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Hervé This, Vo Kientza

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About Aguilera *et al*. (2004): chocolate, migration of lipids, diffusion and capillarity

Hervé This vo Kientza[1,2] *

1. Université Paris-Saclay, INRAE, AgroParisTech, UMR 0782 SayFood, 22 place de l'agronomie, 91120, Palaiseau, France.
2. Inrae-AgroParisTech International Centre for Molecular and Physical Gastronomy, https://icmpg.hub.inrae.fr/ .

*Correspondence: herve.this@inrae.fr

Abstract

An article published in 2004 by Aguilera *et al*. is useful for science and technology education, because it shows the difference between diffusion and capillarity as two important mechanisms of mass transfer. It is also an opportunity to recommend supplementing the physical descriptions of food systems (using the dispersed system formalism) by a thorough analysis of their chemical compositions.

Keywords

chocolate, diffusion, capillarity, microstructure

The purpose of this commentary article is not only to show why an article published about 20 years ago by Aguilera *et al*., although old, remains useful for food science, food technology and food engineering education, but it is also an opportunity to use recent data to examine how the microstructure of chocolate is changing as a function of temperature.

Often review articles begin with an introductory paragraph explaining a question dealt with in an article; they go on explaining its context, then they present the ideas of the article reviewed in the order in which they appear in the article (Gülpınar and Güçlü, 2023), and they conclude by an evaluation of the document, the interpretations being separated from the facts. Here, the organization of this commentary will be different: it will be first explained why the chosen article, about lipid migration in chocolate, is useful for food science and food technology education, but then a scientific question dealt with in the article, about chocolate microstructure, will be discussed. So it is not so much an evaluation but more a scientific discussion.

Diffusion vs capillarity

The title of the article reviewed is *Fat migration in chocolate: diffusion or capillary flow in a*

particulate solid?—A hypothesis paper, by Aguilera *et al.* (2004). Since its publication, the students in our university have been invited to study it, because it explains various concepts that are useful for food science, food technology and food engineering. To make it short, the article discusses - as is well said in the title - diffusion and capillarity in "chocolate" (it will be explained later why quotation marks are used here for the word chocolate), in particular during fat blooming, *i.e.*, the formation of a whitish haze on the surface due to recrystallization of cocoa butter when chocolate is stored at elevated temperatures, depriving it from a smooth appearance, bright color, and gloss (Hartel 1999).

Chocolate is made of cocoa butter, as the most important ingredient, *i.e.*, a mixture of triglycerides for which the fatty acid residues are mainly those of oleic acid (cis-octadec-9-enoic acid, 35 %), stearic acid (n-octadecanoic acid, 34 %), palmitic acid (hexadecanoic acid, 26 %), plus linoleic acid ((9Z,12Z)-octadeca-9,12-dienoic acid) and arachidonic acid ((5Z,8Z,11Z,14Z)-5,8,11,14-eicosatetraenoic acid) (Longchampt and Hartel, 2004).

Having different compositions in their three fatty acid residues, the various triglycerides of cocoa butter can melt at different temperatures. At "room temperature" (again, the reason why there are quotation marks will be discussed later), some triglycerides - those melting at temperatures lower than "room temperature" - can make a liquid phase, whereas others, melting at higher temperatures, can make a solid phase. By the way, as the first are "oils", the title of the article should perhaps have included "oil migration", instead of "fat migration" (IFST, 2023), as in Galdamez *et al.* (2009).

