

Chapter 1

General introduction

1.1 Introduction

A foam is a dispersion of gas bubbles in a liquid, semi-liquid or solid continuous phase [Rajeev K. Thakur ET AL., 2003]. As a two phase system, foams are thermodynamically unstable, meaning that the two phases become completely separated when given enough time; however, depending on the system considered, the kinetics of foam breakdown can vary tremendously, from seconds up to hours. Aerated systems are encountered in a rather wide range of products and technologies, including personal care products, fire fighting substances, fermentation broths, enhanced oil recovery, and, perhaps most commonly, as a component of foods. Foamed food products are often at the apex of culinary art and include such consumer favourites as meringues, soufflés, cappuccinos and various confections, just to name a few. These products are primarily valued for their unique textures, which are often described with words such as light, delicate, smooth, etc. [Jack P. Davis ET AL., 2005]. The air inclusion or aeration process can be considered as one of the fastest growing operations in the food industry. The reasons for air inclusion embrace product functionality, enhanced consumer appreciation owing to the novelty value, a good volume-to-weight relationship, or a combination of these. The relevant element is the presence of air, incorporated as small bubbles, to provide specific texture [Massey A.H. ET AL., 2001].

As stated above, aeration is one of the fastest growing food processing operations. Specifically, it can be defined as a process in which air or carbon dioxide or any other gaseous mixture is included in a food system, to produce a gas phase surrounded by a condensed phase (solid or liquid) [Niranjan K. ET AL., 1999]. This type of process can give unique textures, like for sponge cake, bread, ice cream or other confectionery products, but the operating condition becomes very complex with food such as meringue, angel cake or nougat, because stability must be maintained during the adding process. Regarding meringue, the foam must show little expansion or collapse when heat-setting causes drying, and converts the foam from a liquid to a solid. In angel food cake, the protein foam is mixed with wheat flour (starch and protein) and sugar, then the mixture is baked to produce a cake. During baking, the foam-flour-sugar mixture must expand to a desired volume before heat-setting causes drying and

converts the foam from a liquid to a solid. Nougat presents the additional complication of maintaining a foam structure in a high sugar/low moisture environment [Lau K ET AL., 2004].

Once a foam is formed, it can be characterized by air phase volume (overrun), rheological properties and stability. But the purpose of aeration is not only aimed to confer specific organoleptic properties or enhance the shelf-life, but, from a manufacturing point of view, the aeration can be seen as a direct profit because it reduces the amount of food matter in the product, but also because it is possible to produce novel texture with potential market advantage [Niranjan K. ET AL., 1999].

Aerated food emulsions form an important class of food products. Examples are whipped cream, aerosol cream and ice cream. Macroscopically, aerated emulsions have a white opaque appearance and a relatively low density due to the high quantity of gas bubbles in the system. The integrity of these systems is mainly due to interactions between the main structural units, which are gas bubbles, emulsion droplets and in the case of ice cream, also ice crystals [George A. van Aken ET AL., 2001]. Then, some products benefit from air incorporation (ice cream, confectionery, salad dressings and mayonnaise), but for all these applications, it is important to preserve the size distribution of the air bubbles as well as the spatial distribution of the gaseous phase over the shelf-life of the product, which can go from a few minutes to months. Moreover, the classes of aerated foods are very wide and each type of alimentary foam has specific problems. For this reasons it is important, in the context of food processes, to divide the study of aeration into three types, depending on the viscosity and other rheological properties of the medium being aerated [Niranjan K. ET AL., 1999]:

- *Aeration of low viscosity Newtonian liquids*: e.g. carbonation of drinks and certain foams;
- *Aeration of dough*: at the higher end of viscosity, where viscous and elastic effects may operate simultaneously, there are air/carbon dioxide or other gas dispersions in materials such as dough;
- *Aeration of intermediate viscosity systems*: substances that have viscosity at least ten times greater than aqueous solutions, but which are not as viscous as bread dough. Examples are dairy – based creams, batter used to produce sponge cake, meringues, ice cream, etc.

Depending on the rheological properties of the continuous phase, the bubbles may be stabilized against dissolution by interfacial rheological properties (low viscosity systems such as drinks), bulk rheological properties (semisolid systems such as dough or hard cheese), or a combination of both (soft solid systems such as desserts) [Kloek W. ET AL., 2001].

The purpose of the present work is to make a fundamental study of this argument from an engineering point of view as opposed to the current phenomenological approach. This in turn may be helpful to

obtain information on the ingredients, phases and process for aerated food formation and stabilization, which is considered of great interest to the food industry.

Excluding foodstuffs like beer and/or milk shake, in which foam stabilization occurs by elastic interfacial properties, therefore limited-to surface tension, in this work the stabilization of cellular materials for products like *whipped cream* will be described, in which both interfacial and bulk properties are important, and like *doughs*, for which structure stabilization is controlled by elastic bulk properties.

In fact, the work is focused on systems like:

1. *dough*, system solid-like, constituted of a three-dimensional protein network of gluten (insoluble in water), incorporating all the other components like hydrated starch, the principal responsible for the mechanical behaviour, and gas bubbles, which determine volume expansion during the rising and/or baking phase, stabilized by the protein membrane that avoids gas leakage. As well as air, the bubbles also contain water at thermodynamic equilibrium with water inside the paste, and possibly other substances (like the reaction products of rising agents, NH_3 and CO_2) again at thermodynamic equilibrium. In the long run the equilibrium is broken by the operating conditions due to the thermal profiles and humidity to which the system is subjected, and by the chemical reactions. It is possible to assume that the bubbles grow during the rising and /or baking, initially, in an infinite medium, and then they start to interact with each other, at the end reaching coalescence conditions with the possibility of collapse and opening. This complex mechanism of growth-collapse, which happens in the first baking instants, will determine a porous structure, with a particular texture, from which derive the sensorial properties of the final product.
2. *food emulsions*, always having an aerated matrix, are characterized by a viscosity lower than the previous systems. In fact, it can be said that systems like doughs for bread, cake or biscuits, have rheological bulk properties that influence the matrix stability and the structure, while a food system like “soft solid”, such as desserts or whipped creams, both rheological bulk properties and interfacial properties air/matrix influence the stability and matrix structure. It is a question of dispersed systems constituted of two immiscible liquid phases. The drop size of the dispersed phase ranges from 0.1 to 10 μm approximately. The alimentary emulsion oil in water, in which the oil or the fat is the continuous phase, has become an increasingly important system, especially in the last few years as consumers show an increasing interest in instant food products, like cream or ice cream.

1.2 Process of foam formation

The mechanisms that influence bubble behaviour are very important: these are determined by the aeration conditions and by dispersion characteristics, from the pressure gradient between the inside of the bubble and the continuous phase (or dispersed medium). The interaction between the bubbles and the continuous phase plays a very important role, which is more important when the number of bubbles is high and homogeneously distributed inside the matrix. The bubbles are the units separated by thin films and in the alimentary field it is possible distinguish two large foams families:

1. the system in which the bubbles are spherical and occupy about 50-70% of the volume, like ice-cream or batter;
2. the system of polyhedral foam with a high void fraction, superior to 85% (beer froth) [W. KLOCK ET AL., 2001].

The “foamability” and the shelf-life of the foam depend on the matrix inside which the bubbles are dispersed, but most are from proteins, surfactants, emulsifiers, texturing agents [W. KLOCK ET AL., 2001] and from aeration technology.

A foam is a dispersion of gas bubbles in a liquid- or solid-like medium. In general, there are several methods to make a foam. Firstly, a foam can be produced by agitation of a mixture of a given amount of ingredients (e.g. such as flour, sugar, eggs, etc.) and an certain amount of available gas. During this stage the gas is entrapped in the matrix as large bubbles which are successively broken down into smaller ones by mechanical forces. The whipping process for whipped cream can be considered finished at this stage and the structural stability of the air bubbles is influenced by recipe and process parameters. The foam, which is generated by mechanical dispersion of the gas, is partly stabilised by fat globules, which build a network of agglomerated fat at the air bubble interface. Depending on the structure, especially the air bubble structure, the texture of ice-cream varies over a wide range [H. Rohenkohl ET AL., 1999]. For other food products, like cake, the bubbles included during mixing into the matrix will be nuclei of gas bubbles developed during baking. In fact, in this type of foodstuff, there is a second stage of the process: leavening, when both compressed or naturally rising agents react. Then, the gas generated, like carbon dioxide, diffuses through the paste reaching the initial air bubbles that will grow considerably owing to the simultaneous water diffusion [de Cindio et al., 1995].

Since bubble mechanics determines the relationship between aerating conditions and dispersion characteristics, it is important to study the optimisation of process design, then select the right type of

aerator, correctly size and optimise the performance in order to produce the desired dispersion [NIRANJAN K. ET AL., 1999].

Experimental results have shown that the foaming-ability of the raw materials at a given rotational speed depends on the paddle diameter or shear stress applied by the paddles on the mixture. It appears that a raw material with high viscosity and paddles with a high diameter (narrow gap between paddle head and column wall) favour foaming in continuous processes [G. Djelveh ET AL.,1999].

A second method to make a foam also involves agitation. Contrary to the first method, in this case the required amount of gas can be dosed. An example of this method, which is frequently used in continuous processes in industry, is gas injection into a liquid, often through orifices.

