is in turn related to concentration [20].

$$\mu_i = \left. \frac{\partial G_i}{\partial n_i} \right|_{T,P,n_j} = \mu_i^0 \left(T, P \right) + RT \ln a_i \qquad (14)$$

where μ_i and a_i are the chemical potential and activity of component i , G_i is the Gibbs free energy, T is the temperature, P is the pressure, μ_i^0 is the potential for pure vapor, n is the number of molecules and R is the universal gas constant in J mol^{-1}K^{-1}. In this specific case the migrating component is water vapor which is denoted with w as a subscript instead of i.

The sorption of water within the dispersed phase in chocolate will have a significant impact on the diffusion. The rate at which sorption equilibrium is reached will dictate the type of diffusion mechanism involved. It is reasonable to assume that there is an equilibrium between mobile water and adsorbed water at the sugar and cocoa particle interface at every location in the chocolate [21]. Thus, the concentration profile of water will thus not be homogenous, but will rather have two distinct concentrations, one of the mobile water and the other of the adsorbed water. If these concentrations are denoted c and c_1 for the mobile and adsorbed molecules respectively, Fick's second law can be expressed as:

$$\frac{\partial c\prime}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (15)$$

where c′ = c + c_1. In order so solve this equation analytically more information is needed than for the simple case in equation (4). This can be gathered by constructing a mathematical equilibrium relationship between c and c_1. In case of chocolate the equilibrium equation is given by a moisture sorption isotherm.

2.5.2.1 Moisture Sorption Isotherm

A moisture sorption isotherm is the relationship between water content, given as mass of water per unit mass of dry chocolate and the water activity at constant temperature [22]. The water content versus activity data is obtained by sorption experiments and the moisture sorption isotherm is modeled based on that. It can be modeled using several equations from which the most commonly used is the BET equation, named after Braunaur, Emmet and Taylor. It is given by:

$$m = \frac{m_0 C a_w}{(1-a_w)(1-a_w+Ca_w)} \qquad (16)$$

where m is the moisture content, a_w is the water activity, m_0 is the BET monolayer moisture value and C is the BET constant. The downside of the BET equations is that it only provides reasonable values of the moisture content for water activities between 0 and 0.5 [23]. The water activity of moist fillings in chocolate confectionary products can easily exceed 0.5, thus making the BET equation insufficient. Another possible way to model the moisture sorption isotherm is to use the GAB equation (Guggenheim, Anderson and DeBoer) given below:

$$m = \frac{m_0 C a_w}{(1-K a_w)(1-K a_w+CK a_w)} \qquad (17)$$

where K is the GAB multilayer constant in addition to the terms in the BET equation. When K=1 the GAB equation is reduced to the BET equation. The extra parameter of the GAB equation makes the model a better fit overall, covering the water activity range from 0 to 0.8 [24].

A couple of studies have been made on sorption properties of chocolate. Just to name one, Ogunamoyela and Birch (1984) studied sorption behavior of chocolate containing different sweeteners. They found that the equilibrium for adsorption and desorption was reached in 14 days and that L-sorbose and fructose adsorbed significantly more moisture than other sweeteners [25]. The most important study about dark chocolate was conducted by Biquet and Labuza in 1988. It was found in the study that the equilibrium time for the system ranges between 40 and 60 days, which was significantly higher than that reported by Ogunamoyela and Birch (1984). Furthermore they used the GAB equation to model the moisture sorption isotherm by determining the fitting parameters of the equation. The GAB parameters determined by Biquet and Labuza (1988) are given in table 2.2 and the resulting moisture sorption isotherm is given in figure 2.11.

Table 2.2 Fitting parameters for the GAB equation for dark chocolate determined by Biquet and Labuza (1988).

Mode of sorption	Initial a_w	a_w range of test	m_0 (gH_2O/100g dry material)	K	C
Adsorption	0.01	0.01-0.808	0.545	1.024	103.857
Desorption	0.81	0.754-0.112	1.067	0.785	34.262
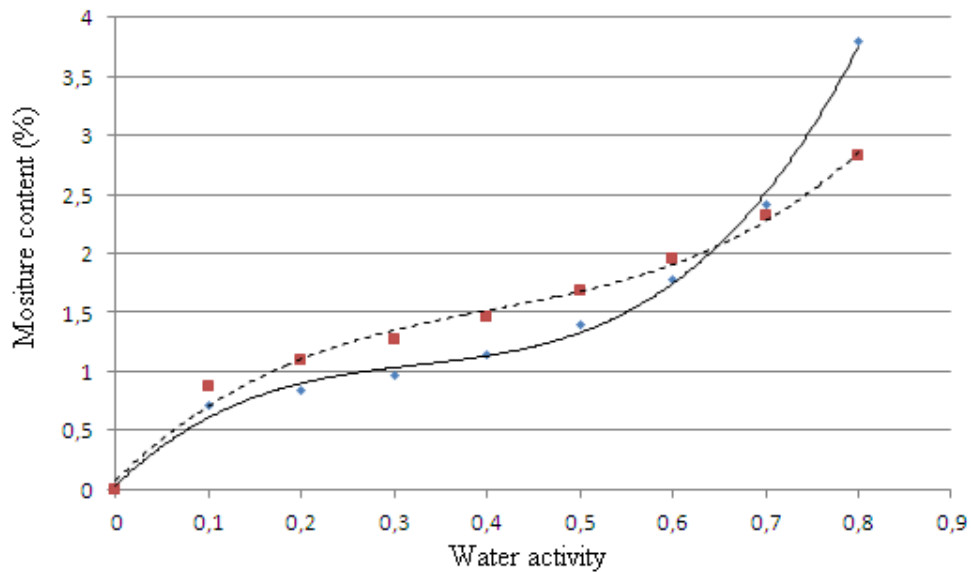
Figure 2.11 Reproduction of the moisture sorption isotherm for dark chocolate at 20°C adapted from Biquet and Labuza (1988) using fitting parameter from table 2.2.

The moisture sorption isotherm given above was used as a reference when studying the moisture sorption of dark chocolate for water activity values under 0.8. For higher water activity the moisture sorption increases rapidly and obtaining values for the moisture content is not easy. However, in their study Roca et.al (2008), managed to construct a moisture sorption isotherm for water activity values ranging from 0 to 0.98, shown in figure 2.12
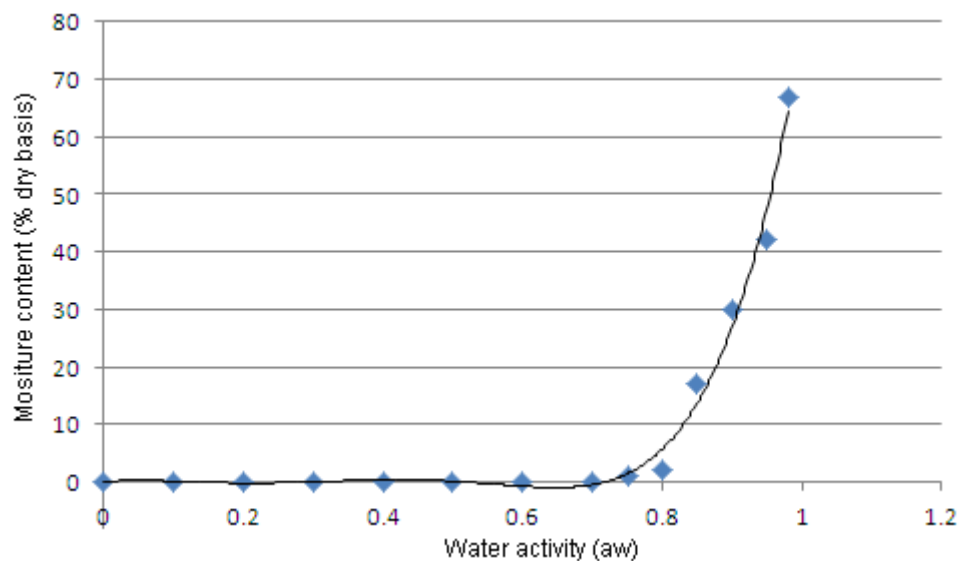
Figure 2.12 Moisture sorption isotherm for dark chocolate adapted from Roca et.al. (2008) [37].

The moisture sorption isotherm constructed by Roca et.al. could be used in addition to the one in figure 2.11 for water activities over 0.8.

2.5.2.2 Analytical Measuring Techniques

For measuring the moisture migration, the chocolate samples are brought in contact with humid air i.e. contains the migrating component. The samples are stored at constant temperature and relative humidity until equilibrium in moisture content in reached. This is usually done by a so called

standardized cup method, where chocolate is sealed in and one surface is put in contact with the migrating species. The moisture content is then generally determined by a Karl-Fischer titration.

In addition it is important to mention that moisture migration in chocolate is often associated with Water Vapor Transmission Rate (WVTR), a parameter commonly used for describing water permeability properties of polymers. WVTR represents the average amount of adsorbed water over one day and one m^2. It can be determined from the data gathered in a standard cup experiment by combining Fick's and Henry's law for gas diffusion in a semi-permeable medium. It is a measure of how fast moisture is absorbed into a system thus being a measure of the diffusion rate.

2.5.2.3 Factors Affecting Moisture Migration

There are many factors affecting moisture migration in chocolate such as water activity gradient, temperature, composition of the chocolate, thickness of the sample, pre-crystallization process and subsequent solid fat content (SFC) and crystal structure.

Solid fat content and crystal structure. There are only few studies that tried to link the polymorph structure of the chocolate with moisture permeability properties. It is expected that closed packed crystal systems will have the lower permeability rate i.e. the α polymorph will have higher permeability than β which in turn will have higher permeability than β' polymorph. However in their study Kester and Fennema (1989) found that the α polymorph had lowest moisture permeability of all polymorph forms [26]. This can possibly be attributed to the increased porosity for higher melting polymorphs (β and β') thereby promoting water migration through capillary rise. Studies done at SIK, by Svanberg (2011), Nestius-Svenson (2011) and Galler (2011) showed how moisture migration depends on the pre-crystallization process. Untempered chocolate, with significantly reduced SFC compared to pre-crystallized samples, showed the least resistance for moisture migration [27][28][29]. Furthermore, samples with different temper degrees were tested for moisture migration properties and the results showed similar permeability to those reported by Kester and Fennema (1989) with under-tempered chocolate being the best moisture barrier at 20°C.

The migration through liquid fat is orders of magnitude faster compared to that through solid fat, as shown in figure 2.13 a). Hence the decrease in solid fat content will significantly increase the diffusion rate. Effects of the solid fat content on the moisture migration were studied by Ghosh et al. (2005) and the results of that study show that the WVTR increases rapidly when the solid fat content decreases to 60% and lower. Figure 2.13 a) shows the WVTR as a function of SFC as studied by Ghosh et al. (2005)

Temperature. As diffusion is caused by random motion of migrating molecules it is expected that the diffusion rate or WVTR is dependent on temperature with a relationship equivalent to Arrhenius equation. This is however not observed in the study made by Labuza and Biquet (1988). In their study the WVTR did not change when the temperature was increased from 10 to 20°C but later increased significantly when the temperature was increased to 26°C. The increase from 20 to 26°C must therefore be accompanied by a structural change mainly caused by reduction of SFC. According to figure 2.13 b) the SFC decreases for about 10% when heating from 20 to 26°C, but less than 5% when going from 10 to 20°C. The significance of the temperature dependence is more due to the decrease in SFC than the pure increase in diffusivity of the migrating species through faster random motion.
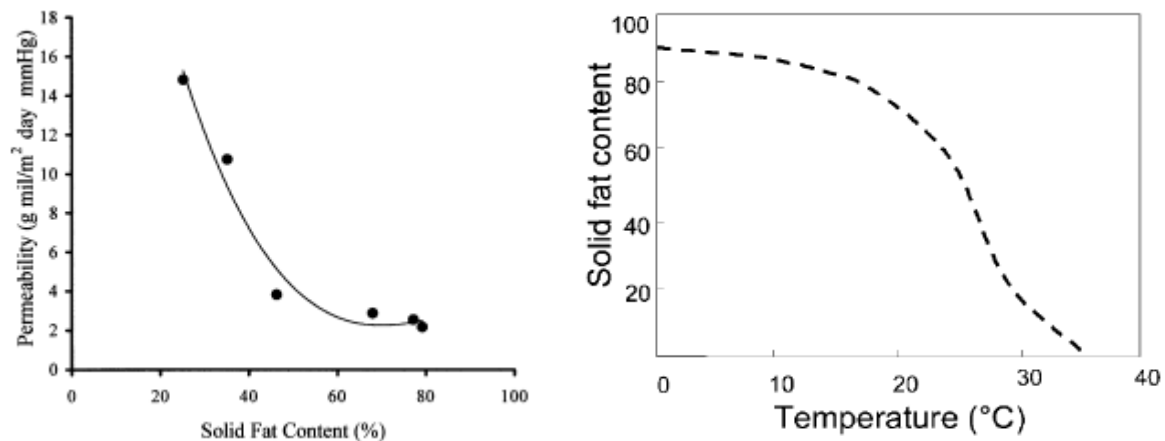
Figure 2.13 a) Water vapor permeability as a function of solid fat content [30]. b) Solid fat content as a function of temperature [3].