In certain circumstances, the oil (*i.e.*, liquid) fraction of lipids migrates inside the "crystal structure" made by the lipid crystals (Miquel *et al.*, 2001; Howard, 2020). The main question discussed by Aguilera *et al.* is: how does this "migration" take place? This question is very broad, because the possible mechanisms for molecular motions and mass transfers are many, but the authors discuss in particular the question:
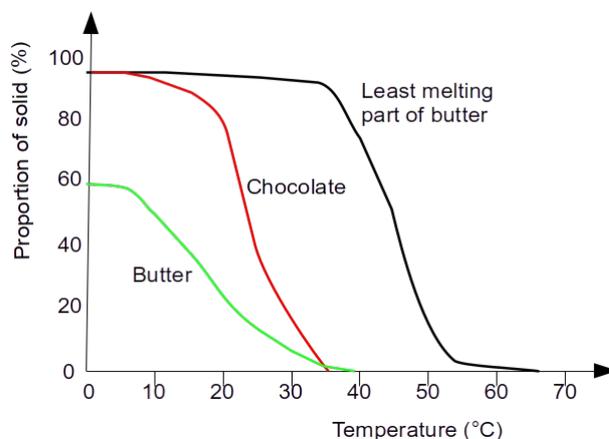

Figure 1. For lipids, the solid content decreases regularly from 100 % at about -10 °C toward 0 % at more than 55 °C, due to the great number of different triglycerides, each having a particular melting point (from This, 2022). Here the melting curve of cocoa butter is compared to the one for butter and for the fraction of butter that melts at the highest temperature, as determined by various analytical methods such as nuclear magnetic resonance spectroscopy (from Shenk and Peschar, 2004; Lopez and Ollivon, 2009; This, 2014).

can we speak of "diffusion", or is it better to speak of "capillarity"? The word "diffusion" is ubiquitous in molecular gastronomy studies (Burke *et al.*, 2021), and, more generally, in food science, food technology and food engineering. A review of the scientific literature in these fields shows that one should be cautious about this word, and also about the meaning of "diffusion coefficients"... because often it means an effective coefficient rather than what is recommended by the International Union of Pure Chemistry and Applications of Chemistry (IUPAC).

One of the best starting point, for such a discussion of the terminology, is the consultation of the *Compendium of Chemical Terminology* (so called ''Gold Book'') of IUPAC (2009a). It provides various definitions including the word "diffusion", beginning with "*The spreading or*

scattering of a gaseous or liquid material. [...] Molecular diffusion is the net transport of molecules which results from their molecular motions alone in the absence of turbulent mixing; it occurs when the concentration gradient of a particular gas in a mixture differs from its equilibrium value".

Diffusion phenomena are quantitatively characterized by diffusion coefficients, but according to IUPAC, "the diffusion coefficient is the proportionality constant D, relating the flux of amount of entities B to their concentration gradient":

$$J_n = -D \nabla c_B$$

There are other diffusion coefficients, such as rotational diffusion coefficient, differential diffusion coefficients, chemical diffusion coefficient, interdiffusion coefficient, and, most importantly, the self-diffusion coefficient D^*_i, which is defined as the diffusion coefficient of species i in the absence of a chemical potential gradient. It is related to the diffusion coefficient by:

$$D^*_i = D_i \frac{\partial \ln(c_i)}{\partial \ln(a_i)}$$

where a_i is the activity of i in the solution, and c_i is the concentration of i.

Aguilera et al. do not go into such details, but they could have done it, because when the oil in chocolate makes a continuous liquid phase, and even when it is restricted to small oil isolated pockets within a solid framework, the triglycerides of this oil exhibits molecular diffusion.

But the authors should not be criticized, because the article focuses on mass transfer, occurring often faster than by diffusion (Quéré et al., 1999). Indeed, to understand their goal, the best is to quote them: "Molecular or Fickean diffusion is widely used (and abused) by food engineers as a general model for mass transfer, most notably in drying, leaching, and frying. The approach has the advantage that by plotting experimental data in the form of log (unaccomplished ratio of mass transferred) against time, an apparent or effective diffusion coefficient, D_{eff}, can be determined from the straight portion of the curve (Schwartzberg, 1987). The simplicity of the method has resulted

in that during a 20-y period over 170 papers from only 5 journals have reported data of D_{eff} or moisture transfer in food materials (Saravacos and Maroulis, 2000). The parameter (which may be correctly redefined as a mass transfer coefficient) actually encompasses all possible forms of mass transfer involved in the process, not only diffusional ones. A major drawback of this practice is that no efforts are made to resolve microstructural aspects, understand the process, and find out actual mechanisms of mass transfer involved (Aguilera and Stanley 1999)."