Thirdly, foam can be produced by the generation of gas bubbles in a liquid. These bubbles can be formed in situ when the liquid is saturated with gas. Bubbles can also be formed out of gas supersaturated liquid by means of heterogeneous nucleation. This occurs during the foam formation of carbonated beverages and aerosol whipped cream, where gas is dissolved under pressure in the liquid, when the pressure is released.

In the present work the physics of instant foam behaviour in two different viscoelastic mediums, i.e a liquid-like and a solid-like material, is extensively studied. Thus this study refers to soft ice-cream and bakery products, like biscuits, throughout their production steps.

1.3 Bakery Products

The theme of the emergence of biscuits is closely interlaced with another, more ancient and just as charming history: that of bread. Whereas for bread it is possible to date the origin to some extent (Humerus mentioned this over 2000 years before Christ), the same is not possible for the biscuit. Perhaps the first reference to something similar to the biscuit was found in "De Agricultura" of Marcus Porcius Cato (234 – 149 BC). The Suavillum illustrated, complete with recipe, something that was in effect biscuits of wheat flour, cheese, eggs, honey and poppy seeds.

Sporadically chronicles and memories furnish news and reference to biscuits, distanced by centuries one from the other. On 25 June 1368 at the Violante wedding banquet, to celebrate the marriage of the daughter of Galeazzo Visconti with Lionel of Clarence, Edward III of England's child, gilded "pinoccate" were used. In September 1513 Pope Leo X (in the world Giovanni dei Medici) received as visitors a crowd of his relatives to be fed, the powerful Medici family. The colossal banquet closed with biscuits, "pinolate" and Cyprus wine.

moving much nearer to our own day, the demand for food with a long shelf-life emerged. The dough of durum wheat, cut into a rectangular and riddled shape, was dried to eliminate every trace of water: the dough was then cooked twice, in fact, the word biscuit comes from the Latin and the etymology is BIS, two, and COCTUS, cooked. But this type of food is not real biscuit because among the ingredients sugar and butter are absent. However, it is clear that biscuits and sweets generally were reserved for rich people. Only the substitution of sugar cane with sugar beet permitted a major diffusion and production. In 1800 the confectionery and biscuit factory started to develop, thanks to the Industrial Revolution. In this period large factories with high levels of production sprang up thanks to new technology. The United Kingdom is the European country with the greatest seafaring tradition. But it was the country where the Industrial Revolution started giving also an advantage with respect to Europe. It is not by chance, therefore, that the biscuit producer to be considered the first in the world, is Huntley & Palmer, founded in the first quinquennium of the XIX century [www.ilbiscottiere.it/storia.htm].

Today the great confectionery industries attempt to satisfy the increasing demand for these products, laying great stress on the characterization of the ingredients, both in terms of quality and quantity in the recipe. In fact, the slightest change in raw materials or in the processing conditions is enough to obtain a different product that, potentially, allows a new share of the market to be gained. Depending on the final product, the process and the ingredients assume great importance in the realization of a specific industrial food. Industrial products, like biscuits, are the final result of a series of operations that optimize and control the final food in terms of taste and texture. The objective is the creation of a product able to satisfy the consumer demands and the search for the correct ingredients, with the correct doses, in the appropriate work conditions.

Specifically, the increasing demand for the reduction of production costs induces companies to use low cost ingredients and the search is focused on reducing the impact of these substitutions on the final product recipes. The initial phase for the realization of a confectionery product is the choice of the ingredients and of the doses: every ingredient and the relative quantities have a notable importance both on the mix and on the quality of the final product. Subsequently detail about the ingredients and the factors that influence the rheological behaviour of a dough and the quality of the biscuits will be dealt with. The second stage is the mixing: the ingredients are usually mixed in kneaders and also the mixing time and the rotation speed of the kneader shovels have a notable influence on the final dough, because this step is important for the structural formation since it makes gas bubbles develop during the following rising stage and guarantees the maintenance of the desired height during the baking. The

rising stage becomes very important when a specific height and porosity is desirable: this step is greatly influenced by the temperature. Specifically, low temperatures require long rising times and give a low development of gas cells in the dough; higher temperatures reduce the times of leavening and promote the development of the bubbles. Naturally the times of leavening and the temperatures at which this has to happen depend on the final characteristics that are desirable for a specific product. Finally, the cooking step is very important to confer a specific texture to the final biscuit thanks to appropriate temperature ramps and humidity controllers.

1.3.1 Dough Biscuits Types

The enormous alimentary, but also economic importance, which the cereal sector enjoys, and particularly the bakery products sector, over the years has encouraged numerous research tasks. At different levels these have allowed the interpretation both of the mechanisms that determine the dough formation and the factors that influence the properties and then the quality of the final products.

The dough preparation requires the use of ingredients defined as "fundamental", that is, flour and water or, according to the desired final product, can include other ingredients such as rising agents, salt, reducers and/or oxidizing agent, eggs, sugars, fat substances, etc.

In the operation of the water-flour ratio that is typically respected in the preparation of the products based on flour, the following distinction can be made:

1. *dough systems* (like bread, pasta, pizza), in which the proportion of flour to water is around 1:0.6 and the gluten proteins constitute the principal structural matrix;
2. *batter systems* (mainly cake batter), in which the proportion of water to flour is superior in comparison to the preceding case.

Wheat flour has had a fundamental role in the history of human alimentation. In the Mediterranean basin flour was an essential food for the Egyptian, Greek and Roman civilizations. The word "flour" derives in fact from the Roman term "far", that means "spelt", another cereal that at that time was much used for the production of flour. Currently wheat is the most cultivated cereal in the world, thanks to its adaptability to different environmental and climatic conditions. Today therefore the term "flour" usually denotes the wheat flour. Flours can also be obtained from other cereals or from vegetables, such as oat, spelt, Saracen wheat, corn, bowline, potato, rice and rye. With the grinding of wheat wholemeal flour is produced (which contains the bran). With further workmanship (called "sifting") the flour is produced, which is then the product that can be purchased in the shop. The level of sifting defines the type of flour: it is possible to range from wholemeal flour (darker, with more bran), to the

flour type 00 (whiter, nearly deprived of bran). In flour production are used hard wheat (*Triticum durum*, which contains more vegetable proteins, 13%), destined to the production of the pasta or tender wheat (*Triticum aestivum* that contains less vegetable proteins, 12.3%), destined to the production of bread and sweets. Wheat flour contains a meaningful quantity of starch and vegetable proteins: gliadin, "glutenina". The vegetable proteins of wheat with water cause a filiform and elastic mass, called gluten, which structures the dough. Specifically, the "glutenina" confers tenacity to the dough, the gliadin guarantees its elasticity. Starch, which absorbs around 36% of the water, probably forms bonds of an electrostatic nature, making the dough homogeneous. Water is a necessary ingredient in the formation of a dough; it is necessary to solubilize the other ingredients, to hydrate the proteins and the carbohydrates and to develop the gluten network. The addition of water causes the dough to undergo an abrupt decrease in consistency and a small reduction of the relaxation time.

If the water content is too low there is a brittle, not consistent dough, which during cooking exhibits a marked "crust" effect, because of the rapid dehydration of the surface [Maache-Rezzoug Z. et al., 1998]. In dough sugar addition causes softening because of the competition between the addition of sugar and the availability of water in the system, the viscosity and the relaxation time diminishes with an increase in cohesion. Instead, sugar addition to biscuits leads to thickening and weight diminution and length increase. It was observed that biscuits with a high sugar content are characterized by a crunchy texture and that the sugar makes the biscuit fragile, because it controls the hydration and tends to disperse the proteins and the starch molecules, preventing the formation of a continuous mass [BEAN and SETSER, 1992]. The fat contributes to the dough plasticity as a lubricant. When it is present in large quantity the effects are so pronounced that a small quantity of water is necessary to have a soft consistency. When fat is mixed with the flour, before their hydration, it prevents the formation of a gluten network and produces a less elastic dough. In effect a highly elastic dough is not desired to make certain types of biscuit, because it creates difficulty in the process of lamination [FAUBION And HOSENEY, 1990]. The addition of fat to the dough provokes viscosity and reduced relaxation time, whereas, to biscuits it leads to a reduction of the thickness and weight and to an increase in the length. The fat also makes the biscuit friable, and it favours mastication by the consumer. The salt in the dough, like "water and flour", helps to improve the organoleptic qualities and it determines an increase of the quality and quantity of the gluten (it has the effect of improving the consistency and the elasticity of the dough, increasing the ability to detain the gas and, in conclusion, the volume of the final product). Moreover, the salt has an inhibiting effect in the dough, reducing the secondary fermentations and it serves to confer a marked coloration to the product crust as well as

making it crunchier. The optional ingredients are usually added to increase the general quality of the end-product. But there are many differences between the doughs. The following principal differences have been pointed out (above all at the structural level) among "water-flour", "for dry biscuits", "short " and "batter" types of dough.

1.3.2 Water- flour doughs

Water-flour dough can be considered as a particular state of aggregation due to the flour constituent, because during its blending with water it realizes an almost solid-like system, approximately constituted of a three-dimensional protein network of gluten (insoluble in water), which englobes all the other components among which the granules of starch, the principals responsible for the mechanical behaviour and gas bubbles, also responsible for the volume during the rising and/or the baking stage, stabilized by a protein membrane that prevents any gas leak.