2.5.2.4 Mechanisms of Moisture Migration

The mechanism of moisture migration in chocolate is yet to be fully understood. Certainly it is governed by the microstructure of the chocolate as well as thermodynamic factors. The moisture migration will greatly depend on the crystal structure of the continuous fat phase as well as liquid fat content as migration is faster through liquid fat. Poor permeability of the fat compared to the solid particles will make the diffusion through the continuous phase a slow rate determining step. The moisture has to diffuse through the continuous phase in order to come in contact with the dispersed particles. This also means that higher content of particles will increase the diffusion rate as the distance between particles is decreased as a result of higher packing density. When the moisture gets in contact with cocoa particles it will get absorbed and the amount is given by the moisture sorption isotherm. Sugar with its high crystallinity will not absorb the moisture but will provide an addition diffusion path along its surface. The diffusion that takes place through and at the surface of the particles is significantly faster than that through the lipid phase. Particles absorbing moisture might undergo swelling which will change the structure of chocolate and non-Fickian diffusion mechanism will dominate. Cocoa particles rather than sugar are responsible for the swelling phenomenon. This is due to the porosity and composition of cocoa particles consisting of starch granules and hygroscopic fibers both of which have the tendency to swell during moisture absorption [30]. Swelling may also cause the chocolate to crack creating canals through which the moisture can quickly diffuse. Additionally adsorption of moisture on the water/sugar interface may cause dissolution of sugar. As a consequence, sugar bloom may form when the moisture reaches the surface and recrystallization occurs. When sorption equilibrium within the particles is reached, the moisture migration continues towards the point of lower water activity in the system. A Schematic representation of the migration mechanism is shown in figure 2.14.
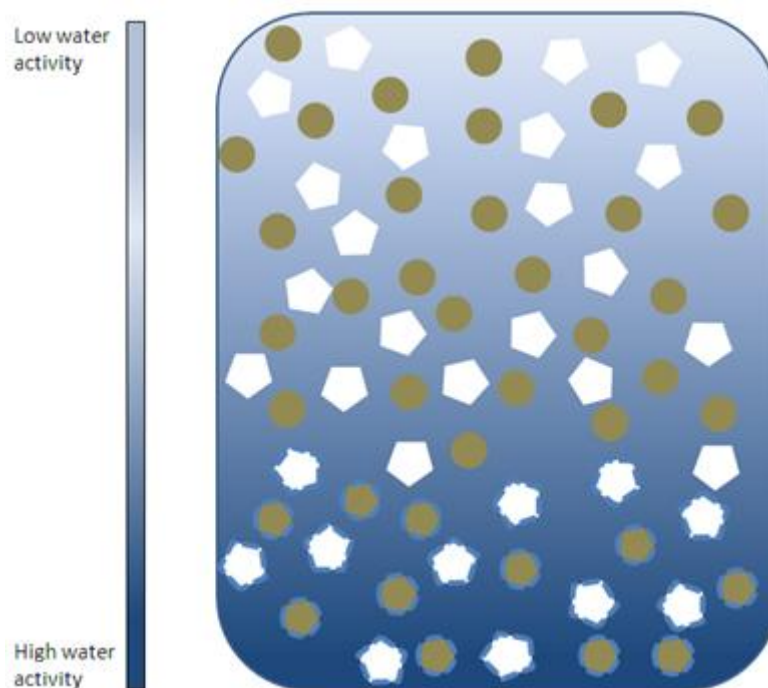
Figure 2.14 Schematic representation of the moisture migration through chocolate where the brown circles represent the cocoa particles and the white pentagons the sugar. The thick dotted lines indicate swelling of cocoa particles as well as moisture adsorbed on the sugar surface. The direction of the migration is from higher to lower water activity.

Another crucial aspect of the migration mechanism is the nature of the diffusion coefficient. It was mentioned earlier in chapter 2.5.1.2 that the effective diffusion coefficient can be determined experimentally as well as estimated mathematically. Most notably Biquet and Labuza (1988) calculated a diffusion coefficient for dark chocolate according to equation (7) and the result are given in table 2.3.

Table 2.3 Effective diffusion coefficient of moisture though dark chocolate at 20°C [15].

Sorption mode	Initial a_w	Relative Humidity (%)	Thickness (mm)	$D_{eff} \cdot 10^{13}$ (m^{2}s^{-1})
Adsorption	0.01	75.4	0.607 (0.05)	1.08 (0.22)
		64.8	0.594 (0.04)	0.82 (0.31)
Desorption	0.81	54.4	0.607 (0.04)	0.87 (0.09)
		33.0	0.599 (0.04)	1.33 (0.13)

The diffusion coefficient is not strongly dependent on the relative humidity of the atmosphere. However it is generally dependent on the moisture content or water activity. In their work Biquet and Labuza (1988) measured the moisture uptake by the cup method with a desiccant inside for different relative humidity of the atmosphere and their result is shown in figure 2.15.
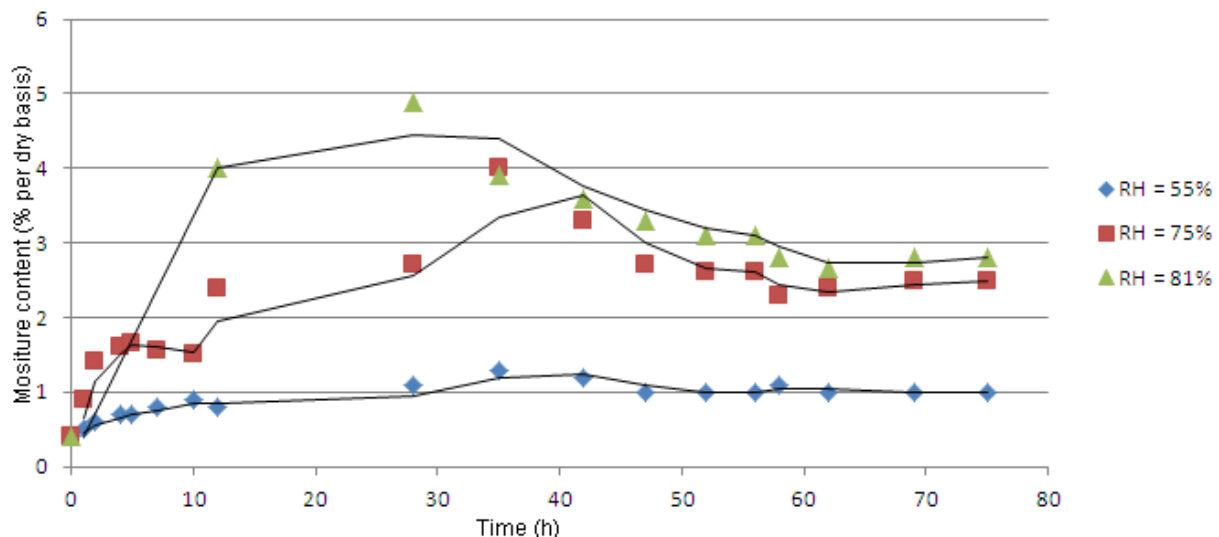
Figure 2.15 Moisture sorption for dark chocolate at 20°C with varying relative humidity adapted from Biquet and Labuza (1988) [15].

The moisture content first reaches a maximum before it decreases to an equilibrium concentration. This type of behavior is not predicted by linear solutions of equation (4) thus a linear model will not be sufficient for predicting this type of behavior. Models incorporating non-linear factors such as non-Fickian diffusion will probably give a better fit for the data produces by Biquet and Labuza (1988).

2.6 Modeling

Mathematical modeling is the process of developing descriptions of a phenomenon in mathematical terms and concepts. The models are used to asses and predict behavior under various conditions without the need of experiments. Biggest advantage of using models to study a process is that models are both time- and resource-efficient. In order to develop a model, mathematical tools are required to either solve the PDE's analytically or numerically.

There are many different classifications of models. Linear models are models where all variables and parameters exhibit linearity. If one or more parameters or variables do not exhibit linearity, the model is non-linear. The reason for classifying the models according to linearity is that Fickian diffusion consists of linear terms only, while non-Fickian diffusion includes non-linear terms.

2.6.1 Modeling of Linear Effects on Moisture Migration

In specific cases the solutions to the Fick's diffusion equation can be obtained analytically, given that few conditions are met. Generally those are given as initial and boundary conditions, which represents the initial concentration profile of the sample as well as the moisture content at the surfaces at any given time respectively. In reality these conditions will represent different chocolate fillings and storage conditions. Additionally all analytical solutions are accompanied with a set of assumptions and simplifications necessary for solving the partial differential equation. One such is the infinite slab approximation, where the geometry of the chocolate is approximated for an infinite slab. Consequently the diffusion only takes place in one dimension with the only significant length being the thickness of the sample. This approximation is valid as long as the diameter of the sample is much larger than the thickness. Another condition that is generally assumed is that transfer of moisture only occurs on one of the surfaces. Hence, the surface in contact with the moisture source

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will have a constant moisture content. Another important aspect of the linear models is the assumption that no swelling is occurring during the diffusion.

2.6.2 Modeling of Non-linear Effects on Moisture Migration

In contrast to the linear models, non-linear models could be sufficient to account for structural changes during the diffusion such as swelling. This is why non-linear models are directly associated with non-Fickian diffusion. There are many ways the non-linearity could be introduced to the Fick's equation, but there is still not a single model that can fully predict non-Fickian behavior. Generally non-linearity arises when concentration dependent diffusion coefficients are present, making equation (4) non-valid for the case. Few models have been developed by Crank amongst others that predict certain aspects of non-Fickian diffusion. One model that is of particular interest is a model based on *History-dependence* developed by Crank in 1953. He suggested that the diffusion coefficient will instantly increase as the concentration of the penetrant increases. The increase will continue until an equilibrium value is reached due to the relaxation process in the crystalline structure. The name *History-dependence* comes from the fact that according to this, the diffusion coefficient in any point of the system depends on the concentration history of that point. The diffusion coefficient is therefore an expression of different time dependent components. The first component is called the instantaneous component D_i which is given by equation (18) assuming that the concentration changes are infinitely rapidly:

$$D_i = D_0 e^{aC} \qquad\qquad (18)$$

where C is the concentration of the diffusing substance while D_0 and a are constants. The second component is the equilibrium component D_e which is given for a certain concentration C at which the diffusion coefficient no long increases with time:

$$D_e = D_0 e^{bC} \qquad\qquad (19)$$

where b is a constant larger than a. D_e is further assumed to be a first-order change, thus:

$$\frac{\partial D}{\partial t} = \alpha(D_e - D) \qquad\qquad (20)$$

The term α in equation (34) is also dependent on concentration and is given by:

$$\alpha = \alpha_0 e^{\sigma C} \qquad\qquad (21)$$

with α_0 and σ being constants.

The expression for the diffusion coefficient then becomes:

$$\frac{\partial D}{\partial t} = \frac{\partial D_i}{\partial C}\frac{\partial C}{\partial t} + \alpha(D_e - D) \qquad\qquad (22)$$

This model has shown success in predicting some features of non-Fickian behavior such as sigmoid type adsorption curves that are typical for foods [11]. However as no literature data is available for chocolate, the multiple parameters embedded in this model need to be fitted to the experimental data.

2.6.2.1 Modeling for Swelling Kinetics

In order to account for the swelling of cocoa particles a moving boundary condition can be included in the model. This is a result of the expansion of cocoa particles due to absorption of moisture. The time dependent boundary will be directly proportional to the diffusion coefficient and the concentration profile.

$$\frac{\partial L}{\partial t} \propto D_{eff} \frac{\partial C}{\partial x} \qquad\qquad (23)$$

Given the time dependent boundary condition it becomes problematical to find an analytical solution to the problem. This can be done through certain assumptions using a method called perturbation presented by Duda and Vrentas in 1968. The solution is obtained for small interfacial velocities using coordinate transformations and series expansions for immobilizing the moving boundary [31]. This method was used by Galdámez et.al. (2009) when studying oil migration in chocolate.