As said, one virtue of this text is to compare Fickean (some write "Fickian") diffusion with capillarity, i.e., the tendency of liquids to be drawn into the confined space of a narrow tube or between at least two surfaces (Von Honschoten et al., 2010). The article considers the case of flow in porous media, generated by an interfacial pressure gradient (as when there is meniscus).

More generally, the article explains both phenomena of diffusion and capillarity, giving examples of food science or food technology where they occur, and it discusses some general equations for mass transfer. In both cases, a fast increase is followed by an asymptotical behaviour, but the slopes in the time-mass diagrams can be different. For the Fickian case, the ratio of the mass at instant t by the mass when equilibrium is reached is proportional to the square root of the time... and the same holds for capillarity as described through the Lucas-Washburn equation (Zhmud et al., 2000; De Gennes et al., 2004).

After discussing this, the articles goes on examining the experimental data obtained at the time it was published, in order to propose the importance of capillarity for liquid lipids ("oil") moving through the solid lipid framework ("a continuous phase of solid and liquid fat"). Here it should be added that other conclusions were favored later (Deka et al., 2006 ; Galdamez et al., 2009): observations of oil migration through chocolate using magnetic resonance imaging have shown that the dominant mechanism is

diffusion, and that if capillary pressure is involved, it is a minor contributor. However it is not the goal of this commentary article to discuss this matter: rather the chocolate microstructure is considered. The authors describe chocolate as a "particulate system", but what does it mean? And is it correct? Comparing chocolate to butter is useful for a better understanding of the microstructure of chocolate.

Butter: which microstructure?

The composition of cocoa butter having been given before, it has now to be observed, for comparison, that the triglycerides content of milk lipids is much more heterogeneous than for chocolate, with a total number of fatty acid residues reaching 400 (Jensen, 2002). The main residues are: butyric, caproic, caprylic, capric, lauric, myristic, pentadecanoic, palmitic, pamitoleic, margaric, stearic, oleic, linoleic, linolenic.

In order to describe the microstructure of butter (and of chocolate), it is convenient to use the "dispersed system formalism" (This vo Kienza, 2021a), using the letters G, O, S, W respectively for describing gas phases, liquid lipid phases ("oils"), solid phases (for example, ice, lipid crystals, etc.) and aqueous solutions. The symbol "/" stands for random dispersion, and the symbol "x" describes the interweaving of two continuous phases. For example, an emulsion is written O/W, or W/O; a dispersion of liquid pockets inside a solid is written O/S, or W/S, and a gelatin gel, with two continuous phases, is described by SxW (when the operator is commutative, the letters are in the alphabetical order). When needed, the physical "dimension" of the various objects being considered is described by D_0, D_1, D_2, or D_3, respectively for dimensions 0, 1, 2, 3, after a reference size is chosen.

Using this formalism, it is possible to analyse what many textbooks in food science and food technology (Friberg *et al.,* 2003; McClements, 2006; Khader, 2016) have been publishing, *i.e.,* that butter is an "emulsion". According to the *Gold Book* of IUPAC, an emulsion is "*a fluid colloidal system in which liquid droplets and/or liquid crystals are dispersed in a liquid. The droplets often exceed the usual limits for colloids in size*". Following the IUPAC definition, milk (from the female of *Bos taurus* in particular) can be an emulsion or not, depending on temperature. Indeed milk is mainly a dispersion of lipids (as D_0 structures) in an aqueous solution $D_3(W)$, but the issue is to know what is the physical state of the lipids: if they are in a liquid phase (O), then milk is indeed an emulsion $D_0(O)/D_3(W)$, but if they make fully solid structures ($D_0(S)/D_3(S)$) or if they make complex structures with both liquid and solid phases, such as in a ($D_0(S)@D_0(O))/D_3(S)$ system, then milk would be a "suspension" (IUPAC, 2009b; 2009c).