The bubbles moreover the air contain water in thermodynamic equilibrium with the "bound water" inside the dough and possibly other substances (reaction products of the rising agents, NH_3 and CO_2) again in thermodynamic equilibrium. The equilibrium is then broken by the process conditions with time, caused by both the thermal profiles and humidity to which the system is subjected and by the chemical reactions. It can be believed then that during the rising and/or cooking stage the bubbles grow, initially, in an infinite medium and then they start to interact among themselves, finally reaching coalescence conditions with the possibility of collapse and opening toward the outside. From this complex mechanism of growth-collapse, which happens particularly in the first instants of baking, a porous structure forms with a specific texture on which the sensory properties of the end-product depend [[DE CINDIO, 2004](#)].

The characteristics of a dough based on water and flour are influenced by various factors: beginning with the flour and its protein content, continuing with the quantity of water added, to finish with the mixing step. In the characterization of these doughs, as in the characterization of doughs in general, there are a lot of problems due to the evolution of the properties because of physical and chemical factors (evolution of the water - flour interactions, enzymatic reactions, relaxation of the induced stresses during the mixing). Oscillatory measures on doughs performed with Australian strong flour pointed out that they are characterized by a small liner viscoelastic region, corresponding to a deformation of about 10^{-3} and, that in a range of frequency that goes from 10^{-2} to 10^2 Hz, G' and G'' follow a power law, with G' , which at low frequencies is much greater than G'' , exhibiting a behaviour typical of a structured material [[PHAN-THIEN et. al., 1997](#)]. On such doughs creep and stress

relaxation tests are very difficult to repeat, because of the evolution of the raw material, and it is not possible to measure the viscosity on them owing to the solid-like behaviour. Time cure tests point out the presence of two transition temperatures corresponding, respectively, to a gelation and a "caramellization".

Representing by a diagram $tg\delta$ vs the mixing time, a trend with a minimum point is generally obtained in the window of times investigated: a minimum in the $tg\delta$ means having a prevalence of solid-like behaviour for the dough. In comparison to this minimum point the obtained curve could be specular, therefore, for values of times smaller than optimal value, there is a situation of under-mixing, whereas for bigger values there is an over-mixing situation. Moreover, at the same $tg\delta$ value, it is possible to have, contemporarily, two situations: doughs with the same properties (because $tg\delta$ does not change between the two materials), but is not yet developed for times shorter than optimal time and unstructured for times longer than optimal.

Empirical techniques base the search for optimal dough consistency on the determination of the maximum in a curve consistency vs window of the times investigated. Also in this case situations of under-mixing and over-mixing are respectively defined for shorter and longer times of optimal mixing time [LÉTANG et al., 1999]. For the gluten and flour isolated, it has been possible to observe that isolated gluten has marked elongation viscosity, moreover at low deformation and this can help in the rising and cooking stage to prevent the breakup of the gas bubbles in expansion. Moreover, the gluten is characterized by a lower relaxation modulus in comparison to those of flour. It seems therefore that gluten and starch are the principals responsible for the rheological properties, but the low repeatability obtained for the data on doughs, shows how in reality also the other components (lipids, soluble proteins in the water) give their contribution [UTHAYAKUMARAN et al., 2002].

1.3.3 Dough for crunchy biscuits

The principal ingredients for a crunchy biscuit dough are: flour, sugar, fat, salt, water, glucose. In a dough for this type of biscuit the gluten development must be such as to allow the workability and reduction in the desired forms, through moulding for sheeting between rolls and "cutting" of the dough sheets obtained.

Oscillatory tests on this dough-type showed a very narrow viscoelastic region, which corresponds to deformation in the range of $10^{-2}/10^{-1}\%$. Moreover, in a frequencies range between 0.1 and 10 Hz, the G' and G'' moduli are linear and they increase with frequency; G' is always greater than G'' at all the temperatures and the value of this modulus is smaller than dough water and flour values. Time cure

tests point out that there is only one transition temperature, corresponding to gelation of the starches. These doughs show a solid-like behaviour and it is not possible to measure viscosity on this.

1.4 Short Dough

Short doughs are different from the other types of doughs because they are incoherent if submitted to tension and fragile to breakup [[HOSENEY et al., 1988](#)], because they contain an appreciable amount of fats and a low quantity of water (<20%). The ingredients just mentioned are opportunely dosed to obtain the right consistency. Saccharose, which is one of the most used ingredients, thanks to its crystalline state, as well as to its large-size crystals, can create some dissolution problems in water and, therefore, give problems of consistency [[A.BALTASAVIAS et al.,1997](#), [S. CHEVALLIER et al., 2002](#)]. From a processing point of view, quality control of the raw materials for short dough is essential and is associated with consistency of the same dough. The optimum of consistency is usually obtained thanks to the operator's experience, there being no methods able to verify the mechanical properties of short doughs.

The study of these types of dough is generally dealt with varying both the content and the quality or kind of added fats, eliminating or replacing the sugar (saccharose), which is believed to be principally responsible for short dough brittleness. In fact, fats and sugar broadly vary in percentage in the different types of recipes:

FAT range 20/60% weight of flour

SUCROSE range 25/55% weight of flour

in confirmation of the fact that they act in a conclusive way on the macroscopic, and microscopic qualities as well as on the texture.

Some results [[A.BALTASAVIAS et al., 1999](#)] that are based on microscopy, suggest that these doughs do not have a continuous protein network: the structure should be constituted of a protein and starch mix and should have the presence of fats, which should act as a filler. Changing the fats percentage, it is possible to act on the degree of voids, increasing this, all the parameters, apart from the break-up deformation, meaningfully prove to be different. Doughs with a high fat content can give rise to a "particularly" continuous structure. A. Baltsavias et al. [[A.BALTASAVIAS et al., 1997](#)] carried out rheological tests on short doughs, changing the types of fats added or removing some fundamental ingredients, to study the characteristics of these when submitted to small amplitude oscillations. All the types of dough studied seem to exhibit the same behaviour of the storage modulus (G') and around the

same amplitude of linearity regions, except in the case in which the fats are added as liquid-oil. In this latter case, in fact, the storage modulus is an order of greatness higher than all the other recipes.

It is deducible then that the type of fat added influences the matrix and that the fats have the tendency to confer rigidity to the dough. The explanation of the G' diminution lies in the fact that the fats are added to the dough in a solid-like form, causing the formation, during the mix, of fatty lumps, while, when adding fat in liquid form, final drops of oil are present in the dough that bind the constituent particles to the flour. The greater continuity of the fat matrix, in the latter case, confers less rigidity on the dough and therefore the storage modulus is smaller [A.BALTASAVIAS et al., 1997].

On the basis of studies carried out [A.BALTASAVIAS et al., 1997] it is found that the short doughs are not only fat-continuous, but also bis-continuous systems. Reducing the content of fats or replacing solid fat with oil, it is possible to obtain fat-dispersed systems. The not-fat phase can be held to be constituted of a solution of saturated saccharose connected to the particles of flour/starch. Certainly the non-fat phase, thanks to the gluten, which exhibits a typical strain-hardening behaviour, contributes to confer a greater resistance at higher deformations. Sugar inhibits the gluten development during the mixing phase with the flour, because of the quantity of water imposed by the recipe, leading to obtaining friable biscuits. Replacing part of the sugar recipe, opportunely reduced, with an oligosaccharide, does not have the same hardening effect on the dough as grained sugar, which has the lowest hardness values compared to those obtainable from standard biscuit doughs. The visual properties, like colour, are invalidated only by the very high sugar substitution [A.BALTASAVIAS et al., 1999].

The curves obtainable from monoaxial compression tests of short doughs appear as in figure 1 [A.BALTASAVIAS et al., 1999].

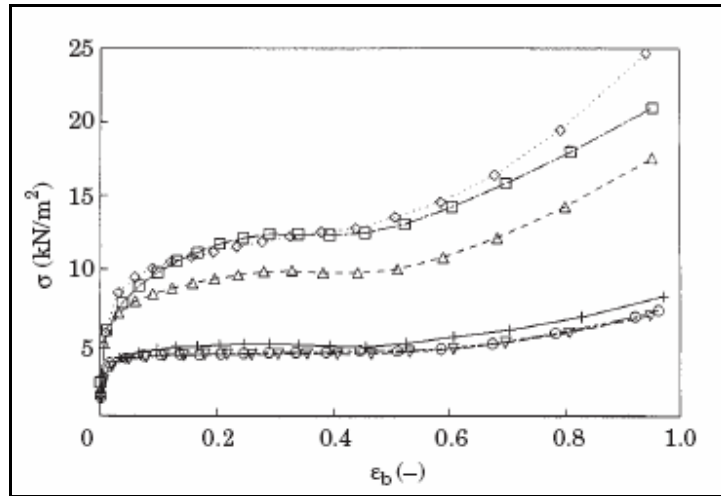


Figure 1.1 - Stress - deformation curves for short dough [A.BALTASAVIAS et al., 1999].