However, when solving PDEs involving non-linarites, numerical solutions could be used instead of analytical. A widely used method for solving PDEs numerically is called the Finite Element Method (FEM)

2.6.3 Numerical Solutions to Diffusion Problems using FEM

Numerical solutions are often used for solving complex problems that either have an unknown analytical solution or the simplifications done in order to obtain it deviate significantly from the reality of the problem. The complexity of the problems generally arrive from non-symmetric geometries in two or three dimensions, and sometimes also from the nature of the process observed (initial and boundary conditions, nonlinearities). Numerical methods provide an approximate solution for the problem and can be used for solving both linear and non-linear PDEs. The exactness of the solution will be heavily dependent on the computational power available for the modeling.

The most commonly used method for numerically solving PDEs in called FEM. Simply put, this method consists of dividing the object of interest (geometry) into smaller element domains creating a mesh. Each of these domains will have a solution to the problem approximated as a piecewise continuous linear function called a basis functions. The basis functions are derived from a series of approximations and boundary conditions, while the overall solution of the problem is given as the linear combination of the basis functions. Additionally, for non-steady state problems, the time dependent term $\frac{\partial C}{\partial t}$ has to be approximated, usually by applying a forwards or backwards Euler scheme [32].

3. Materials and Methods

3.1 Materials

- Chocolate

The chocolate used for this project was purchased by Cloetta AB (Ljungsbro, Sweden) with an approximate composition given in table 3.1.

Table 3.1 Composition of the dark chocolate used.

Ingredient	Content (%)
Cocoa mass	40
Cocoa butter	10
Sugar	50
Lecithin	0.4
Vanillin	0.02

The total fat content of the chocolate was 32% and the batch was stored at 15°C and 30% RH prior to use.

- β_{VI}-seed

The seed was provided by D. Ehlers from ETH Zurich, produced in a SeedMaster device at Bühler Group AG, Uzwil, Switzerland. It was also stored at 15°C and 30% RH prior to use.

3.2 Chocolate Sample Processing

3.2.1 Pre-crystallization

To erase any crystal memory, the dark chocolate was first stored in a climate chamber at 48°C and 50% RH for 24 hours. It was then pre-crystallized using the β_{VI}-seeding method. The chocolate was cooled down to 32°C while being continuously stirred and 4g of seeds were added to the pre-cooled chocolate during 3 minutes. The exact amount of seeded needed to get a well-tempered chocolate was determined during pre-trial, knowing from previous work that around 1% (w/w) gives a desired crystalline structure. The chocolate was stirred during this time plus one more additional minute using a kitchen mixer in order to obtain a homogenous spread of nucleation centers. Care was taken to make sure that the chocolate at the edges was also well mixed. The samples were made in three batches containing 500g of chocolate each. Immediately after the pre-crystallization, the temper degree was measured to make sure that the chocolate was well-tempered.

3.2.2 Measurement of Temper Degree

The temper degree was measured using a MultiTherm Tempermeter (Bühler AG, Uzwil, Switzerland). Alumina cups (15 ml) were filled with chocolate and then places in the tempermeter to measure temperature in center of the cup versus time kept at 8°C. The temper-degree was calculated using the MultiTherm software from the plot of temperature versus cooling time. To verify that the chocolate was well-tempered a temper index (TI), of 5±0.5 was required which according to the built in algorithm corresponds to correct processed chocolate.

3.2.3   Molding

The samples were molded into cylinder shapes using plastic molds with dimensions of 22mm in diameter and 6mm in height. After the chocolate was pre-crystallized it was poured into the molds in order to make samples for migration analysis. Parafilm was used at the bottom to prevent the chocolate from leaking. After the excess of chocolate was scraped off with a spatula, the molds filled with chocolate were put on a vibrating board for 20-30 seconds to eliminate possible air bubbles that appeared during the stirring. The chocolate was then put in a cooler for 15 minutes at 8°C in order to solidify. Finally, the samples were demolded as carefully as possible. One batch produced 50 samples that were used in the experiments.

3.2.4   Storage

The samples were stored in a climate chamber at 20°C and 75% RH. The moisture sorption of the chocolate during storage was measured gravimetrically and by moisture content determination (described in section 3.3.1). Samples were places as triplets in petri dishes and six samples per day were taken out for measurements, three in the morning and three in the afternoon. A total of 150 samples were used during the experiment.

3.3 Analysis

3.3.1   Measuring Moisture Migration

The moisture migration was measured using two different methods. The first method was a simple gravimetric weight measurement. All samples were weighted individually, using a scale with a precision of ±0.00001g (Mettler Toledo), after demolding and again right after they were taken out from the climate chamber. The water content in % (w/w) could then be calculated from the weight gain using:

$$M \; t \;\; = \frac{m_t - m_i}{m_i} \times 100\% + M_0 \qquad\qquad (24)$$

where m_t and m_i are the mass of the sample at a given time t and the initial mass respectively and M_0 is the initial moisture content of the sample.

The second method was done by measuring the weight decrease during the evaporation of the samples. After being taken out from the climate chamber the samples were grinded and placed into a cup and the weight was recorded using the same scale. The samples were then placed in a vacuum oven where they were dried at 70°C for 3 days until all the water has evaporated. The evaporation time was determined by weighing samples each day until no weight drop was detected. After 3 days in the oven the sample were taken out and the weight was once again recorded and the water content was calculated using:

$$M \; t \;\; = \frac{m_i - m_f}{m_f} \times 100\% \qquad\qquad (25)$$

Where m_i is the weight before and m_f is the weight after being in the oven. The initial moisture content needed for equation (24) is also calculated using this method.

The two methods should produce similar results as all gain/loss of weight is attributed to moisture migration. However the evaporation method should be regarded as more reliable. This method has also been verified by simultaneous moisture content measurements using Karl-Fischer titration [29]. The experiments were carried out under the assumption that all of the samples had the same moisture sorption properties.

3.4 Modeling

The modeling was done mainly using Matlab (Mathworks), but also Comsol MultiPhysics (Comsol AB). Comsol, which is based on a FEM solver, was used when modeling for swelling kinetics. The data gathered in the experiments was used for model conformation as well as determining the diffusion coefficient where needed. Data from previous works available at SIK as well as from literature were also used and compared in order to verify the effectiveness of the model.

Non-linear models will inevitably contain parameters that cannot be measured or calculated. However, these parameters can be determined by fitting the solution to the experimental data. For the purposes of this work, FMINUIT was used for curve fitting to determine model parameters. FMINUIT is a Matlab function derived from the MINUIT Fortran routine developed in the 1970s at CERN [34]. MINUIT is a tool for function minimization and analysis of parameter errors and correlations. It uses statistical chi-squared analysis to determine parameter values so that a given function is fitted to a set of experimental data minimizing the error.

3.4.1 Linear Models

The linear models were distinguished as Model One and Model Two with respects to boundary conditions. For each of the models, the diffusion coefficient was determined using five different equations resulting in 5 curves. Those curves were plotted on the same graph together with the experimental data in order to compare the effectiveness of the model. The relationship between the model and experimental values is evaluated with the coefficient of determination, denoted R^2. An R^2 value of 1 indicates a regression line that perfectly matches the data while close to 0 indicates that the model does not fit the data.

3.4.1.1 Modeling for Uniform Initial and Equilibrium Concentration

Model One is a rework of a model developed by Annie Lechevretel at PERA Technology (Leicester, England). Figure 3.1 shows a simplification of the sample geometry and the orientation of the x-axis:
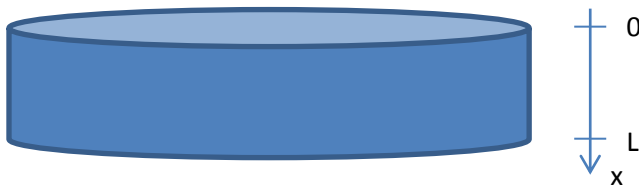

Figure 3.1 Schematic representation of the sample showing the orietation of the x-axis.

The initial and boundary condition are given bellow:

$$C\ x,t\ = C_i \qquad\qquad 0 < x < L, \qquad t = 0 \qquad\qquad (26)$$

$$C\ x,t\ = C_m \qquad\qquad x = 0, x = L, \qquad t \geq 0 \qquad\qquad (27)$$

$$\frac{\partial C}{\partial x}(x,t)\Big|_{x=L} = 0 \qquad (28)$$

where C_i and C_m are the initial and equilibrium concentration respectively and equation (28) indicates no transfer at one of the boundaries i.e. the transfer of water between the mediums occur at x =0. The solution to this equation was purposed by Jost (1960) given by [33]:

$$\frac{C-C_i}{C_m-C_i} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\sin\frac{(2n+1)\pi x}{L}exp\left(-\pi^2(2n+1)^2\frac{D_{eff}t}{h^2}\right) \qquad (29)$$

The total moisture uptake of the sample at any given time is calculated by integrating the flux of vapor over the external surface area i.e. at x=0. Therefore e flux at x = 0 is needed, which is given by:

$$J(0,t) = -D_{eff}\frac{\partial C}{\partial x}(0,t) \qquad (30)$$

And the total amount of moisture absorbed at time t per unit area of the exposed surface is thus given by the integral of the flux at x=0 over time t:

$$Q(t) = \int_0^t J(0,t)\,dt \qquad (31)$$

Usually the moisture content is given as a weight percentage of water as a function of time. Therefore moisture content of the chocolate given in grams of water per 100g of dry material can be calculated as follows:

$$M(t) = M_i + \frac{100}{L}Q(t) \qquad (32)$$

where M_i is the initial moisture content.

Using equations (29), (30), (31) and (32) we have the solution for the moisture content according to Josh:

$$\frac{\frac{M}{100}-M_i}{M_m-M_i} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}exp\left(-\pi^2(2n+1)^2\frac{D_{eff}t}{L^2}\right) \qquad (33)$$

This solution is used for modeling the moisture migration through chocolate in the first model. Additionally, five models were developed for each set of boundary conditions where the diffusion coefficient was evaluated using equations (6), (7), (8), (12) and (13) respectively. Note that equations (6), (7) and (8) are experimental methods which require data of moisture content in order to be used. Equations (12) and (13) are based on structural effects and can be used to theoretically calculate the effective diffusion coefficient. However they do require structural parameters which were taken from the literature [30].

3.4.1.2 Modeling for Uniform Initial Concentration and Different Surface Concentrations

A more general approach to a linear model is to use boundary conditions given as constant concentration at the surfaces for x = 0 and x= L. Also for the initial concentration the most general idea is to have a concentration profile given as a function of the thickness, f(x). Therefore the conditions for Model Two are given by:

$$C(x,t) = f(x) \qquad t = 0, \qquad 0 < x < L \qquad (34)$$

$$C(x,t) = C_1 \qquad t \geq 0, \qquad x = 0 \qquad (35)$$

$$C(x,t) = C_2 \qquad t \geq 0, \qquad x = L \qquad (36)$$

The solution to the non-steady state equation (4) with the given boundary and initial conditions are given by Crank (1975):

$$C = C_1 + \ C_2 - C_1 \ \frac{x}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi x}{L} \exp \ -\frac{D_{eff} n^2 \pi^2 t}{L^2}$$
$$+ \frac{2}{L} \sum_{n=1}^{\infty} \sin \frac{n\pi x}{L} \exp \ -\frac{D_{eff} \pi^2 n^2 t}{L^2} \ \int_0^L f(x) \sin \frac{n\pi x}{L} dx \qquad (37)$$

In order to evaluate the moisture content the boundary and initial conditions has to be known. Depending on the experimental setup the C_1 is usually given as the concentration of the medium in contact with the sample as fast equilibrium is assumed at the surface. In the case of a praline this is given by the water activity of the filling or in the case of storage of dark chocolate C_1 is given by the relative humidity of the surrounding atmosphere. C_2 is generally harder to evaluate, but given the fact that the moisture migration through chocolate is an extremely slow process, C_2 can be approximated with as the arithmetic average of the initial and the steady-state concentration, which is approximately equal to C_1. C_1 is calculated using the moisture sorption isotherms given in figure 2.11 and 2.12. The isotherm constructed by Biquet and Labuza (1988) was used for determining C_1 for modeling the experimental data collected during this work, as the relative humidity was 75%, corresponding to a water activity of 0.75 in an equilibrium between the air the and the surface of the chocolate . For modeling of the experiment conducted by Galler (2011), where chocolate was in contact with a gel with a water activity of 0.83, the sorption isotherm used for determining C_1 was given by Roca et al. (2008).