In order to decide which system describes milk, one has to look at the melting curve of milk lipids (Figure 1). At temperatures lower than - 10 °C, milk lipids are entirely solid (as well as water), and butter is a solid suspension $D_0(S_1)/D_3(S_2)$, S_1 and S_2 standing respectively for ice and for solid lipids, but at temperatures higher than 60 °C, all the milk lipids are melted and butter is either an emulsion ($D_0(O)/D_3(W)$ or $D_0(W)/D_3(O)$) depending on the way it has been obtained) or a biphasic liquid ($D_3(O)σD_3(W)$) (here σ stands for superposition).

What about milk at "room temperature"? This is not well defined, as the summer temperatures in hot countries are very different from the temperatures in cold countries in winter: at a "room temperature" of 15 °C, the solid lipid content would be slightly higher than 50 %, but at a room temperature of 30 °C, it would be less than 15 % (Jacques *et al.*, 1999). Anyway, in both cases, milk is a suspension (because of the solid component of the dispersed structures) rather than an emulsion.

From milk, cream is recovered, and butter is produced by churning. After butter production, some of the aqueous solution (limited to 16 % w by international regulations) (EC, 1998) can remain in the system, but the liquid lipid fraction (O)/solid lipid fraction (S) ratio still depends on temperature, and the system can be a "gel", with

two kinds of liquid droplet ($D_0(O)$, $D_0(W)$) inside a continuous solid lipid matrix $D_3(S)$ (IUPAC, 2009c), or a suspension if the oil phase is continuous. Metastabilizing phenomena such as supercooling effects can occur (Castro-Alayo *et al*., 2023), adding to the allotropy that is well known for lipid crystals, and the proportion and distribution of liquid and solid lipid fractions depend not only on the temperature, but also on the history of the product (Ronholt *et al.*, 2014). Finally sintering of lipid crystals can make it likely that butter is a complex gel (continuous solid phase) when the temperatures are those at which butter is usually consumed by humans (Johansson and Bergenstahl, 1995; This, 2016).

As chocolate includes cocoa butter, the same question arise, concerning its microstructure: is it a suspension, or a gel, with respectively a continuous liquid lipid phase, or a continuous solid lipid phase? The melting curve of cocoa butter is narrower than the melting curve for butter (Figure 1), and here, the two solid contents to be considered for answering the question are 90 % at 15 °C, and 20 % at 30 °C. These values can be compared with the maximum packing coefficient (74 %) for spheres all of the same diameter, and the unlikely100 % value when spheres of all sizes are present (so called Apollonian packing) (Kasner and Supnick, 1943), or to other values when polydispersity is taken into account (Howe *et al*., 1997). Of course, the full packing is not possible, because one has to consider the presence of liquid lipids, and a 92 % maximum solid content is more realistic (Kwok *et al.*, 2020).

Aguilera *et al.* seem to assume a suspension system, based on some articles that do not indicate the temperature at which their measurements were made (Loisel *et al.*, 1997; Hartel, 1998; Babin *et al.*, 2005; Hartel *et al.*, 2016; Howard and Maleky, 2022), but keeping in mind the 92 % limit, and taking into account the sugar crystals and plant solid particles, which increase to solid volume fraction, one could doubt of their assumption. Indeed, lipid crystals can undergo sintering in chocolate as in butter (Johansson and Bergenstahl, 1995), and because chocolate is made from an initial melted mass

Figure 2. When an emulsion of chocolate in water is whipped, an aerated system called "chocolate chantilly" is obtained only when the system is cooled: this indicates that a continuous solid network is probably established, as these temperatures (This vo Kientza, 2021b).

(during conching), percolation phenomena should be taken into account in order to envision a possible suspension-to-gel transition (De Gennes, 1979). Moreover the fact that ''chocolate chantilly'' (This vo Kientza, 2021b) can be obtained only when it is cooled corroborates the assumption that a continuous solid network is established at these temperatures (Figure 2).

Let us conclude temporarily this discussion by quoting the old controversy between Plato and Aristoteles: for Plato, chocolate would have been an entity, but for Aristoteles, "chocolate" does not exist, and there are rather chocolates... perhaps with different microstructures depending on the temperature at which they are stored.