From experimental deformation tests effected [A.BALTASAVIAS, 1999] it is impossible to obtain unequivocally the macroscopic fracture point and the Young modulus. The principal characteristics noticed is that if stress is impressed on the sample and it cracks, after the removal of sudden stress, fracture propagation is not noticed. The Stress vs. Strain curve can be divided into three regions, as can be deduced from figure 1:

- a first zone where the stress increases with the deformation;
- a plateau, representing the second zone and denoting a structural rearrangement in progress due to the flow and flexibility processes. This region constitutes the essential part of the whole curve;
- the increase in the stress for deformations greater than 0.7, caused, in part, by the friction between the plates and the material. It is possible to have an effect due to rather elevated deformation on the dough properties, but this is a more marginal effect than the first one.

The matrixes having a well-developed three-dimensional glutinic network respond elastically when subjected to large deformations. Doughs like bread, in fact, exhibit strain-hardening behaviour for Henky deformations greater than 1.2. It is possible to observe, on the contrary, that the effects of the gluten in the answer to large deformations is mostly observed in sugar-free biscuit types and at high deformation values (curve in the upper part of the graph in figure 1). For this motive it was ascertained that saccharose changes the phase structure without fats.

Even though present in small quantities, water is an important ingredient because it acts as plasticizer: at “low activity” the biscuit exhibits a typical fragile material behaviour, whereas at "high activity" a well-separated fracture point is not present.

The factors that influence the mechanical properties of the biscuit are: the degree of void, the inhomogeneity size and the geometric characteristics, as well as the continuity of the fat phase. The fat globules can be deformed and have coalescence, causing an increase of the continuous phase. An elevated biscuit viscosity can interfere with the bubble expansion and can have a crucial role in the degree of void, but also on the greatness of the cells. The mechanical properties of this type of biscuit essentially depends on the matrix properties. For low water contents, the biscuit exhibits a fragile break-up type. The cell breakup initially happens owing to the bending of the cell walls and then following breakup, owing to energy accumulation. The saccharose state, crystalline or rubbery, considerably influences the mechanical behaviour [A.BALTASAVIAS et al., 1999]. The experimental analysis performed by S. CHEVALLIER et al. [S. CHEVALLIER et al., 2002] suggests that the matrix of pasta remains "soft" during the phase of cooking to the oven. This confirms as to reported by MANLEY et al. [MANLEY et al., 1991] for pastas in sugar and fat. During the cooking of doughs sugar-rich, the expansion period is followed by a marked collapse. This behaviour is attributable to the lower contents of water in the dough. The proteins are not hydrate enough to form a network of gluten and, when the dough is heated, the water is insufficient for the gelation of the starch. Therefore the classic model based on the gluten network is not applicable in this case. Because the matrix of the dough doesn't become rigid during the cooking phase, the end of the expansion stadium can be attributed to "Emptying" from the rising agents and/or to the evaporation of the water, with possible breakup of the cells walls inside the biscuit. In every case the phenomenons of expansion require much rigorous studies and the kinetics of gas production remain one of the principal problems [S. CHEVALLIER et al., 2002].

Since the mechanical properties of the biscuit depend on the matrix, it has raised the question on the properties and characteristics of the not-fat continuous phase. The results obtained thanks to DSC, show that the not-fat continuous phase is probably composed of gluten. The gluten T_g in the flour is > 96°C and depends on the water content [A.BALTASAVIAS et al., 1999]. Then the short dough was considered as cellular solid constituted of a structure of "beams" and "flats" (figure 2):

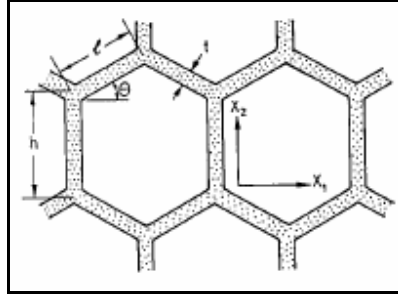


Figure 1.2 – Cellular Structure.

Some authors [NIEDIEK et al., 1988] thought about using valid expressions for cellular isotropic solid, with cells of uniform size and also uniform density and thickness of the walls:

$$\begin{aligned} \frac{E}{E_w} &= C_1 \left(\frac{\rho}{\rho_w} \right) = C_1 (1 - \varphi_{void})^2 && \text{open - cell} \\ \frac{E}{E_w} &= C_2 \left(\frac{\rho}{\rho_w} \right) = C_1 (1 - \varphi_{void})^3 && \text{closed - cell} \end{aligned} \quad (1)$$

where E and E_w are the Young Modulus [Nm^{-2}] respectively of the foam and of the cellular material, where ρ , ρ_w , are the densities and C_1 and C_2 are constants around unitary, depending on the cell shape. This type of equations was applied to alimentary foams.

Another model was applied by Kerner [KERNER, E. H., 1956] to cellular materials; applying these models to the results obtained for short dough biscuits, he verified that the use of the model is applicable to gluten matrixes or icing sugar, or also to a combination of the two. From the experimental results, moreover, it is deduced that the model proposed by Kerner is mostly usable when the filler fraction in the biscuit is low. Whereas, when the biscuits do not have a uniform gas cell size, the results are better represented by the Gibson and Ashby approach. The important factors seem to be Φ_{void} , Φ_{fat} and the geometric characteristics of the dough (closed or open cells). Finally, the addition of fats gives softer and more "delicate" biscuits. This could be due to the fats that increase the fraction in volume of air and, therefore, to a more homogeneous and wide continuous phase. The biscuit bottom shows hemispheric bubbles with a large enough diameter, while the top shows a slight crust. The defects of the material can cause stress and localized strain exhibiting fragile breakup. In conclusion, it is possible to say that the mechanical behaviour of short dough is governed by:

- Φ_{void} , Φ_{fat} , and the geometric characteristics of the dough (closed or open cells);
- size of inhomogeneity (cells of gas);

There are however other factors, such as the matrix state (whether glassy or rubbery) and the fat continuity, which play an important role, in fact, sugar-free biscuits exhibit a less fragile behaviour.

1.5 “Batter” Dough

The principal ingredients that constitute a batter dough are: flour, sugar, water, eggs, oil, rising agents and glycerol. This type of dough has a different structure from that examined in the previous paragraphs: gluten network development is avoided completely in it, preventing water from binding with the flour; this is possible paying attention to the order in which the various ingredients are mixed (in the industrial process the flour is the last ingredient that is added).

This dough shows a liquid-like behaviour and therefore it is structurally weaker than "water-flour" and short dough: it achieves a difference in rheological and mechanical properties. Oscillatory tests on a dough of this type (Jaffa cake) have shown a limited linear viscoelastic region moving toward higher deformation values in comparison to the case of crunchy biscuit dough: the deformation is in the range of 0.1% - 1%. In a frequency range that goes from 0.1 to 80 Hz, the moduli G' and G'' show a linear behaviour and at high temperatures and at high frequencies there is a crossing and inversion of the moduli: for low frequencies G' is greater than G'' , while at high frequencies it is the contrary. The moduli values are much lower than the previous doughs: they increase with frequency and decrease with temperature. Increasing the temperature these doughs are structured and time cure tests show only one transition temperature corresponding to the starch gelation temperature.

These doughs are greatly influenced by the quantity of rising agent: increasing this the structure is weaker. Also the colour, after cooking, is influenced by it: increasing the rising agent the colour becomes darker. While for "water-flour", crunchy biscuit and short dough, it is not possible to measure viscosity, for batter the viscosity is a fundamental parameter for spreading (effect according to which the dough, under the action of its own weight collapses) and for expansion, since this influences the conditions at the start of cooking. In the case of batter dough the form is made with nozzles measuring out a certain quantity of dough or placing it directly on the cooking surface, or in moulds; this depends on the final product that is desired. In the first case, when the dough is directly set on the cooking surface, because of its own weight, it collapses (the expansion that the dough has depends on its viscosity): this is the method that is used for the realization of the biscuits, characterized by a reduced height. In the other case, when the dough is set in appropriate moulds, spreading is avoided, because the dough is confined to an opportune support, and the growth of the product is favoured in height: this

is the method that is used for cakes. Transitory tests on batter dough are very difficult to repeat, above all for linear viscoelasticity; moreover, large deformations alter the structure of the batter with time.

1.6 Mixing and baking stage

The mixing stage plays, as said before, has a primary role, since the phases in question are in intimate contact between each other and the sites are created to favour the growth of the bubbles in a following phase [NIRANJAN, K, 1999]. Generally, the process of a classical baked foodstuff starts with the ingredients mix. The viscoelastic properties shown by the dough mainly derive from the hydration of the gluten and they are influenced both by the starch content and by the dilution medium (water). The dough, moreover, is not a completely compact mass, or rather homogeneous, but it is, instead, a heterogeneous system, with a network, among which the air bubbles are entrapped, therefore, it is characterized by a certain degree of airming. The mixing conditions (expressed in terms of mechanical energy, temperature and time) influence the physical characteristics of the dough, which can be under conditions of optimal development, of incomplete development or of excessive mixing. Under these latter two conditions the development of a glutinic network is not well-stabilized by intermolecular covalent and physical bonds, which contribute to increasing the elastic properties. Excessive mixing also determines a diminution of resistance to extension because of structural damage. It has been verified that in the completely developed dough the wider formation of the protein matrix is obtained, while, contrarily, in the incompletely developed dough it is very low. The viscoelastic parameters depend on the mixing time and this dependence changes with the wheat variety [BOHLIN and CARLSON, 1980]. An increase of biscuit mixing time causes an increase in the elastic effect in the dough (and this indicates that the proteins continue to develop, an undesired effect in a short dough type), an increase of cohesion, stickiness and rigidity and a diminution of the consistency, viscosity and of the relaxation and extrusion time. Whereas the same conditions in the biscuit cause, after cooking, an increase in the length and a weight decrease [MANOHAR and RAO, 1996]. The mixing time has also a considerable effect on the quality of the biscuits. In fact, increasing the latter there is a diminution of the spread in systems like batter, evidently because of an excessive development of the gluten network, an increase of density and therefore a diminution of the friability. Also the sensorial characteristics change with the mixing time: a longer time gives a wrinkled surface biscuit, makes it harder and gives slightly lower values of the sensory colour.