In every case of moisture migration in chocolate confectioneries the initial concentration is almost exclusively a constant value, C_i. This makes the integral in equation (37) easily evaluated and the resulting concentration according to Crank (1975) is given by:

$$C = C_1 + \ C_2 - C_1 \ \frac{x}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi x}{L} \exp \ -\frac{D_{eff} n^2 \pi^2 t}{L^2}$$
$$+ \frac{4C_i}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \sin \frac{(2m+1)\pi x}{L} \exp \ -\frac{D_{eff} \pi^2 (2m+1)^2 t}{L^2} \qquad (38)$$

In order to obtain the total amount of water equations (30) and (31) are used once again resulting in:

$$Q = D_{eff} \ C_1 - C_2 \ \frac{t}{L} + \frac{2L}{\pi} \sum_{n=1}^{\infty} \frac{C_1 \cos n\pi - C_2}{n^2} \ 1 - \exp \ -\frac{D_{eff} n^2 \pi^2 t}{L^2}$$
$$+ \frac{4C_i L}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \ 1 - \exp \ -\frac{D_{eff} \pi^2 n^2 t}{L^2} \qquad (39)$$

The moisture content is then calculated using equations (32) and (39).

This model gives a more general solution to the non-steady state Fick's equation allowing for boundary and initial conditions representing different cases of moisture migration in chocolate. The diffusion coefficient was also, in this case, determined using equations (6), (7), (8), (12) and (13).

3.4.2 Non-linear models

A simple way to study the non-linear effects of moisture migration is to assume a diffusion coefficient linearly dependent on concentration:

$$D = \ D_l + D_n \ C \qquad (40)$$

26

where D_l is equal to the linear diffusion coefficient and D_n is the non-linear term. Substituting equation (37) to equation (3) yields the new non-linear diffusion equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\ (D_l + D_n C)\frac{\partial C}{\partial x} \qquad (41)$$

Usually non-linear partial differential equations do not have analytical solution. Equation (38) is however an exception and could be solved analytically for certain assumptions. This was done by Antunes and Antunes (2000) who assumed that the non-linear effects are small i.e. $D_n C \ll D_l$. Also the concentration is expressed in the following form:

$$C\ x,t\ = C_l\ x,t\ + C_n(x,t) \qquad (42)$$

where $C_l(x,t)$ is the solution of the linear equation (4) with the boundary and initial conditions given by (26) and (27) respectively and $C_n(x,t)$ is a non-linear correction term. In order to solve the diffusion equation for $C_n(x,t)$ another approximation is necessary. It is assumed that $C_l(x,t)$ can be approximated by its constant stationary value i.e. the value at the boundary x=0. By inserting (39) into (38) the diffusion equation for C_n becomes:

$$\frac{\partial C_n}{\partial t} = (D_l + D_n C_{l1})\frac{\partial^2 C_n}{\partial x^2} \qquad (43)$$

with initial and boundary conditions $C_n(x,0) = 0$ and $C_n(0,t) = C_{n1}$. There is also no transfer at x=L in this case as well. Given these conditions the solution to this equation proposed by Antunes and Antunes (2000) is described below:

$$
\begin{aligned}
C\ x,t\ =\ & C_{l1} + C_{n1} \\
& -\frac{1}{2L}\ \sum_{n=0}^{\infty}\ C_{l1} - C_0\ + C_{n1}\exp\ -\frac{D_n C_{l1}\ 2n+1\ ^2\pi^2 t^2}{4L^2} \\
& \cdot\frac{\sin\ \frac{2n+1\ \pi x}{2L}}{\frac{2n+1\ \pi x}{2L}}\ \exp\ -\frac{D_l\ 2n+1\ ^2\pi^2 t^2}{4L^2}
\end{aligned}
\qquad (44)
$$

According to equations (29)(30)(31) the moisture content is therefore given by:

$$
\begin{aligned}
M\ t\ =\ & M_0 + \frac{100}{2L^2}\ 1 + \frac{D_n}{D_l}(C_{l1} + C_{n1}) \\
& \cdot \sum_{n=0}^{\infty}\ C_{l1} + C_{n1}\ 1 - \exp\ -\frac{D_l\ 2n+1\ ^2\pi^2 t}{4L^2} \\
& + \frac{C_{n1}\ 1 - exp\ -\frac{(D_l + D_n C_{l1})\ 2n+1\ ^2\pi^2 t}{4L^2}}{1 + \frac{D_n}{D_l}C_{l1}}\ \frac{4L^2}{(2n+1)^2\pi^2}
\end{aligned}
\qquad (45)
$$

Note that the four parameters in this model, D_l, D_n, C_{1l} and C_{1n} are not physical parameters that can be measured independently, even though $C_{1l} + C_{1n}$ will correspond to the surface concentration of the chocolate. To obtain a solution for the model, parameter fitting is used to determine the equation parameters.

3.4.2.1 Modeling of Swelling Kinetics in Comsol Multiphysics

The dilute species transfer module was used for modeling the time-dependent diffusion. Also, the boundary condition for this model were given as a constant concentration at x=0 (equation (35)) and no flux at x=L (equation (28)) and the initial concentration was assume to be constant and uniform (equation (26)). The swelling of the chocolate was modeled by adding a moving mesh, i.e. a moving boundary. However, as equation (23) suggests a proportionality constant need to be determined in order obtain proper results. In contrast to modeling with Matlab, parameter fitting was not used with Comsol the proportionality constant was determined *ad hoc* to fit the data.

Another advantage of using Comsol Multiphysics was that solutions could be obtained for higher geometries. Therefore a model in three dimensions corresponding to an approximate geometry of the samples, shown in figure 3.1, was developed in addition to the one dimensional case. The boundary conditions were in that case expanded over whole domains instead of single points. The diffusion coefficient was determined using equation (13).

4. Results and Discussion

4.1 Pre-crystallization and Temper degree

A total of 150 samples were made from three different batches and the temper degree is shown in table 4.1 and the temper curves are shown in figure 4.1.

Figure 4.1 Temper curves of the produced chocolate samples.
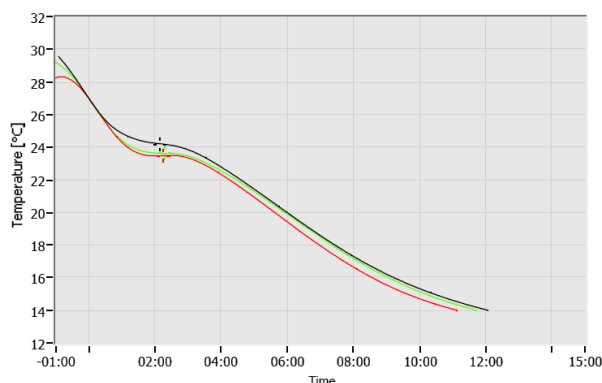
Table 4.1 Temper degree of samples used.

Batch	Color of temper curve	Temper degree (TI)
1	Green	5.08
2	Red	4.62
3	Black	5.81

As the table shows, the temper degree varied across the batches where batch 1 was almost ideally well-tempered, batch 2 was slightly under-tempered while batch 3 was over-tempered. Even though the same ratio of chocolate mass and seeds was used the variation still occurred. This is most likely due to the nature of the production technique involving parameters that were hard to control. The process was highly temperature sensitive and controlling the temperature profile was hard due to the openness of the chocolate to the colder surroundings. The inability to control the temperature profile over the production process was the main reason for the deviation of the temper degree. However a small variation in the temper degree will not impact the experimental result significantly [27][29].

4.2 Sample Morphology

Although each sample were shaken on a vibrating table to remove air bubbles and textile gloves were used to protect the chocolate surface, many of the samples made did not have a perfectly smooth surface as was desired for the experiment. Samples contained defects on the surface such as roughness and cracks, but also in the bulk in form of air bubbles, shown in figure 4.2. These imperfections in the samples would probably increase the rate of diffusion or the WVTR. Partly because the roughness of the surface increases the total surface area, hence the amount of diffusing substance and also because the resistance to migration in air bubbles is considerably lower compared to that of the liquid fat phase in chocolate.

Figure 4.2 One of the samples, showing uneven surface and holes made by escaping air

4.3 Moisture Migration

The moisture migration properties were assessed through moisture sorption of the chocolate sample in a humid atmosphere. The moisture content of the chocolate in contact with the humid air at a specific time was measured using two different methods and the results are shown in figure 4.3.
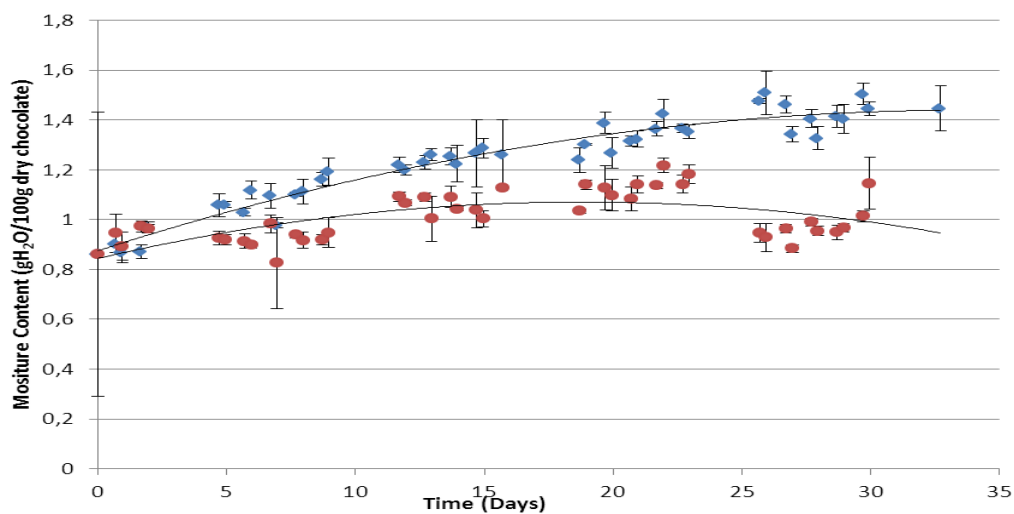
Figure 4.3 Moisture content of chocolate per dry basis as function of time. The moisture content was calculated using two methods described in section 3.3. The blue points represent the weight change method while the red points represent the evaporation method. Points are fitted with second degree polynomial trend curve with R^2 values of 0.9342 and 0.4147 for blue and red respectively.

The same results were expected independent of the method used to determine the moisture content, as all of the weight gain/loss was assumed to be due to water sorption and evaporation. However figure 4.3 shown that the results differ in both values of the moisture content and in the shape of the curve.

The moisture content determined by measuring the weight gain of the samples (blue points) is in fact dependent on the initial moisture content as shown in equation (24). This initial concentration was

determined experimentally by evaporating water from a sample in the vacuum oven before any of them were put in the climate chamber. The resulting value was 0.28%±0.07 gH2O/100g dry chocolate, which is significantly lower than literature value for dark chocolate (0.4% – 1% w/w) as well as values earlier reported at SIK [15][29]. Therefore the value of the initial moisture concentration was replaced with 0.86%±0.57 as reported by Galler (2011). Although the standard deviation is high, 0.86% is a more reasonable value for the initial moisture content. The value can be applied to the data collected for this work as the chocolate used in the study of Galler (2011) had the same composition and fat content.

Given that the values of the first method can be compensated by having a higher initial moisture content, the curves do have a similar shape for t<20 days. After that point the moisture content of the samples start to decrease according to method 2. This is most likely due to errors in measurement, but could also be a sign of non-linear diffusion behavior. The decrease in moisture content is however too large, which points towards an error in measurement.

The equilibrium value for moisture sorption in 75% RH is approximately 2.3 gH$_2$O/100g dry, which significantly higher than final value of 1.5 gH$_2$O/100g dry, of the moisture content reported. This could very likely mean that the equilibrium was not reached after 35 days, which is consistent some previous studies [15].

4.4 Mathematical Models of the Moisture Migration

The mathematical models were evaluated by plotting the moisture content versus the time for model values compared to experimental data. There were a total of 8 sets of experimental data that were used for this study, shown in table 4.2.