Back to capillarity

Aguilera *et al.* promote the idea of capillarity as a mechanism for oil migration within the chocolate "matrix", but what is this matrix? As seen before, an important preliminary question is to know if

they assume that it is a continuous one. For sure, capillarity can occur both with suspensions between the solid particles, or with connected gels, inside the solid network (This vo Kientza, 2021c), and mercury porosimetry can be performed for the two systems (Loisel *et al.*, 1997). But another question is to know if capillarity is occurring in the same way or differently in the two kinds of systems? It is interesting that whereas the chemical bonds between the triglycerides of the liquid fraction and the compounds making up the surface of the "solids" in presence are highly determinant, as well as the size of the "pores", the chemical question is not discussed: the discussion in the article is mainly from a physical point of view. For sure, the classical dichotomy diffusion/capillarity is well analyzed (even if there are other possibilities than the Lucas-Washburn equation), but can the oil migration be discussed without going down to molecular description? And what about other mechanisms, such as depletion mechanisms, Ostwald ripening, etc. (Zhao and Tahkar, 2017)? What about the influence of sugar crystals (perhaps covered with a water layer) and plant particles (Shen *et al.*, 2023)?

All that being written, I shall continue to advise students to read the article reviewed here, for it is a direction in which they will not stray, in particular if they go beyond what was written when it was published (about 20 years ago): they will be invited to use any word of the article as a possibility to ask scientific questions, and to discover the advances since the time of its publication. They will be invited to question every word and every concept, and to supplement their reading with bibliographical research into recent works on chocolate, in particular using new analytical tools such as confocal microscopy, electron miscrocopy, small angle X-ray or neutron scattering (Metilli *et al.*, 2020; Jeffries *et al.*, 2021; Pugh *et al.*, 2023). But they will also be invited to look beyond the physics-chemistry dichotomy and always seek out the relationships between the two separate descriptions: let's stand on our two feet, physics *and* chemistry!

Two experiments are proposed, as a conclusion to the discussion given here. The first is giving a hint to the solution of the gel versus suspension question: it consists in putting chocolate into oil; as a suspension will be diluted, solid particles would separate spontaneously, whereas a gel will keep its structure. The second experiment is to put a piece of chocolate in water, and to observe the whitening of the surface. Why? Indeed, chocolates (observe the plural) are still wonderfully mysterious.

References

Aguilera JM, Michel M, Mayor G. 2004. Fat migration in chocolate: diffusion or capillary flow in a particulate solid?—A hypothesis paper, *Journal of food science*, 69(7), R167-174.

Bouteille R, Gaudet M, Lecanu B, This H. 2013. Monitoring lactic acid production during milk fermentation by in situ quantitative proton nuclear magnetic resonance spectroscopy, *Journal of Dairy Science*, 96(4), 2071-2080. DOI: 10.3168/jds.2012-6092.

Burke R, Kelly A, Lavelle C, This vo Kientza H. 2021. *Handbook of molecular gastronomy*, CRC Press, Boca Raton (FL). https://doi.org/10.1201/9780429168703.

Castro-Alayo EF, Balcazar-Zumaeta CR, Torrejon-Valquia L, Medina-Mendoza M, Cayo-Colca IS, Cardenas-Toro FP. 2023. Effect of tempering and cocoa butter equivalents on crystallization kinetics, polymorphism, melting, and physical properties of dark chocolates, *LWT - Food Science and Technology*, 173, 114402. DOI: 10.3390/foods11121769.

De Gennes PG. 1979. *Scaling concepts in polymer physics*, Cornell University Press, New York.

De Gennes PG, Brochard-Wyart F, Quere D.

2004. *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*, Springer, Heidelberg (Germany, chapter 5.

Deka K, MacMillan B, Ziegler GR, Marangoni AG, Newling B, Balcom B. 2006. Spatial mapping of solid and liquid lipid in confectionery products using a 1D centric SPRITE MRI technique, *Food Research International,* 39, 365–371. DOI: 10.1016/j.foodres.2005.08.009.