It can be said then that the principal aims of the mixing operation are:

- to guarantee interaction among the different ingredients to get a homogeneous system;
- to assure the development of the gluten network in the wheat dough or where necessary;
- to incorporate air in the dough mass.

In the end, a two-phase mixing system is obtained, composed of the paste (continuous phase) and from the air, that is entrapped during mixing. The presence of the air bubbles is essential for the following phase of leavening, because it is well-known that void formation happens owing to the diffusion of CO₂ in the bubbles created during the mixing and not to nucleation. In fact, studies conducted by [Baker and Mize \(1947\)](#), on the origin and the structure of the gas cells in the dough showed that the latter do not originate from the air obstructed in the flour or from the gas produced by the rising agents, but they are produced in the mixing phase. The CO₂ produced in the fermentation phase diffuses then in the pre-existing cells of expanding air, but does not create additional cells.

In conclusion, the final characteristics of many oven products depend on the volume and control of the structure of the gas bubbles in the uncooked matrix. The quantity of incorporated air during the mixing changes with the type of mixer used. The application of a partial vacuum decreases the gas absorption while working at pressures higher than atmospheric, gas occlusion increases. It is not only the incorporated air quantity which is important, but also the size and the number of the created bubbles, since they have a strong influence on the final product.

It is known that the application of a partial vacuum in the mixing produces a thin and uniform structure of cells, while working under pressure a final structure having a major percentage of open cells is obtained. Since these differences in the final structure of the dough can be imputed to the working pressure during mixing, the control of this pressure is to be considered as a possibility for the control of the structure of the final product [[NIRANJAN K, 1999](#)]. Another important factor to be considered is the mixer blade drawing, because the combination of the rotation speed and a correct blade drawing can very much influence the process of dough aeration. In conclusion, it can be said that the process to obtain bakery products is among the most complex in the food industry, because the variables in question are several and because a true standardization of the process and raw materials does not exist.

1.7 Emulsions

Emulsions are dispersed systems constituted of two liquid phases immiscible with each other. The drop size of the dispersed phase can go from around 0.1 to around 10 µm. The alimentary emulsions of oil-

in-water are important; in this type of emulsion the oil or the fats are the dispersed phase and the water is the continuous phase, such as cream, ice-cream, salad dressing, flavour emulsions, meat emulsions and cream liquors. Examples of emulsions of the water-in-oil type are butter or margarine. The emulsions are inherently unstable because of the free energy that is at the interface between the two phases. The increase of the interfacial area or the diminution of the particle number or the addition of other dispersed material such as fats, requires a great deal of energy at the interface to avoid drop coalescence. The presence of fat crystals can both stabilize and destabilize the emulsion droplets, depending on their presence in the continuous phase or in the intra-globular zone. If the fat crystals are in the continuous phase, they can be in contact with the interface and being adsorbed on the surface of the droplet, this potentially stabilizes the emulsion. The crystals can originate from the solidification of the surface-active agents to the interface [primarily mono-acid-glycerol] and/or from crystal migration, formed in precedence, toward the droplet. The dispersed phase, the lipids, in a state of partial crystallization, can substantially increase the destabilization of the emulsion. During the treatment and/or the deposit, the intra-globular fat (in the cream) can induce formation of crystals, which can go through the interface and produce the coalescence of droplets [ROUSSEAU D. (1999)].

There are some molecules called surfactant or emulsifying and these lower the interfacial tension and decrease the necessary free energy of the system to keep the two phases separate.

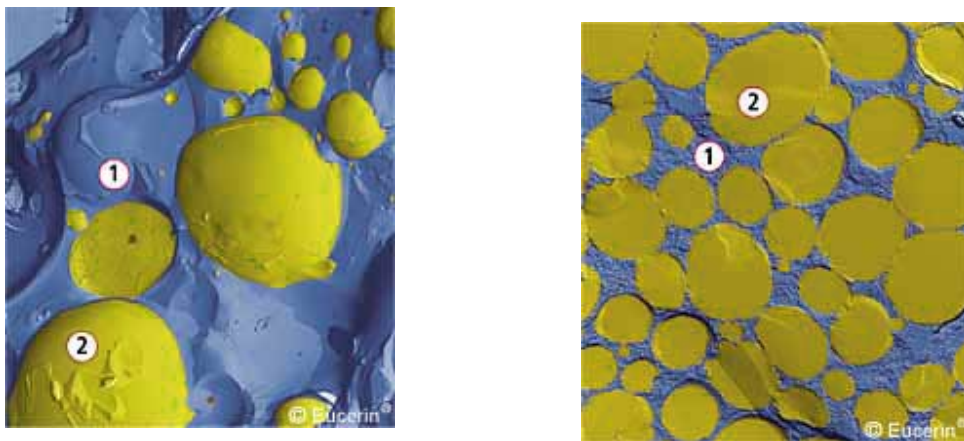


Figure 1.3 - On the left image by electronic microscope of an emulsion O/A: 1) external watery phase; 2) inside oily phase (kept by the site: www.eucerin.co.uk); on the right image by the electronic microscope of an emulsion O/A with larger oil content: 1) external watery phase; 2) inside oily phase (kept by the site: www.eucerin.co.uk)

The only way to put together some immiscible fluids (gas or liquid) can be to mix them all together, if the interfacial layer that surrounds the dispersed droplets is occupied from an adsorbent layer of molecules that stabilizes the droplets or the bubbles against coalescence. Figure 4 show the importance

of the interfacial layer in the foams and in the emulsion systems, and it shows the two principal classes of active molecules that stabilize the surface.

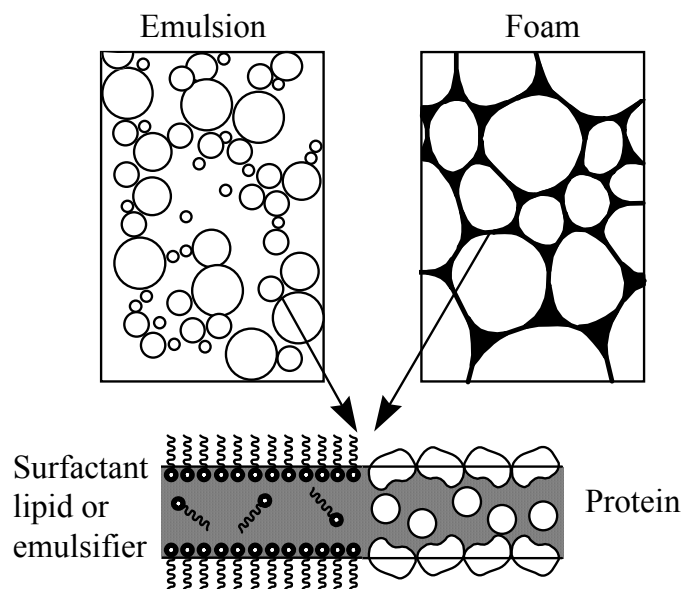


Figure 1.4 - The importance of active molecules at the surface in the foams and in the emulsions. The two classes are surfactants (lipids and emulsifiers) and proteins.

The low molecular weight surfactants, the lipids and the emulsifiers are simple amphiphilic molecules with a hydrophobic tail and an absorbent head group. These are assembled alone and in a simple way on the interfaces, now associating the proper part of the molecule with the absorbent phase to the hydrophobic phase, therefore, they reduce the interfacial tension, which is the strength that exists between the two phases of the emulsion. The emulsifiers promote a destabilization of the fat part of the emulsion and this gives a smooth product, dry and with good fusion properties. The emulsifiers are a group of components that help in the development of an appropriate fat structure and a suitable distribution of necessary air to have good flow and fusion characteristics in the end-product.

The proteins on the other hand are larger and more complex macromolecules, with a series of amino-acids of different hydrophobic degrees. Figure 5 shows how these two very different types of molecule stabilize the foam and the emulsion.