Table 4.2 The experimental data used for model verification.

Data set nr.	Found in	Pre-crystallization	Temper degree (TI)
1	Galler (2011)	No pre-crystallization	untempered
2	Galler (2011)	Seeded with 2% (w/w) seed	6
3	Galler (2011)	Tempered	5
4	Galler (2011)	Tempered	3
5	Galler (2011)	Seeded with 0.7% (w/w) seed	5
6	Galler (2011)	Seeded with 0.2% (w/w) seed	3
7	Hondo(2013)	Seeded with 0.8% (w/w) seed	5
8	Hondo(2013)	Seeded with 0.8% (w/w) seed	5

There is a major difference within the experimental setup in the work of Galler (2011) compared to this work. In Galler (2011) the samples were stored in 50% RH and they were placed on a gel with a constant water activity of 0.83. The majority of the moisture transfer occurred from the gel to the sample. In this work the samples were only stored in 75% RH with one surface in contact with the air and the other isolated for moisture migration. The transfer in this case occurred from the humid atmosphere to the sample.

4.4.1 Linear Models

4.4.1.1 Model One

The boundary and initial conditions for this model is given in section 3.4.1.1. The experimental data defined in table 4.2, and linear model one with diffusion coefficient calculated according to equation (6), (7), (8), (12) and (13) is presented in figure 4.4 and 4.5 as well as in tables 4.3 through 4.10.

Table 4.3 R^2–value for data set number 1

Data set	D_{eff} according to equation	D_{eff} [m^2s^{-1}] x10^{13}	R^2
1	(6)	14.179	0.9266
	(7)	6.6143	0.5327
	(12)	12.619	0.8989
	(13)	33.884	0.5602
	(8)	17.361	0.9072

Table 4.4 R^2–value for data set number 2

Data set	D_{eff} according to equation	D_{eff} [m^2s^{-1}] x10^{13}	R^2
2	(6)	10.099	0.8445
	(7)	6.2005	0.7161
	(12)	12.619	0.8108
	(13)	33.884	-
	(8)	17.361	0.5714

Table 4.5 R^2–value for data set number 3

Data set	D_{eff} according to equation	D_{eff} [m^2s^{-1}] x10^{13}	R^2
3	(6)	8.3256	0.8674
	(7)	5.7148	0.8146
	(12)	12.619	0.6974
	(13)	33.884	-
	(8)	17.361	0.2605

Table 4.6 R^2–value for data set number 4

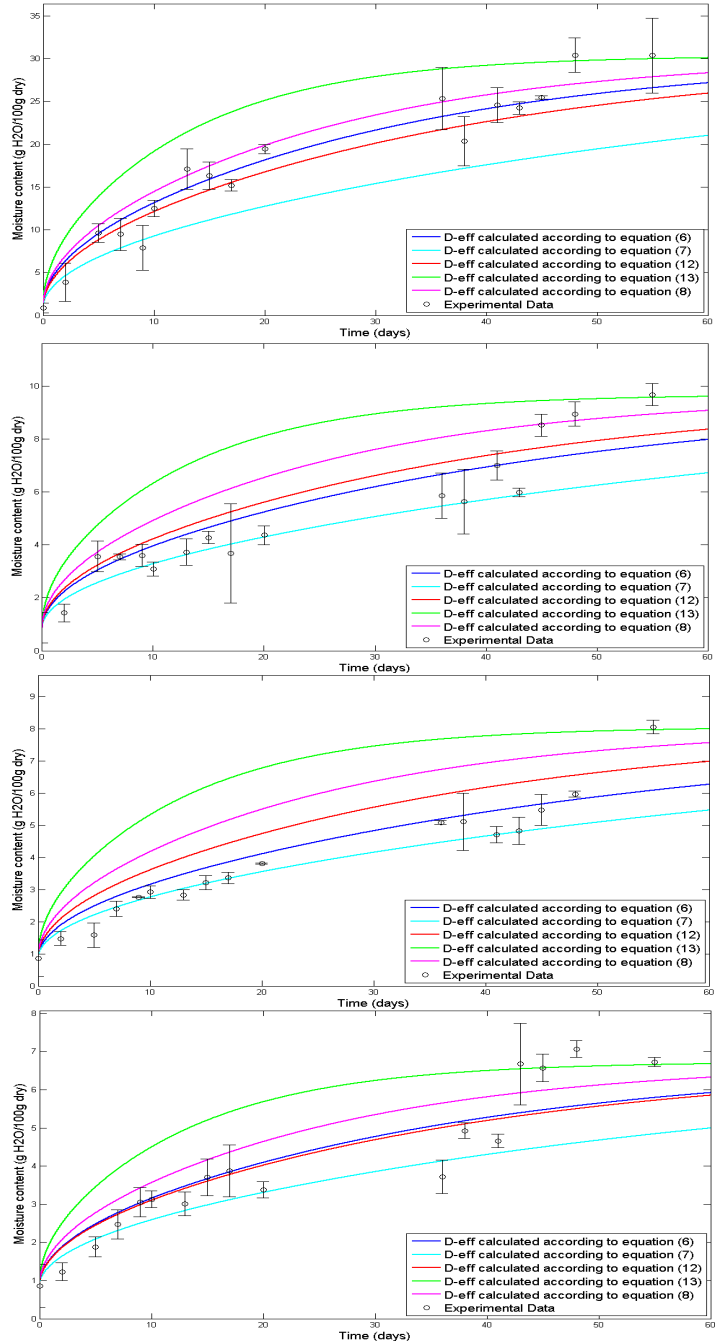| Data set	D_{eff} according to equation	D_{eff} [m^2s^{-1}] x10^{13}	R^2
4	(6)	12.484	0.8330
	(7)	7.1005	0.6337
	(12)	12.619	0.8298
	(13)	33.884	0.3830
	(8)	17.361	0.7799

Figure 4.4 a) – d) Mositure content versus time for Model One with experimental data sets 1 – 4, as described in table 4.2.

Table 4.7 R^2–value for data set number 5

Data set	D_{eff} according to equation	D_{eff} [m²s⁻¹] x10¹³	R^2
5	(6)	10.282	0.8772
	(7)	6.2469	0.6218
	(12)	12.619	0.8916
	(13)	33.884	0.2429
	(8)	17.361	0.7839

Table 4.8 R^2–value for data set number 6

Data set	D_{eff} according to equation	D_{eff} [m²s⁻¹] x10¹³	R^2
6	(6)	13.835	0.7839
	(7)	7.4176	0.7542
	(12)	12.619	0.8186
	(13)	33.884	0.1312
	(8)	17.361	0.6783

Table 4.9 R^2–value for data set number 7

Data set	D_{eff} according to equation	D_{eff} [m²s⁻¹] x10¹³	R^2
7	(6)	5.7445	-
	(7)	12.822	0.4324
	(12)	12.619	0.3521
	(13)	33.884	0.8599
	(8)	21.231	0.8166

Table 4.10 R^2–value for data set number 8

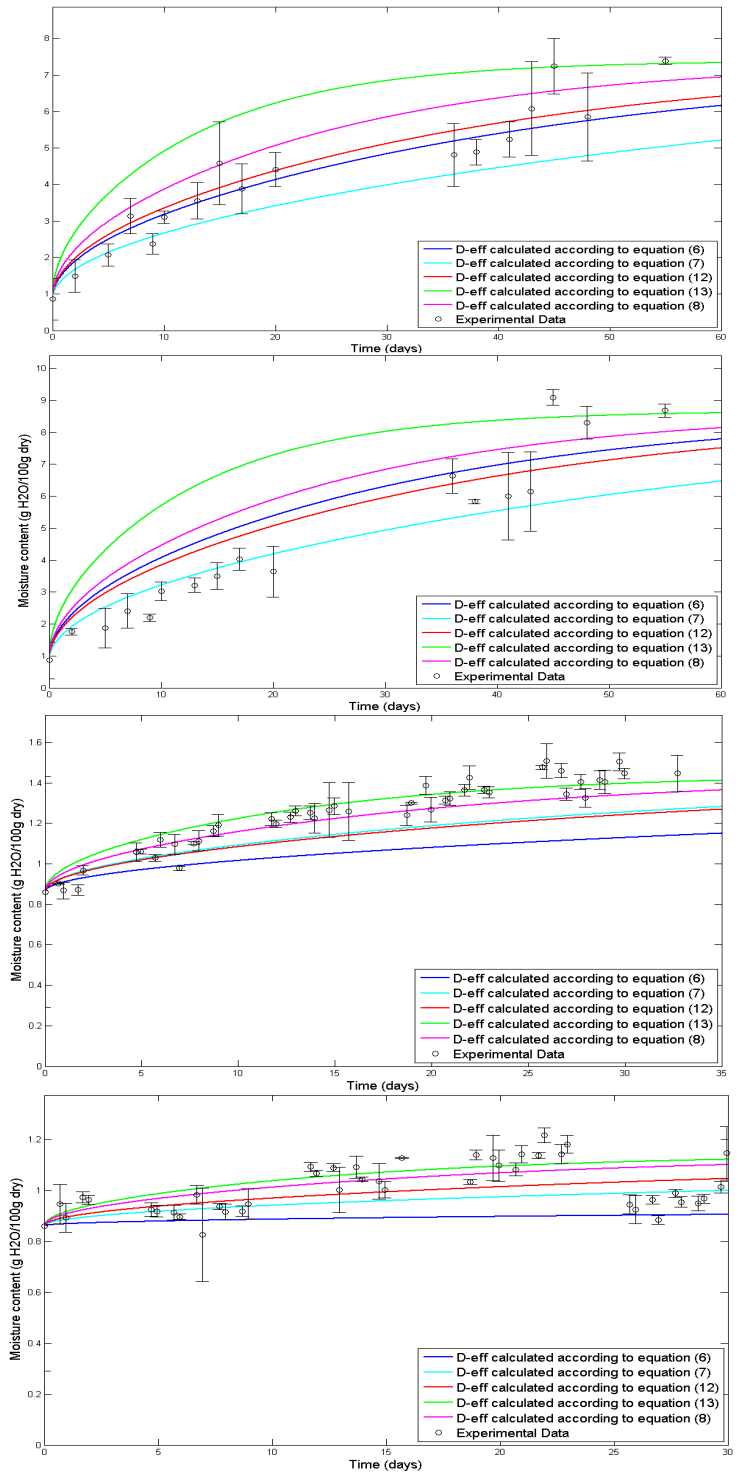| Data set	D_{eff} according to equation	D_{eff} [m²s⁻¹] x10¹³	R^2
8	(6)	0.6790	-
	(7)	6.5094	-
	(12)	12.619	0.1807
	(13)	33.884	0.0326
	(8)	23.180	0.1862

Figure 4.5 a) – d) Mositure content versus time for Model One with experimental data sets 5 – 8, as described in table 4.2.

The R^2 value does not tell much about the goodness of fit of the experimental data. Howerver, it does serves as a tool to compare how well the different methods of determining the diffusion coefficient were in predicting the moisture sorbtion behavior.

As tables 4.3 – 4.10 suggest the model that overall fits the experimental data best was the model with a diffusion coefficient calculated with equation (6). It was the best fit in four cases, but failed to predict experimental data collected during this work, table 4.9 and 4.10. Determining the diffusion coefficient with equation (6), (7) or (8) would expectedly give similar results as all three methods are focused on calculating an average diffusion coefficient from experimental data. This is can be seen to some extent in table 4.4, 4.6, 4.7, and 4.8. In other cases the R^2 for the models where D_{eff} was calculated using these equations was very different. Using equations (6), (7) or (8) will result in models that are case-specific for each experimental setup and cannot be used to generally describe moisture diffusion through chocolate. The only case these equations would represent the general model is if the diffusion coefficient does not vary significantly with concentration and can thus be estimated as an average diffusivity.

Equations (12) and (13) are based on theoretically determining the diffusion coefficient using structural parameters. It was expected that equation (13) would give a better description for the diffusion of moisture through chocolate as the diffusion through the dispersed phase is much faster than through the continuous cocoa butter phase. However, this was only true in one case, shown in table 4.9. This might be an indication that the model is not adequate as a general representation of moisture migration through chocolate. It is important for a general model that all model parameter can be derived from the literature and can be used without any experimental data. Equation (13) gave a good prediction for some of the data in this work (data set 7) which were collected in a different experimental setup compared to Galler (2011). As a general model for moisture migration through chocolate, Model One showed limited capability of predicting experimental data. An exception was moisture uptake in a humid atmosphere where model one, coupled with equation (13), showed good results, shown in figure 4.5 c) and table 4.9.