EC. 1998. 98/582/EC: Council Decision of 6 October 1998 amending Commission Decision 97/80/EC laying down provisions for the implementation of Council Directive 96/16/EC on statistical surveys of milk and milk products, *Official Journal,* L 281, 17/10/1998 P. 0036 - 0038.

Friberg S, Larsson K, Sjoblom J. 2003. *Food Emulsions*, CRC Press, Boca Raton (FL).

Galdamez JR, Szlachetka K, Duda JL, Ziegler GR. 2009. Oil migration in chocolate: A case of non-Fickian diffusion, *Journal of Food Engineering,* 92, 261–268. DOI: 10.1016/j.jfoodeng.2008.11.003.

Gülpinar O, Güçlü AG. 2023. How to write a review article?, *Turkish Journal of Urology*, 39(S1), 44-8. doi:10.5152/tud.2013.054.

Hartel RW. 1999. Chocolate: Fat bloom during storage. The influence of structural elements. *Manufacturing Confectioner,* 79(5), 89–99.

Hartel RW, Jin J, Jaures E. 2016. Particulate effects on storage bloom in chocolate, *Manufacturing Confectioner*, 96, 59-64.

Howard BD. 2020. *Shear and Composition Effects on Porous Network Properties and the Permeability of Lipid Films*, Master's thesis, Ohio State University, 2020. http://rave.ohiolink.edu/etdc/view?acc_num=osu1593680466745792.

Howard BD, Maleky F. 2022. Quantification of

Porous Properties of Shear Crystallized Lipids, *Molecules*, 27, 631. DOI: 10.3390/molecules27030631.

Howe AM, Clarke A, Whitesides TH. 1997. Viscosity of emulsions of polydisperse droplets with a thick adsorbed layer, *Langmuir*, 13, 2617-2626. https://doi.org/10.1021/la960871f

IFST. 2023. *Oils and fats*, https://www.ifst.org/resources/information-statements/oils-and-fats.

IUPAC. 2019a. diffusion, *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"), 61, 2167. https://doi.org/10.1351/goldbook.

IUPAC. 2009b. emulsions, *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"), 62, 2167. https://doi.org/10.1351/goldbook.

IUPAC. 2009c. suspensions, *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"), 61, 2167. https://doi.org/10.1351/goldbook.

IUPAC. 2009d. gels, *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"), 61, 2167. https://doi.org/10.1351/goldbook.

Jacques H, Gascon A, Arul J, Boudreau A, Lavigne C, Bergeron J. 1999. Modified milk fat reduces plasma triacylglycerol concentrations in normolipidemic men compared with regular milk fat and nonhydrogenated margarine, *American Journal of Clinical Nutrition*, 70, 983–91. doi: 10.1093/ajcn/70.6.983.

Jeffries CM, Ilavsky J, Martel A, Hinrichs S, Meyer A, Pedersen JS, Sokolova AV, Svergun DI. 2021. mall-angle X-ray and neutron scattering, *Natural Reviews Methods Primers 1*, 70, https://doi.org/10.1038/s43586-021-00064-9.

Jensen RG. 2002. The composition of bovine

milk lipids : January 1995 to December 2000, *Journal of Dairy Science*, 85, 295-350. doi: 10.3168/jds.S0022-0302(02)74079-4.

Johansson D, Bergenstahl B.1995. Sintering of fat crystal networks in oil during post-crystallization processe, *Journal of the American Oil Chemist's Society*, 72(8), 911-920. DOI:10.1007/BF02542069.

Kasner E, Supnick F. 1943. The Apollonian packing of circles, *Proceedings of the National Academy of Sciences*, 29 (11) 378-384.

Khader V. 2016. Textbook of food science and technology, *Indian Council of Agricultural Research*, New Delhi.

Kwok S, Botet R, Shglabow A, Cabane B. 2020. Apollonian emulsions. *EPL - Europhysics Letters*, 130 (3), 38001.