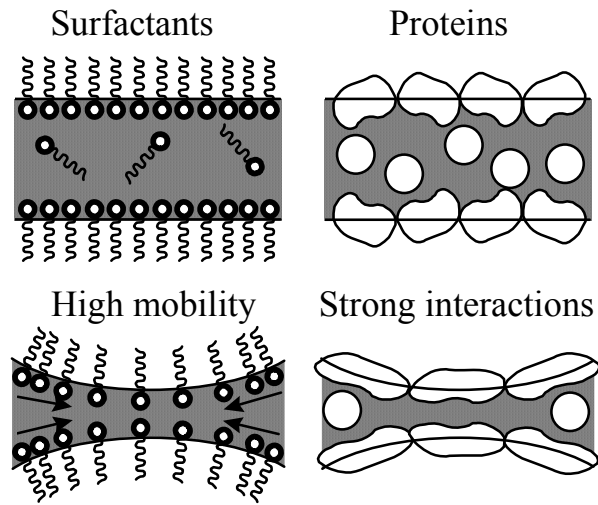


Figure 1.5 - Mechanisms of stability for proteins and surfactants.

The surfactants act thanks to a rapid diffusion eliminating some troubles at the interface. This rapid motion will drag some fluid into the inter-lamellar space between droplets or bubbles, to maintain the separation. This is known as the Gibbs-Marangoni mechanisms. The proteins on the other hand develop strong interactions, forming a viscoelastic gel at the interface that can get deformed and so stabilize the system against coalescence. The principal difference among the interfaces stabilized by proteins and surfactants is the interface viscoelasticity (figure 6).

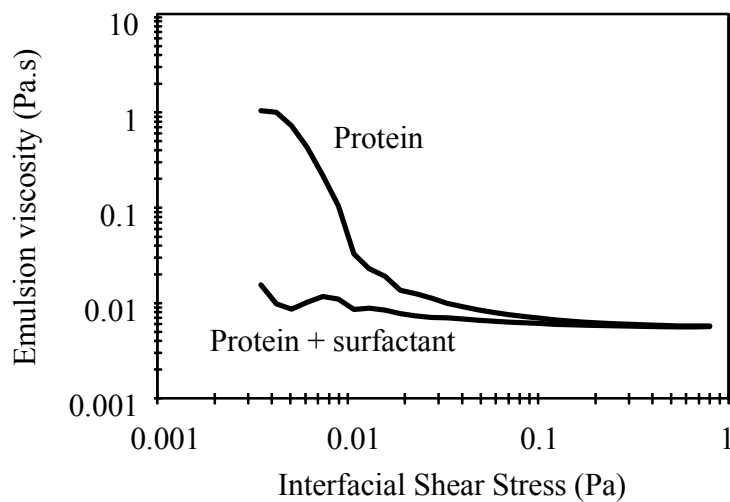


Figure 1.6 - Emulsion viscosity stabilized by proteins in the presence or in the absence of surfactants.

1.8 Foams and emulsions stability

The physical stability of foams and emulsions is a really important subject for the food industry, since it means assuring a good quality of the product during food preservation and checking instabilities during the process. As already stated, the foams and the emulsions are meta-stable systems in which a phase (air for the foams and oil for the oil in water emulsions) is dispersed in another phase (liquid); they are subject to changes in the state because of various processes. Some of these processes change the distribution of the dispersed and continuous fat phase (creaming, drain) while others invalidate the stability (disproportionation, aggregation and coalescence).

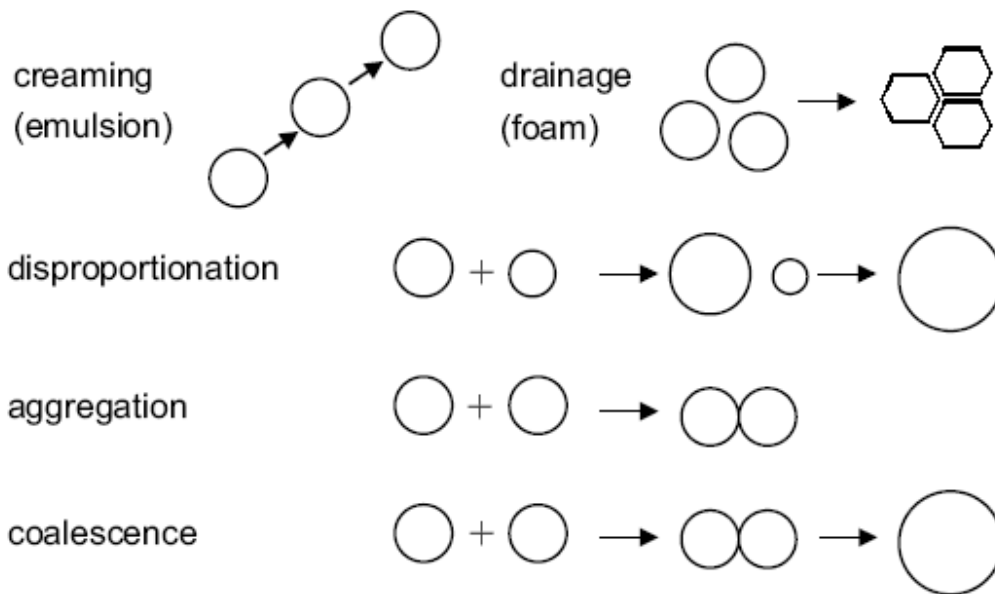


Figure 1.7 - Instability mechanisms of emulsions and foams.

Creaming and aggregation normally are not important for foams. Stability against creaming can be realized mechanically reducing the droplet size of the emulsion with the homogenizer. Drainage is the process thanks to which a liquid flow is obtained through the foam. For instance, observing the foam of a beer glass it can be noted that the bubbles become larger as soon as the liquid among them drains in the glass. This process happens because the smallest bubbles join up and the resulting larger ones furnish wider channels through which the liquid can flow out. The coalescence is the fusion of two bubbles into a larger one. Disproportioning (or Ostwald ripening) involves gas transport from smaller bubbles to larger ones due to the difference in the Laplace-pressure. Large bubbles will therefore grow

at the expense of smaller bubbles, which decrease in size and eventually disappear. This process leads to coarsening of the foam.

The mechanical resistance of the protein film can be in opposition to the change of area that is generated during the disproportionation. The destabilization of an emulsion will be influenced strongly by composition, environmental condition (temperature, pH etc.) and process conditions. Many works in the literature which consider the stabilization of emulsions have examined the improvement in kinetic stability with the use of emulsifiers and thickening agents. The emulsifiers play two roles in the kinetic stability of an emulsion:

- they lower the interfacial tension between the phase oil and the phase water;
- they mechanically form a cohesive interfacial film around the droplets that prevents the coalescence.

The surface-active agent can impart dynamic properties to the interface that allows it to resist against tangential stress. Moreover, the emulsifiers can be proteinic (sodium caseinate) or at low molecular weight (polysorbate, phospholipide). Also some thickening agents such as gum Arabic and adragantes rubber have stabilizing effects. These agents can influence interfacial phenomena like surface tension, viscosity and surface elasticity (or viscoelasticity).

It is known that in a lot of food emulsions solid particles are necessary to confer stability to the system (crystals of ice in ice-cream, particles of egg yolk in mayonnaise and fat particles in mounted whipped cream). The influence of fat crystals in the (in)stability of an emulsion depends on whether they are surrounded by the continuous or dispersed phase.

The ability of an emulsion to resist coalescence depends largely on its interface properties. An extremely viscous and rigid interfacial film will delay the adsorption and therefore this promotes its stability. It has also been observed that xantan rubber causes a less orderly fat structure, in alimentary emulsions, with consequent increase of instability [ROUSSEAU D. (1999)].

The soluble proteins in water accumulate and they are bound in a strong enough way to the liquid interface.

The interfacial adsorption of the proteins forms a surface with viscoelastic characteristics. The rheological properties of this layer are of interest for the formation and stabilization both of emulsions and of foams. A key factor for an answer to the stability can be the interfacial protein film and its answer to interfacial expansion and compression tests [Martin AH, 2002].

Two kinds of surface deformation are important: the change of area (dilatation/compression) and the change of form (shear). Dilatation is associated with the adsorption / desorption of the active surface agents, together with the relaxation processes to constant surface concentration and to the strengths of cohesion and interaction among the protein molecules.

Interactions among the proteins are investigated better by the shear deformations. Both types of interfacial deformations are remarkable for the emulsions and for the foams. In fact, some correlations have been found among the surface rheological properties and the foam properties : a higher apparent viscosity in interfacial shear, a slower drainage and a more stable foam [[Martin AH, 2002](#)]. A surface tension gradient is a prerequisite for the stability against coalescence during foaming because coalescence requires film break-up and the breakup speed depends on the thickness of the film and on mechanical properties, particularly on the stress at which the film breaks.

The interfacial properties are various and at each is imputed an influence on the "foamability" and on the foam stability, but their influence is not very clear.

1.9 Examples of typical alimentary foams

The alimentary foams, used daily, can be produced from mixture agitation of a stated amount of liquid and an unlimited amount of gas or be ready in an aerosol spray and their use will foresee only a preventive agitation. Instant foams are for example the desserts, which require a certain preventively dosed amount of gas. An example of this latter method, frequently used in continuous process-type industries, consists in the injection of a gas in a liquid, often through an orifice. Instant desserts can be replaced in this way with fresh whipping creams.

A first example of instant product is whipped cream. Whipped cream is an emulsion with a fat content that can vary between 35 and 40%. The departure emulsion is shaken with a mixer in a bowl and during agitation air is incorporated.