Regardless of what equation was used to calculate the diffusion coefficient, the model failed to fit to the last set of data used, shown in table 4.10. As shown in figure 4.3 the moisture content of the samples decreases after some time, which was not expected. This type of behavior cannot be modeled with a linear model, hence the low R^2 values. Another thing to note about data sets 7 and 8 is that the time for the experiment was 35 and 30 days respectively. According to Biquet and Labuza (1988) the time it takes for moisture sorption of chocolate to reach equilibrium is between 40-60 days. Therefore the equilibrium might not be reached in the experiment. This is particularly affecting Model One as the equilibrium concentration is a model condition, shown in equation (27).

4.4.1.2 Model Two

The boundary conditions and description of this model can be found in section 3.4.1.2. The experimental data for data sets 5 and 7 defined in table 4.2, and linear model two with diffusion coefficient calculated according to equation (6), (7), (8), (12) and (13) is presented in figure 4.6 and table 4.11. The results for all data sets can be found in Appendix C.
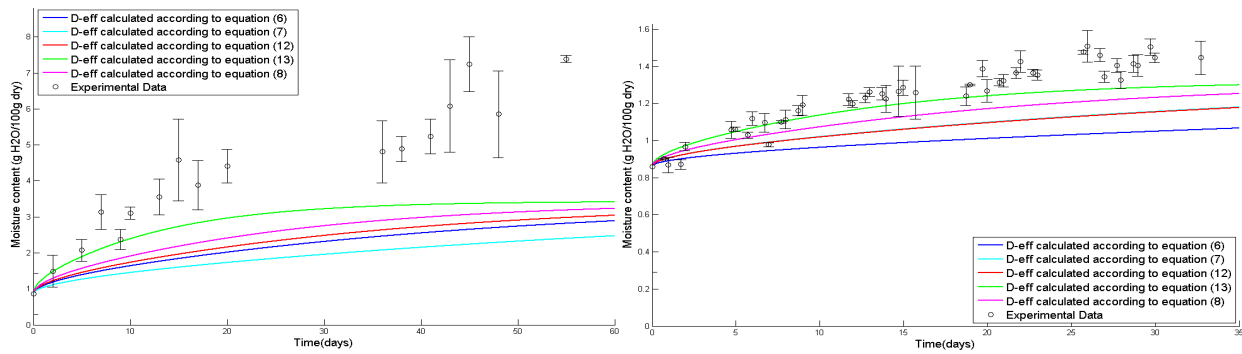
Figure 4.6 a) Moisture content versus time for Model Two plotted against experimental data set 5. b) Moisture content versus time for Model Two plotted against experimental data set 7.

Table 4.11 Calculated values for the initial and boundary conditions for the results shown in figure 4.6.

	Data set 5	Data set 7
Water activity	0.83	0.75
C_0 (kg/m^3)	8.5985	8.5985
C_1(kg/m^3)	85.7810	22.5510
C_2(kg/m^3)	47.1897	15.5797

Both data sets 5 and 7 were chocolate sample that were seeded in order to get a well-tempered chocolate. When considering this model it is important that parameters such as tempering degree are constant when comparing results. This is because the boundary conditions are determined from the moisture sorption isotherms which are very structure dependent. This is even more important when dealing with high water activities, where even a slight change in the structure of chocolate can drastically change the actual boundary condition. Taking this into account it is hard to compare the data sets in between as the moisture sorption isotherms are given for well-tempered chocolate. The model should therefore match the data for tempered chocolate the best while being far away from the data for untempered chocolate (data set no 1 in table 4.2).

This is to some extent observed as the model does predict the data better for tempered chocolate compared to untempered, however the results are not satisfactory. This model fails to predict the data and shows significantly lower values for the moisture content than actually observed. Comparing 4.6 a) and b), the model gives a better fit for 4.6 b) which had a lower water activity at the boundary, but still does not give a satisfactory match for the data. Additionally, the diffusion coefficient calculated using equation (13) is closest to predicting the data. This was expected to begin with, but was not predicted by Model One.

The problem for this model seems to be in the nature of the boundary conditions. Allowing both ends of the sample to have a constant concentration will allow the moisture to migrate out of the sample at x = L. This means that the equilibrium moisture content is always significantly lower than C_1. This model can still be a general representation of moisture migration through a praline where the water activity of a fruit filling is one boundary condition and the humidity of the air is the second. In such conditions the transport of water is not limited just to occur at one boundary, but can instead take up or release moisture at the air/chocolate interface. However this was not represented by the experimental setup done for this work as well as in Galler (2011). The experiments in both these works were designed such as the migration dominantly occurred at one surface of the sample. This changes the model in a way that C_1 stays the same, but C_2 is replaced by boundary condition for no flux, as shown in equation (28). The model then becomes very similar to Model One, the difference being that the boundary concentration is not determined from the experimental data, but rather from the moisture sorption isotherm.

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4.4.1.3 Modeling Linear Models in Comsol Multiphysics

The initial and boundary conditions used for modeling linear models in Comsol Multiphysics were a mix between Model One and Model Two and were given by equations (26), (35) and (28). In order to get a model as general as possible the diffusion coefficient was calculated using equation (13). Additionally, approximate 3D sample geometry was used, shown in figure 3.1. The experimental data for data sets 5 and 7 defined in table 4.2 and a model using 3D and 1D geometry are presented in figure 4.7.
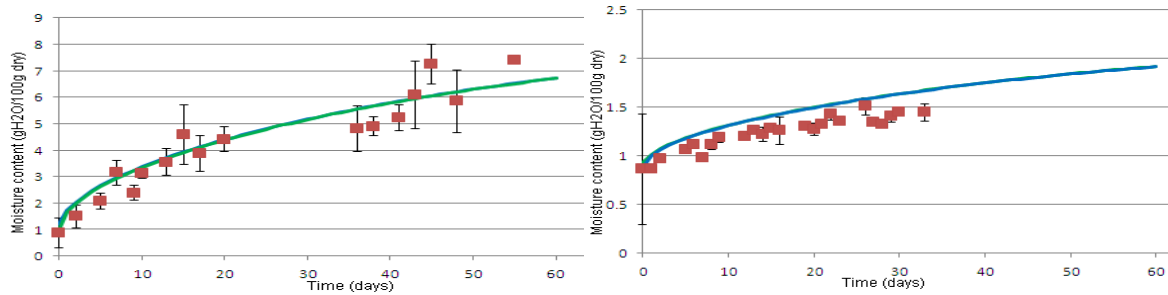

Figure 4.7 Moisture content versus time for a linear model developed in Comsol MultiPhysics in 1D (blue line) and 3D (green line), plotted against experimental data: a) set 5, aw = 0.83, $D_{eff} = 33.88 \times 10^{-12} \, m^2 s^{-1}$, $R^2 = 0.3051$. b) set 7, aw = 0.75, $D_{eff} = 33.88 \times 10^{-12} \, m^2 s^{-1}$, $R^2 \approx 0$.

Note that the blue and the green line are almost completely overlapping in both cases, which is why it seems there is only one curve. This means that with the boundary conditions used one can say that increasing the geometry will not affect the results as no significant radial diffusion is observed. Thus the infinite slab approximation seems to be valid in this case of moisture transfer.

According to figure 4.7 the model gives a decent fit for data set 5, showing that the diffusion coefficient can be approximately determined using equation (13). The data fits the curve better for lower value of the moisture content (for t<20 days), which is an indication that the diffusion coefficient is fairly constant at low moisture contents, but changes for higher values. For data set 7 the resulting curve is unexpectedly high and gives a poor fit for the data as indicated with the R^2 value. An R^2 similar to Model One and equation (13), shown in table 4.9, was expected in this case as the difference in the models is just in the value of one boundary condition. This shows how a slight change in the concentration at high water activities can have a big impact on the result. The unexpected R^2 value can also be due to the difference between the analytical and numerical solution methods. However it is highly unlikely that this would affect the results greatly as a very refined mesh was used when modeling in Comsol. In both cases the model gives a better prediction than Model Two, shown in figure 4.6.

Furthermore the boundary and initial conditions used for this model should represent the experimental set up designed for both this work and the work of Galler (2011). This implies that any inaccuracy of predicting the data is most likely due to the value of the diffusion coefficient or less likely that the data itself is inadequate. As assumed the diffusion coefficient is exponentially dependent on concentration, and therefore on water activity, and will increase rapidly for water activities over 0.8. This is suggested by the moisture sorption isotherms in figures 2.11 and 2.12. Equation (13) can be used for determining the diffusion coefficient for lower water activities when the sorption is fairly constant compared to equilibrium concentrations when $a_w > 0.8$. Given that the data is accurate this model could thus be used to determine an average diffusion coefficient for high water activities assuming that there is no swelling and that the diffusion is not accompanied by another transport mechanism. The diffusion coefficient could be determined by coupling the

experimental data with the optimization tool in Comsol MultiPhysics within the model. This was not done during this work. However the diffusion coefficients were determined by roughly fitting the data, except for data sets 5 and 7 where equation (13) was used again. The results are shown in table 4.12 as well as in the following section and in Appendix D.

Table 4.12 Estimated diffusion coefficients using a linear model in Comsol MultiPhysics

Data Set	D_{eff} (m^2s^{-1}) $x10^{12}$
2	12.5
3 and 4	2.50
5	33.88
6	5.25
7	33.88

4.4.2 Swelling Kinetics

Swelling kinetics was implemented as an addition to the previous linear model done in Comsol Multiphysics. One-dimensional geometry was used as it reduced the computing time substantially and still produced the same results as indicated by figure 4.7. The proportionality constant for the moving boundary was set to be -1 (the value is negative as the volume increase is in the negative x-direction) and the diffusion coefficients were taken from table 4.12. The results comparing the models with and without swelling kinetics are shown in figure 4.8 and in Appendix D.
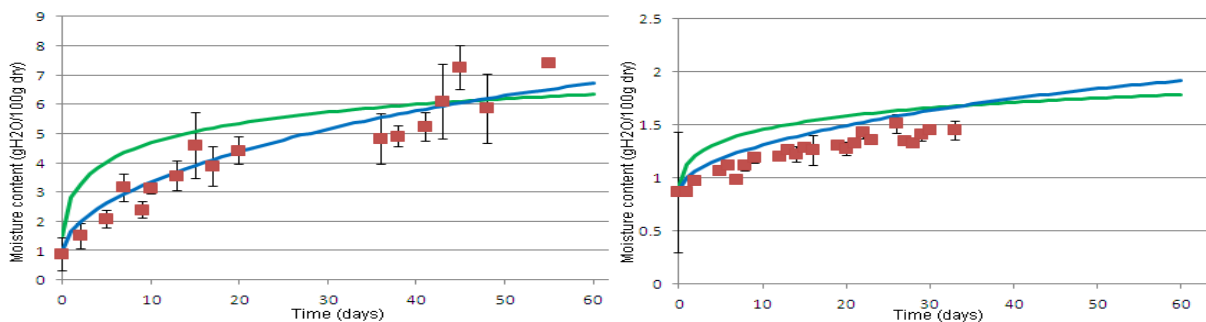

Figure 4.8 Moisture sorption versus time for a linear model (blue line) and a non-linear model including swelling kinetics (green line), both done in Comsol. a) experimental data set 5 b) experimental data set 7. D_{eff} was taken from table 4.12.

The R^2 values were not calculated for the models presented in figure 4.8 as it was expected to be a value close to 0. The model with swelling kinetics generally shows a worse fit than the linear model. However this does not show that the model including swelling kinetics is not an accurate representation of the moisture migration, because the diffusion coefficient was estimated using equation (13). What can be said about the model including swelling kinetics is that equilibrium is reached faster, which is a problem with the linear model. The blue lines in figure 4.8 a) and b) goes much slower towards equilibrium than the green line. It could be said that neither the blue nor the green lines in 4.8 reaches equilibrium in 60 days, predicted in the literature [15]. Nevertheless, it is clear from the figure that equilibrium is reached faster for the green line. This might be an indication that swelling kinetics is an important mechanism in the moisture migration through chocolate. But in order to fully evaluate if swelling kinetics has an impact in the modeling of moisture migration through chocolate, more needs to be known about the diffusion coefficient. In addition to the diffusion coefficient, the swelling proportionality constant must be determined as well. Similarly as with the linear model in Comsol, this model could also be used to predict the diffusion coefficient assuming that swelling kinetics is affecting the diffusion.