Lonchampt P, Hartel RW. 2004. Fat bloom in chocolate and compound coatings, *European Journal of Lipid Science and Technology, 106, 241–274. https://doi.org/10.1002/ejlt.200400938.*

Loisel C, Lecq G, Ponchel G, Keller G, Ollivon M. 1997. Fat bloom and chocolate structure studied by mercury porosimetry, *Journal of Food Science,* 62(4), 781-788.

Lopez C, Ollivon M. 2009. Triglycerides obtained by dry fractionation of milk fat. 2. Thermal properties and polymorphic evolutions on heating, *Chemistry and Physics of Lipids,* 159, 1–12.

McClements DJ. 2006. *Food Emulsions*, CRC Press, Boca Raton (FL).

Metilli L, Francis M, Povey M, Lazidis A, Marty-Terrade S, Ray J, Simine E. 2020. Latest advances in imaging techniques for characterizing soft, multiphasic food materials, *Advances in Colloid and Interface Science*, 279, 102154. https://doi.org/10.1016/j.cis.2020.102154.

Miquel ME, Carli S, Couzens PJ, Wille HJ, Hall LD. 2001. Kinetics of the migration of lipids in composite chocolate measured by magnetic resonance imaging, *Food Research International,* 34 (2001) 773-781.

Pugh MJ, Hamlett CAE, Fairhurst DJ. 2023. A short overview of bubbles in foods and chocolate, *Advances in Colloid and Interface Science*, 314, 102835. https://doi.org/10.1016/j.cis.2023.102835

Quéré D, Raphaël E, Ollitrault JY. 1999. Rebounds in a capillary tube, *Langmuir*, 15 (10), 3679-3682.

Rønholt S, Kierkensgaard JJK, Mortensen K, Knudsen JC. 2014. Effect of cream cooling rate and water content on butter microstructure during four weeks of storage, *Food Hydrocolloids*, 34, 169-176.

Shen L, Jin J, Ye X, Li Y, Zhang C, Jiang L, Zhao L. 2023. Effects of sucrose particle size on the microstructure and bloom behavior of chocolate model systems, *Food Structure,* 36, 100323.

Schenk H, Peschar R. 2004. Understanding the structure of chocolate, *Radiation Physics and Chemistry*, 71, 829-835.

This H. 2014. *Mon histoire de cuisine*, Belin, Paris (France).

This H. 2016. What can "Artificial Meat" be?, Note by note cooking offers a variety of answers, *Notes Académiques de l'Académie d'agriculture de France / Academic Notes from the French Academy of Agriculture (N3AF)*, 2(4), 1-10. https://doi.org/10.58630/pubac.not.a196614.

This vo Kientza H. 2021a. DSF. In Burke R, Kelly A, Lavelle C, This vo Kientza H, *Handbook of molecular gastronomy*, CRC Press, Boca Raton (FL).

This vo Kientza H. 2021b. Chantillys. In Burke R,

Kelly A, Lavelle C, This vo Kientza H, *Handbook of molecular gastronomy*, CRC Press, Boca Raton (FL).

This vo Kientza H. 2021c. Gels. In Burke R, Kelly A, Lavelle C, This vo Kientza H, *Handbook of molecular gastronomy,* CRC Press, Boca Raton (FL).

This vo Kientza H. 2022. *Calculating and problem solving through culinary experimentation*, CRC Press, Boca Raton (FL), 237.

Van Honschoten JW, Brunets N, Tas NR. 2010. Capillarity at the nanoscale, *Chemical Society Reviews*, 39, 1096–1114. https://doi.org/10.1039/B909101G.

Zhao Y, Takhar PS. 2017. Freezing of Foods: Mathematical and Experimental Aspects. *Food Engineering Reviews*, 9, 1–12. https://doi.org/10.1007/s12393-016-9157-z.

Zhmud G, Tiberg F, Hallstensson K. 2002. Dynamics of capillary rise, *Journal of Colloid and Interface Science*, 228(2), 263-269.