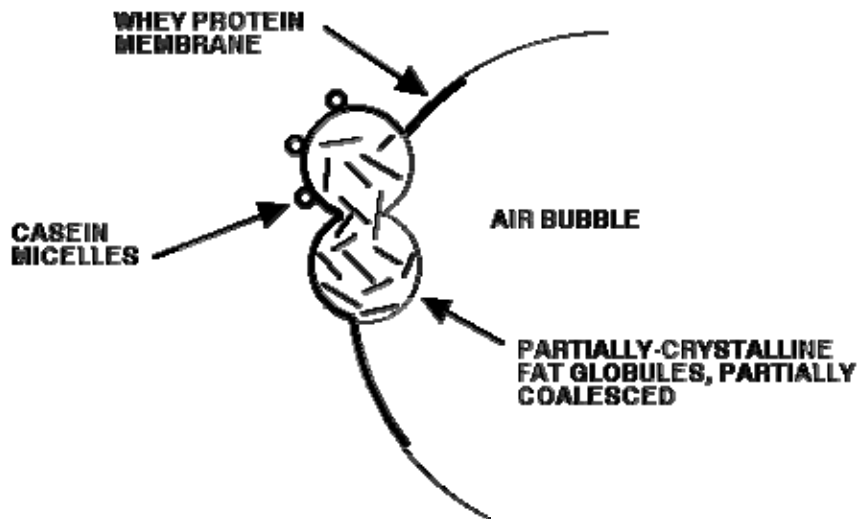


Figure 1.8 – Cream structure.

During the process the fat globules coalesce partially in chains and clusters and they are distributed around the air bubbles, this causes a stabilization of the air bubbles and, since the fats join up between them in chains, an aerated and stable compact structure also originates, with the classical soft aspect. Water, lactose and proteins are trapped in the spaces around the air/fat-stabilized bubbles.

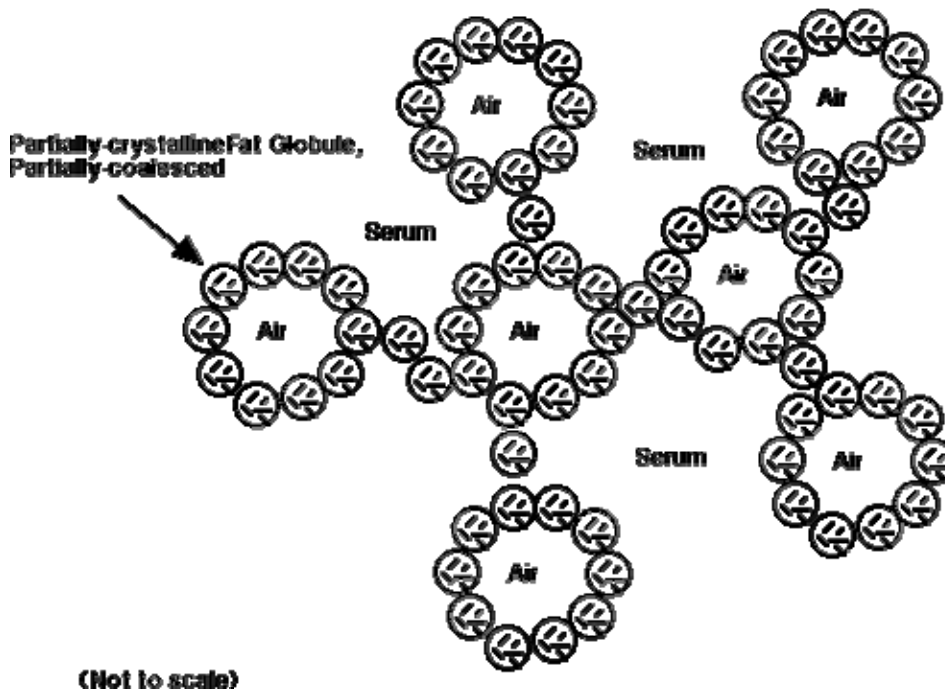


Figure 1.9 - Schematization of the whipped product structure.

The structure of a whipped cream analyzed through scanning electron microscopy (SEM) is shown in figure 9: in figure A., the relative size and prevalence of the air bubbles and of the fat globules (f) can be noted; in figure B, the inside structure of the air bubbles, the layer of partial coalescence of the fats that stabilize the bubbles; in figure C, the details of a fat particle that originating the film around the bubble.

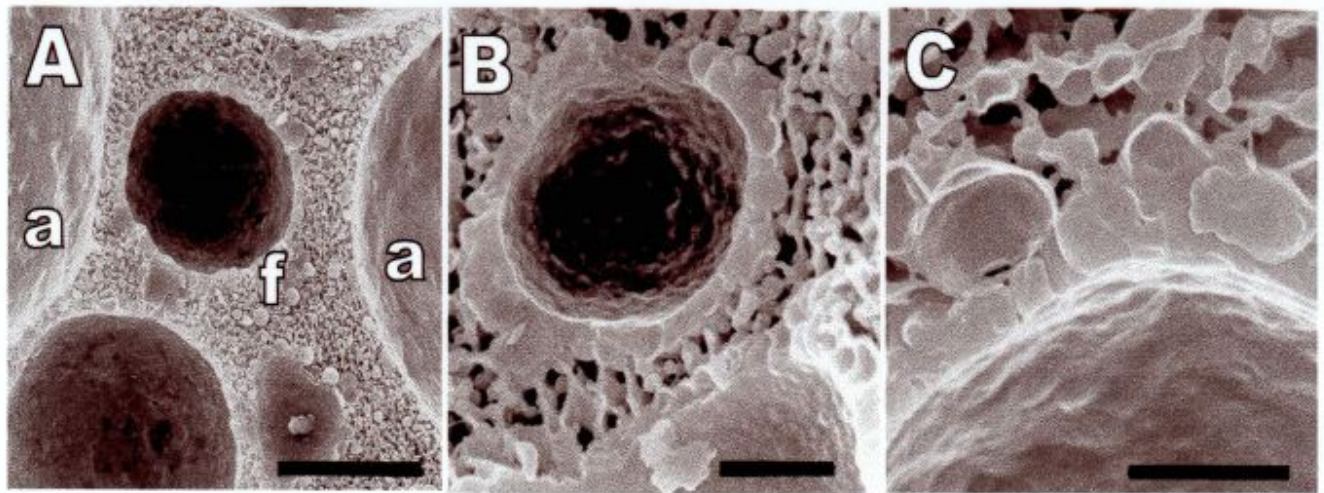


Figure 1.10 - Images of whipped cream. A) Bar=30 µm, B). Bar=5 µm; C) Bar=3 µm (Dayri Science and technology University of Guelph).

A similar product to fresh whipped cream is the so-called aerosol whipping cream, a product manufactured in an aerosol spray. The formation process of a ready-whipped cream provides for a series of steps. Before the cream enters inside the spray, the cream undergoes various trials: UHT (ultra high temperatures), which consists in a sterilization of the cream with the least thermal damage (the treatment increases the shelf-life of the product), then the cream becomes slightly homogenized to reduce the fat globule size and consequently to reduce creaming. The homogenization process causes an increase of the viscosity with time (rebodying) that can happen during transport and the shelf-life of the sprays. The cream is finally introduced antiseptically into the sprays that are closed by a valve. The propellant generally used is nitrogen protoxide, added to the spray by the valve. The spray is then shaken to allowing the dissolution of the gas in the cream and therefore to prevent the development of an excessive pressure in the spray. Nitrogen protoxide has a solubility in the cream about 50 times greater than air. Thanks to the high pressure inside the spray (5-10 bar), most of the gas is dissolved. It is advisable, moreover, to shake the aerosol spray before use mostly to disperse the inhomogeneities,

such as for instance coalesced fat, globules that could be present inside the cream. The pressure drop between the inside of the aerosol spray and the external environment will induce an instant expansion of the bubbles present inside the aerosol spray, thus whipping up the product. The process of instant formation and therefore the properties of the foam of aerosol whipped cream will be influenced by the amount of gas dissolved in the cream inside the confection. The foam is characterized by an elevated overrun, which can vary for good products from 100 to 120% [K. Smith, 1999]. Unfortunately the whipped cream in an aerosol spray is not very stable. In fact, after around 15 minutes of its formation it collapses, decreasing in height and showing a degeneration of its classical form to "rose". It seems that the deterioration of aerosol whipped cream is caused by the process of disproportionation, which is strongly promoted by an elevated gas solubility [WIJNEN and PRINS, 1995].

Often fresh whipped cream is compared with that in the aerosol spray, since the two products have some substantial differences.

When air is incorporated, during the process of whipping of fresh whipped cream, the bubbles are somehow stabilized by the milk proteins [BROOKER, 1993]. During the assemblage phase, the solid and liquid fat globules are adsorbed at the interface. The process that involves the fresh whipped cream prevents the coalescence since solid fats are also present. Temperature plays an important role in the process, since it helps the formation of the network conferring greater rigidity to the fat globules. This network helps the stability of the foam against the phenomenon of the disproportionation. The stability of the fresh whipped cream is due both to the bonds of the globules of fat, which have joined and that connect the air bubbles and to the absorption of single globules or groups on the walls of the bubbles. Unfortunately however the overrun proves to be lower than that of instant whipped creams.