4.4.3 Non-linear Model

The results for the non-linear model described in section 3.4.2 are given in figures 4.9 and 4.10. A summary of R^2 values, i.e. estimate of how well experimental data fit the model, for the experimental data sets (table 4.2) are presented in table 4.19

Figure 4.9 a) – d) Mositure content versus time for the non-linear model with experimental data sets 1 – 4, as described in table 4.2.

The fitting parameters described in section 3.4.2 were determined using FMINUIT and they are given in Appendix B. They were fitted freely i.e. independently of each other and without requirement that any parameter is constant for all data sets. This is a significant simplification as $C_{1l} + C_{1n}$ should represent the boundary condition at x = 0. The simplification was done in order to get a better fit for the curves.
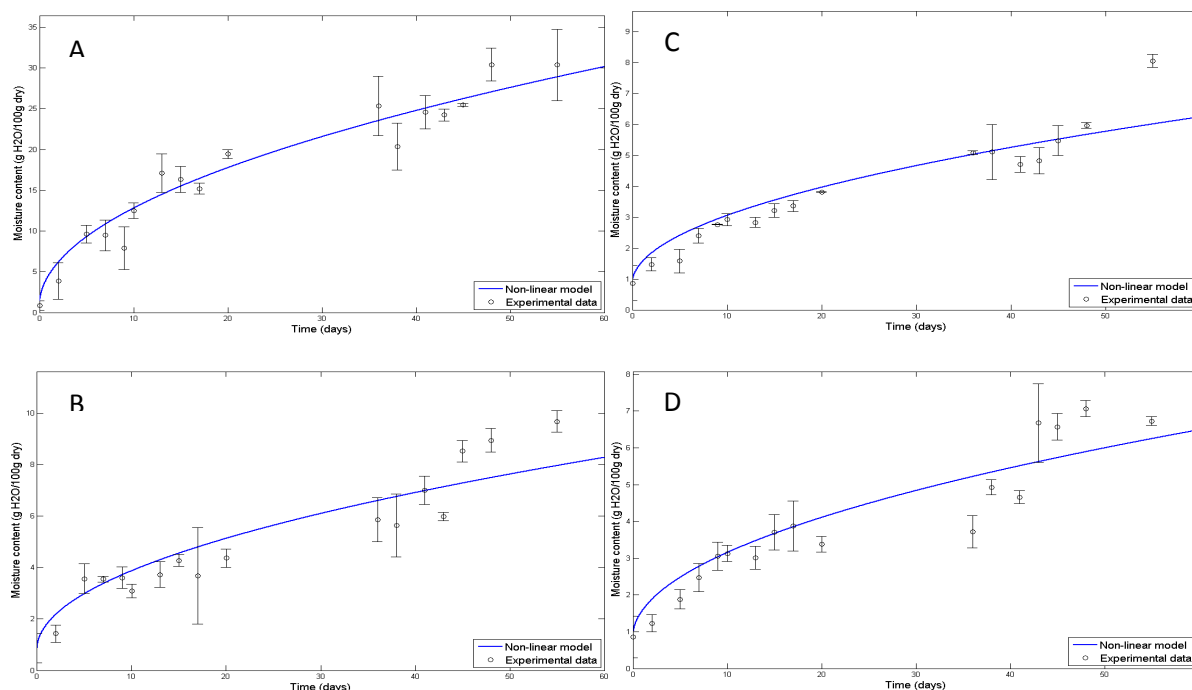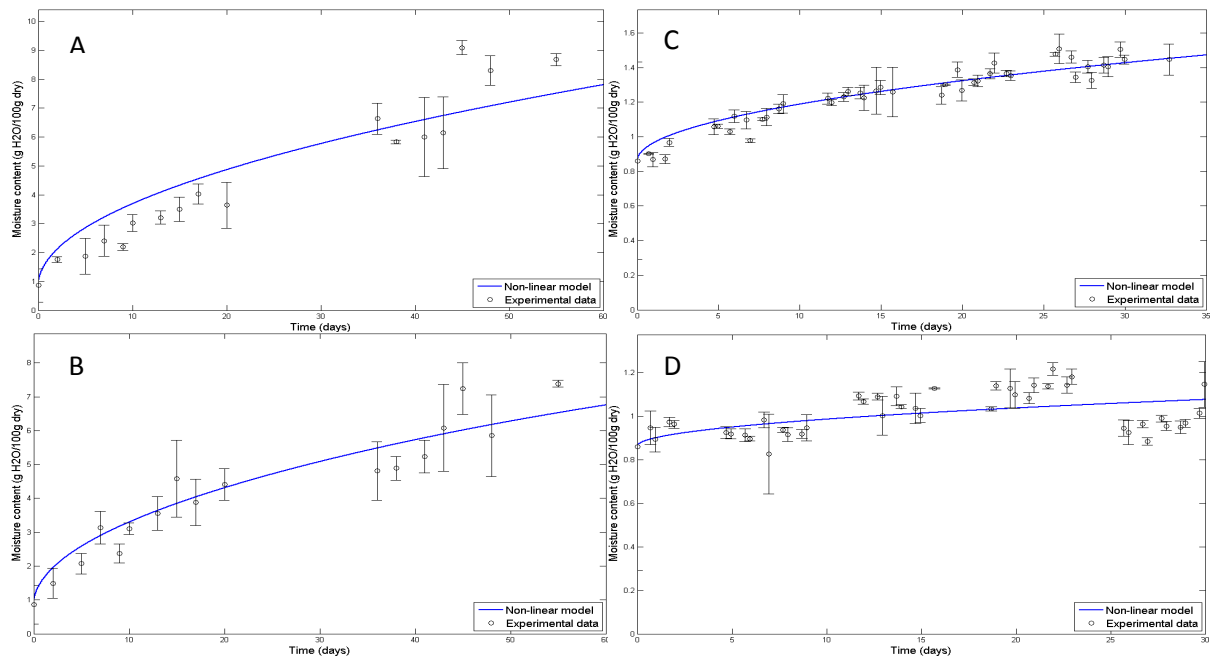
Figure 4.10 a) – d) Mositure content versus time for the non-linear model with experimental data sets 5 – 8, as described in table 4.2.

Table 4.19 R^2-values for the non-linear model

Data set	R^2
1	0.94371
2	0.86411
3	0.88253
4	0.86233
5	0.90444
6	0.84917
7	0.90655
8	0.22139

The purpose of this non-linear model was not to give a general expression of the moisture migration through chocolate. The model parameters were determined by least square fitting and they do not presenent any physical parameters that can be measured or calculated in any other way. However, if this model gives a better fit to the data than the linear models, it is an indication that a linear expression for the diffusion coefficient, given by equations (6), (7), (8), (12) and (13), might be inadequate for predicting moisture sorption behavior in dark chocolate.

Comparing table 4.19 to the results of the linear models one can say that there is no significant difference in the results, although the non-linear model fits the data slighly better. The non-linear model was expected to fit the data better, but the R^2 values were not indicating a perfect fit of the curve. A better results was expected for data set 8, shown in figure 4.10 d) as a non-linear model should be able to predict a maximum point as observed at t =23 days. However as the figure shows, the model values for moisture content increases throughout the whole time range.

There could be two explanastions why the model did not fit the data perfectly even though curve fitting was used. The first comes from the inconsistency of the data as inacurate measurment are inevitable within the experimetal design. This problem is easiest solved by doing more measurments

and use more samples for each data point. A consistent set of data is of outmost importance when validating a model. The second reason for the mediocre fit is that the model might be inadequat under the assumptions used. Equation (40) was used to describe the non-linear diffusion coefficient which is most likely not a representation of the actual case. The diffusion coefficient is most probably exponentialy dependant on concentration, opposed to linearly, as suggested in section 2.6.2. Equation (40) was used because an approximate analytical solution was known for that particular example of non-linear diffusion. This was not the case for a exponentially dependant diffusion coefficient described in equation (27). In order to obtain a better non-linear model more understanding about the diffusion coefficient is needed. The modeling itself can be solved by using a FEM-based software such as Comsol MultiPhysics rather than finding an analytical solution of the non-linear diffusion equation.

5. Conclusion

The aim of this thesis was to find a mathematical representation of the moisture migration through chocolate that predicted the collected data as accurately as possible. This was done by developing five different models and verifying them using experimental data collected during this work and the work of Galler (2011). Additionally the diffusion coefficient was determined using five different methods.

The first model, which was based on a Fickian diffusion mechanism and only allowed moisture to migrate across one of the surfaces of the sample, showed overall the best fits for the experimental data. However, the model can only be used in specific cases. This is mainly because the diffusion coefficient that gave the best fit was determined as the average diffusion calculated from experimental data. However, for some of the data sets, the expected theoretical equation for the diffusion coefficient gave the best fit. This equation gives a more general model as experimental data is not necessary to calculate the diffusion coefficient. In overall the Fickian diffusion model showed good fits for the data but limited capability of generally describing moisture migration through chocolate, as the diffusion coefficient that gave the best fit and the equilibrium concentration was calculated from the experimental data

The second model, which was also used to model Fickian diffusion, completely failed to predict the data. In contrast to the previous one, this model had boundary conditions set as constant concentrations at both ends of the sample. Mathematically this produces results with an equilibrium concentration between the two constant values at the surface and a transfer at both surfaces is allowed. This was not an accurate representation of the experimental setup and therefore the model showed much lower values of the moisture content than indicated by the data. Nevertheless the model could still be useful in cases where the boundary conditions are more applicable. Both models based on Fickian diffusion were developed using Matlab.

The next model was an adaptation of the first one, where the boundary condition for the Fickian diffusion was taken from the moisture sorption isotherm rather than the experimental data. This model as well as the fourth was developed using Comsol MultiPhysics. This model was mainly used to show that increasing the geometry from 1D to 3D did not have a significant impact on the results. There was a difference in the results between this model and the first model which was assumed to be due to the inability of the model to predict the diffusion coefficient. Another problem was that the equilibrium moisture content was not reached within 60 days according to this model, a time duration earlier reported by Biquet and Labuza (1988). This particular problem could be fixed by introducing swelling kinetics of the cocoa particles, a non-Fickian phenomenon. This was done in the fourth model and the moisture content went significantly faster towards equilibrium. However the problem with the diffusion coefficient remained which resulted in poor fits for the data. The results in this work gave a clear indication that swelling kinetics is an important mechanism in moisture diffusion through chocolate although further research is required before any general conclusions can be made.

The final model was a curve fitting experiment done in order to see if using a non-linear diffusion coefficient had a significant impact on the results. The results showed a better fit than for the first model, which was expected, but the difference was not significant. Though, the non-linearity of the diffusion coefficient can still be observed from the results of the other models. The models seem to agree better with the data for lower values of moisture content. This is an indication that the diffusion coefficient is fairly constant at low water concentrations but increases rapidly for higher. The reason for this is that structural changes, such as swelling or crack formation occur, which increases the rate of moisture migration. Mathematically, a diffusion coefficient that is exponentially

dependent on concentration would fit this description. In order to fully understand the moisture migration through chocolate and in order to develop accurate models, the diffusion coefficient needs to be further studied. The results of this work indicate that migration is accompanied by structural changes and non-Fickian diffusion occurs. To model this non-Fickian diffusion, a concentration dependent diffusion coefficient needs to be determined.

6. Future Work

In order to improve the mathematical models for moisture migration through chocolate a few more studies could be conducted. Most importantly a detailed study of the diffusion coefficient of moisture migration through chocolate is needed in order to develop a general model. The aim of the study could be to determine the effective diffusion coefficient as a function of the moisture content. This can be done by studying the *regular regime* in the moisture sorption process. The regular regime is a stage in the sorption process when the concentration profile becomes independent of the initial conditions. This is true for many cases of concentration dependent diffusion coefficients. The regular regime sorption curve is then governed by the diffusion coefficient, boundary condition and geometry [36]. Additionally the diffusion coefficient will vary differently for swelling and non-swelling systems which can also be taken into account. A detailed study about the regular regime and concentration dependent diffusion coefficient was conducted by Schoeber in 1976. The concentration dependent diffusivity can also be studied experimentally using pulse field gradient NMR as well as MRI [2].