Ice-cream is one of the most widely-consumed products today. There are a lot of stories based around ice-cream. It is not known exactly when ice-cream was invented. It is said, however, that already in 500 BC, the Chinese had discovered how to preserve winter ice to be able to use it in summer. In India, the Moghul emperors sent riders on the mountains of the Hindukush to bring ice and snow to Delhi for fruit sherbets of the court. Another interesting piece of news is that in the most distant centuries, among some peoples, such as the Babylonians, the Egyptians, the Arabs and the Romans, there was the habit of refrigerating some sweet substances, as for example, fruit juice. Even the Arabs in Sicily used to mix the snow from Etna with fruit juices, creating something that can be considered the ancestor of ice-cream and that was called Sherbeth. The cone was introduced in 1904 during the World exhibition of St Louis. An ice-cream vendor, having finished the containers inside which he placed the ice-creams for his clients, tried to use some wafers sold near his stall. It was an enormous success.

Commonly ice-cream today has the following composition (percentage in weight) web [page 2]:

- Percentage not inferior to 10% of milk cream, by law, usually between 10% and 16% milk cream in excellent ice-creams;
- Less than 12% of skimmed milk dust: this component contains proteins (casein and sieroprotein) and carbohydrates (lactose) present in the milk;
- 12-16% sweeteners: usually a combination of saccharose and glucose;
- 0.2-0.5% stabilizing agents and emulsifiers;
- 55-64% water that comes from the milk or from the other ingredients.

These are percentages in weight. However it should not be forgotten that approximately half the volume of the ice-cream is air [web page 1].

The milk cream is important in ice-cream for the followings reasons:

- it increases the rich taste of the ice-cream;
- it produces a characteristic smooth "texture" making it flow on the palate;
- it helps to give strength to the ice-cream, because of its role of destabilized fat;
- it helps to give good melting properties.

The limitations of an excessive use in the mixture include:

1. cost,
2. not so easy making;
3. high calorific value.

The triglycerides in the fat (milk fat) have an ample interval of fusion, from +40°C to -40°C, for which reason there is always a combination of liquid and crystalline fat [web page 2].

The dust milk skimmed (MSNF) contains lactose, casein, sieroproteins, mineral and contained in ash varying according to the product from which it has been obtained. It is an important ingredient for the following advantages :

- improves the "texture" of the ice-cream, because of the presence of proteins;
- helps to give strength and mastication resistance to the end-product;
- can be a convenient source of total solid.

The limitations on the use of dust skimmed milks include a loss of taste that can be due to some products, and an excess of lactose can produce the defect of "sandy taste" during crystallization. The excessive concentrations of lactose can also lower the freezing point of the end-product to an unacceptable level.

The proteins are around 4% of the mixture and they offer an important contribution to the development of the structure of the ice-cream, including:

1. properties of emulsification of the mixture;
2. properties of workability of the ice-cream;
3. ability to bind the water that improves the viscosity and a lowering of the freezing point.

The crystallization of the lactose, can induce instead:

- a temperature decrease that promotes a rapid crystallization and therefore an increase of over-saturation;
- a temperature decrease that promotes the slow crystallization and therefore involves an increase of viscosity, reduces the kinetic energy of the particles and involves a decrease of the percentage of beta lactose that changes into alpha.

However, the over-saturated state can exist because of the elevated viscosity, and it is probable that a great part of the lactose present in the ice-cream is in a non-crystalline state. The stabilizers help to keep the lactose in an over-saturated state since they improve viscosity.

Citrate and phosphate ions (citrate of sodium, phosphate disodic decrease the tendency to coalescence, kick and ions of magnesium have the opposite effect, they promote a partial coalescence. Calcium sulphate gives rise to a drier ice-cream. Calcium and the magnesium cause an increase of the degree of aggregation of the proteins. Salts can also influence electrostatic interactions. The fat globules have a small clean negative charge, these ions can make to increase or to decrease this charge [[web page 2](#)]. Typically the consumer desires a sweet ice-cream, consequently, sweeteners are added to the mixtures with a 12-16% percentage in weight. The sweeteners, moreover, improve the "texture" and "palatability" of the ice cream, they improve the taste, and, usually, they are the most convenient source of total solid. Sugars, including lactose, contribute to lower the freezing point binding the water with the object of very low temperatures typical of the service temperature, between -15° and -18°C.

Saccharose is the most used sweetener, because it imparts an excellent taste. It is a disaccharide obtained from glucose and fructose.

It is common in the food industry to replace all or a portion of the content of saccharose with sweeteners obtained from corn syrup (dextrose). This sweetener is added to give more consistency and a greater chewiness to the ice cream, moreover it is a source of solid and improves the shelf-life of the end-product. Addition of dextrose produces an increase of sweetness and a diminution of the average molecular weight, this brings a lowering of the freezing point in the food in which it is present. Corn syrup contains more dextrin that binds more water in the mixture and this contributes to having a better

stability. The purpose is then to have an equilibrium among sweetness, total solid and freezing point [[web pg. 2](#)].

Stabilizers are a group of components, usually alimentary polysaccharide gums, which are responsible for the viscosity increase of the mixture. These bring a series of benefits, among which, without stabilizers, the ice-cream would quickly become frozen because of the migration of the free water and the growth of the ice crystals already present.

The functions of the stabilizers are:

- in the mixture: to stabilize the emulsion to prevent the fat creaming and, in the case of the carrageen, to prevent the separation of the serum due to the incompatibility of the polysaccharides with the milk proteins and also to keep the liquid aromas in suspension.
- on the frozen surface of the ice-cream: to stabilize the air bubbles and to maintain the taste.
- in the ice-cream during setting: to prevent the crystal growth of lactose and prevent or reduce the crystal growth of ice, to prevent the contraction or the collapse of the air bubbles and to prevent the migration of humidity in the packing and of sublimation from the surface.
- in the ice-cream during consumption: to offer consistency to contact with mouth, without being rubbery, and to have a good taste.

Limitations on their use include:

- excessive viscosity of the mixture before freezing.
- production of undesirable melting characteristics, because of the very high viscosity.

The stabilizers in use today in the food industry include:

- Guar gum, obtained from the endosperm of the guar seed , a bush, which grows in India and in a limited zone of Texas.
- Locust seed gum, synonymous with carob seed gum, a soluble fibre obtained from the endosperm of the seeds of an exotic plant that grows especially in Africa
- Xanthan gum, produced in crop by the microorganism *Xanthaomonas campestris*, used in small quantities
- Sodium alginate, extract of sea alga, used also in small quantities
- Carragenina, an extract of Irish musk or red algae

Each of these stabilizers has characteristic properties and often, two or more of them, in combination, are used for lending synergistic properties and to improve their general effectiveness. Guar, for example, is more soluble than locust seeds at lower temperatures, so it finds more applications in

pasteurization processes . Carragenina is not used alone but rather as a secondary colloid and is used for preventing the elimination of the milk serum from the mixtures that is usually promoted by the other stabilizers [web pg. 2]. The traditional emulsifier used in ice-cream is the egg yolk, while today there are two mainly used emulsifiers:

- Mono - and di-glycerids of fat acids, produced by the partial hydrolysis of fats or oils of animal origin;
- Polysorbate 80, an ester that is a molecule of a glucose alcohol with a fat acid with oxyethelene groups added to improve solubility in water.

The other possible sources of emulsifiers include serum and glycerol ester. All these components are the most important components present in the greater part of foods [web pg. 1]. Today, however, another type of ice-cream is frequently to be seen on the market: soft ice-cream. This type of product has the aspect of a whipped cream, but the taste of a true ice-cream, a soft and velvety aspect. The tendency is to try to produce this type of ice-cream in simple aerosol sprays to use quickly at home.

1.10 Aim and outline of the thesis

The thesis proposed intends to fill a lack of knowledge, tackling the study of cellular materials with a heterogeneous approach that distinguishes the two phases of gas and matrix. This allows the rheological properties to be introduced and therefore experience and ingredients to be linked together. On the contrary, the homogeneous approach fails, because it is not capable of inserting these latter very crucial properties.

The result is extremely interesting for aerated alimentary systems, the characteristics of which are strongly affected by bulk properties of the system or by both bulk and interfacial properties.

To do this, a starting point can be studying the expansion of a single bubble in a viscoelastic infinite medium, to try to understand what is the remarkable aspect of the aeration phenomenon and, more precisely, on the one hand, the rheological behaviour of the glutinous membrane, for systems like dough, and on the other hand, the behaviour of the membrane formed by the fat globules for systems like desserts. This study can be extended to the system of interactive bubbles to study in this way the coalescence phenomena ,of collapse and of stabilization for systems like biscuits. This allows the study to be extended to the system as a whole and to write a predictive model for viscoelastic systems. Each of these steps need the definition of the kinematics and dynamics of motion, and of the proper

rheological characterization that determine it. The final result is the control during the process of the texture evolution.

With the purpose of tackling the study of the proposed alimentary systems, the extrusion of food emulsion has also been studied and illustrated, particularly the case of soft ice-cream production, which can be extruded through nozzles. In this thesis an attempt is made to unravel the overall process of foam formation and the aim is to obtain more physical knowledge about the stability and foam formation of aerosol whipped cream, looking at the situation in the aerosol can.

1.11 References

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