Furthermore, to get a complete model, temperature dependence of the moisture migration needs to be studied. Structural parameters such as the diffusion coefficient and solid fat content depend greatly on the temperature which affects the moisture migration. As mentioned in 2.5.2.3, there are studies that demonstrated the moisture sorption dependence on the temperature and this needs to be incorporated into the model. The temperature dependence of the diffusion coefficient can also be determined by studying the regular regime.

Using numerical solution for the models will allow for more complicated boundary conditions and geometries to be used. These can be a better representation of the reality of the problem and should be preferred over using analytical methods. Comsol MultiPhysics proved as a valuable tool for modeling of the diffusion of diluted species and should be used in future work as a replacement for of Matlab or Excel. It can also be coupled with Matlab if more data analysis is required. Using Comsol MultiPhysics will save a lot of time spend writing scripts and functions in Matlab. Instead the focus of a study could be to develop experimental methods to carefully determine the boundary conditions for the problem that are given as surface concentration of moisture at the filling/chocolate and chocolate/atmosphere interface. At least one of the concentrations is not constant with time, which was neglected in this work.

Moreover, it is also important to collect accurate data. Experimental work such the one conducted by Galler (2011) needs to be extended by more data points. The moisture content should be measured more frequently over 50-60 days with at least one measurement per day for the first half of the experiment.

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Appendix

Appendix A. Data from the Moisture Sorption Experiment

Table A1. Data calculated using equations (24) and (25) used for the plot in figure 4.3.

Time (days)	Average moisture calculated by the weight change method (gH$_2$O/100g dry)	Standard deviation (gH2O/100g dry)	Average moisture content calculated by the evaporation method (gH2O/100g dry)	Standard deviation (gH2O/100g dry)
0	0.861246	0.570245	0.861246	0.570245
0.708333	0.902765	0.001265	0.945741	0.077236
0.958333	0.866937	0.041504	0.892586	0.056054
1.708333	0.871168	0.027078	0.972533	0.022057
1.958333	0.968528	0.023078	0.962667	0.017422
4.708333	1.057916	0.045662	0.924602	0.027228
4.958333	1.060806	0.012852	0.91911	0.021758
5.708333	1.028802	0.015628	0.913169	0.029389
5.958333	1.118442	0.036179	0.897116	0.010676
6.708333	1.095997	0.049177	0.983004	0.035478
6.958333	0.978424	0.010214	0.826122	0.183367
7.708333	1.101838	0.007502	0.937992	0.011512
7.958333	1.113021	0.050394	0.916284	0.032075
8.708333	1.161087	0.02664	0.918987	0.019551
8.958333	1.191361	0.054259	0.947114	0.059416
11.70833	1.221144	0.031104	1.092752	0.018445
11.95833	1.19843	0.019716	1.067569	0.012221
12.70833	1.230114	0.027392	1.090249	0.015871
12.95833	1.262002	0.023646	1.00321	0.089339
13.70833	1.253182	0.033444	1.0908	0.04241
13.95833	1.224737	0.0741	1.043796	0.008164
14.70833	1.266431	0.136047	1.037336	0.069692
14.95833	1.286536	0.040767	1.003234	0.032963
15.70833	1.259191	0.142994	1.127603	0.001826
18.70833	1.23952	0.049456	1.034143	0.008381
18.95833	1.300497	0.003819	1.139936	0.019504
19.70833	1.388613	0.043011	1.127315	0.089234
19.95833	1.269193	0.061372	1.098459	0.061889
20.70833	1.315391	0.01964	1.083307	0.046758
20.95833	1.323569	0.033435	1.141869	0.033126
21.70833	1.364678	0.029239	1.136878	0.012374
21.95833	1.425656	0.057773	1.217952	0.02847
22.70833	1.366201	0.018221	1.142926	0.03742
22.95833	1.353537	0.027674	1.182082	0.036184
25.70833	1.476659	0.009851	0.945449	0.036945
25.95833	1.508705	0.085905	0.928576	0.056303
26.70833	1.461402	0.034409	0.963626	0.017324

26.95833	1.342665	0.030375	0.884083	0.016016
27.70833	1.405325	0.03559	0.989545	0.015551
27.95833	1.325837	0.046048	0.955044	0.01965
28.70833	1.414304	0.045592	0.948886	0.029066
28.95833	1.404093	0.057792	0.967573	0.018055
29.70833	1.504165	0.042851	1.014319	0.022455
29.95833	1.446241	0.026803	1.146028	0.103689
32.70833	1.446234	0.090838		

Appendix B. Fitting Parameters for the Non-linear Model

Table B.1. Fitting parameters for the non-linear model determined using FMINUIT with initial guess value $D_l = 1e^{-12}$, $D_n = -1e^{-12}$, $C_{1l} = 0.5$, $C_{1n} = -0.5$

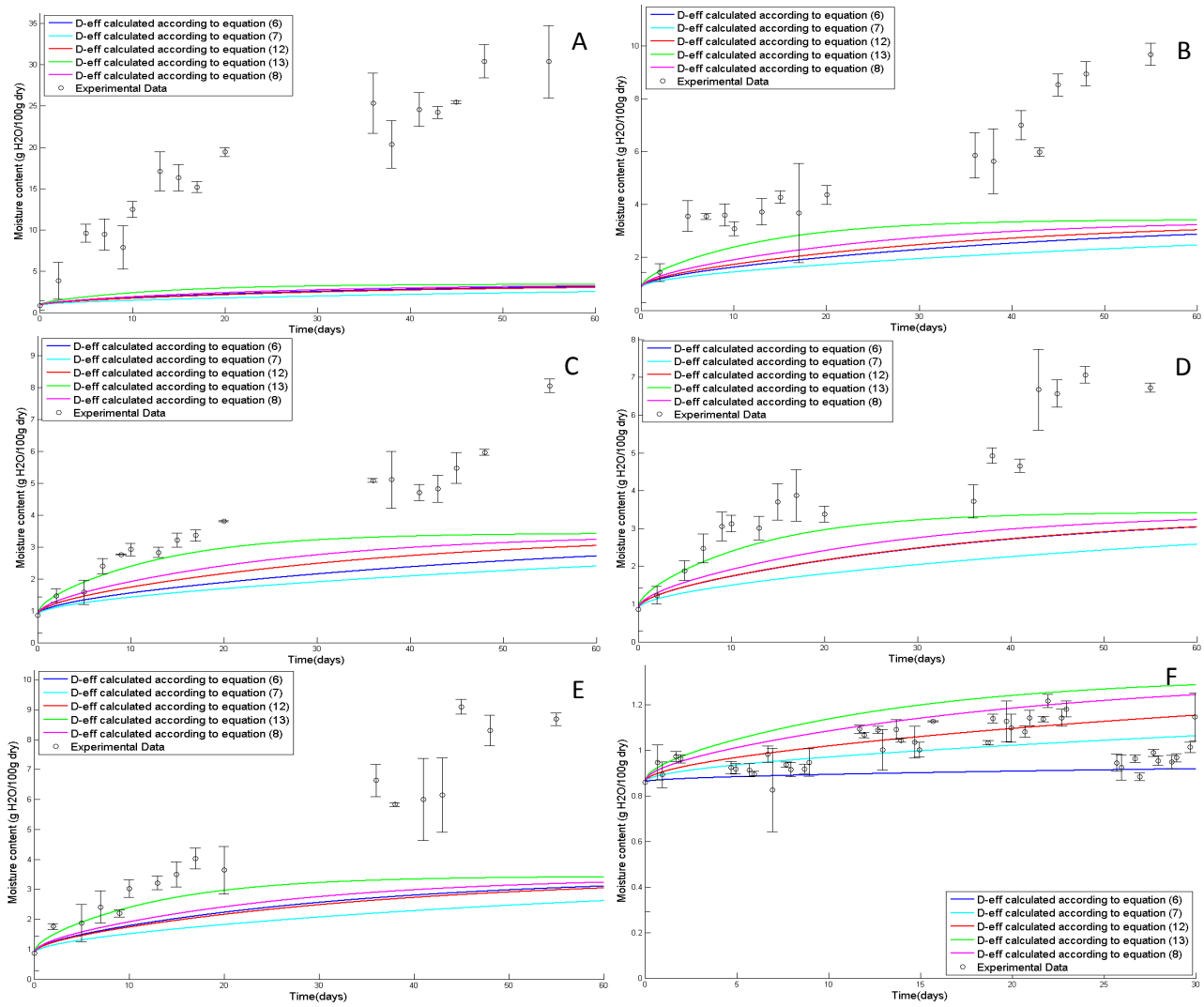| Data set	D_l	D_n	C_{1l}	C_{1n}
1	0.66122e-12	-0.44427e-13	2.4564	2.2425
2	0.15856e-13	0.15045e-12	0.44362	0.38718
3	0.78865e-13	0.65249e-11	0.60149e-1	0.11494
4	0.58185e-13	0.30027e-12	0.25660	0.37605
5	0.24939e-11	-0.10149e-11	0.20301	0.20304
6	0.37693e-13	0.20673e-12	0.44194	0.33946
7	0.12563e-11	-0.93111e-12	0.66925	-0.42340
8	0.12170e-11	-0.93767e-12	0.64489	-0.44193

Appendix C. Results from Model Two

Figure C.1 Moisture content versus time for Model Two plotted against experimental data: a) set 1, b) set 2, c) set 3, d) set 4, e) set 6, f) set 8.

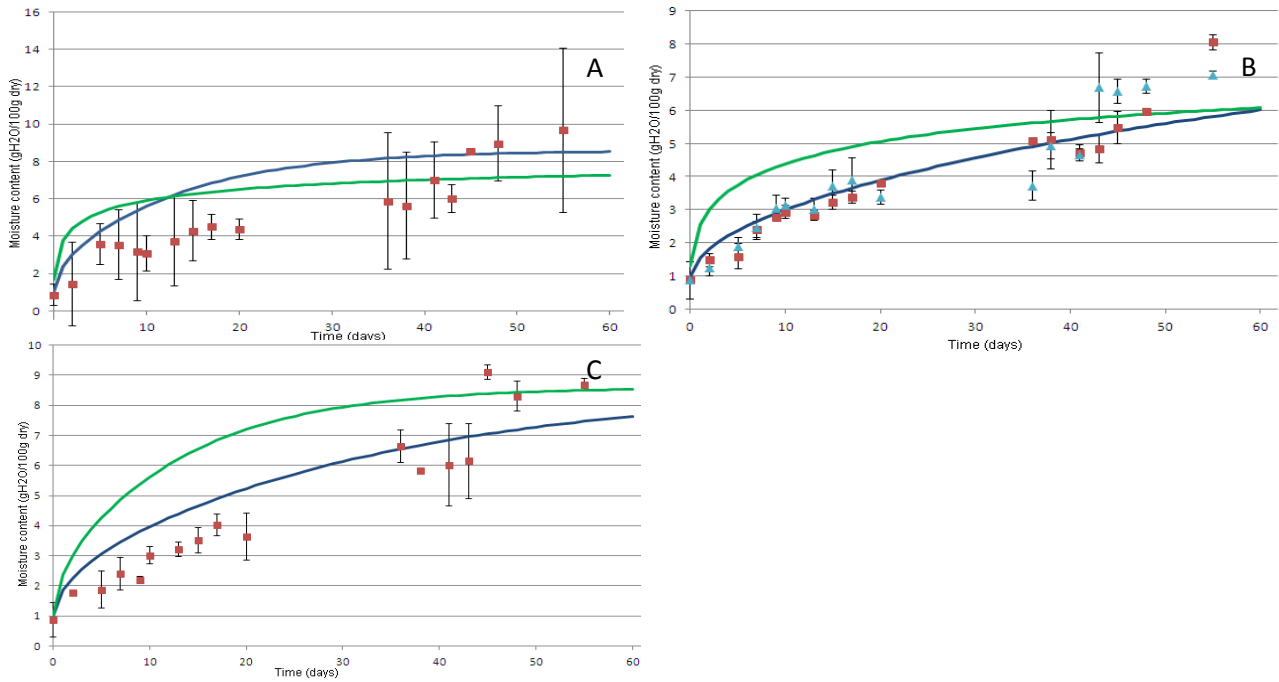# Appendix D. Results from the models done in Comsol MultiPhysics

Figure D.1 Moisture content versus time for a linear model (blue line) and a non-linear model including swelling kinetics (green line), both done in Comsol. a) experimental data set 2, b) experimental data set 3 and 4, c) experimental data set 6. D_{eff} was taken from table 4.12.