# Origine et devenir des gaz dissous dans le fromage

## Origin and Fate of Gas in Cheese

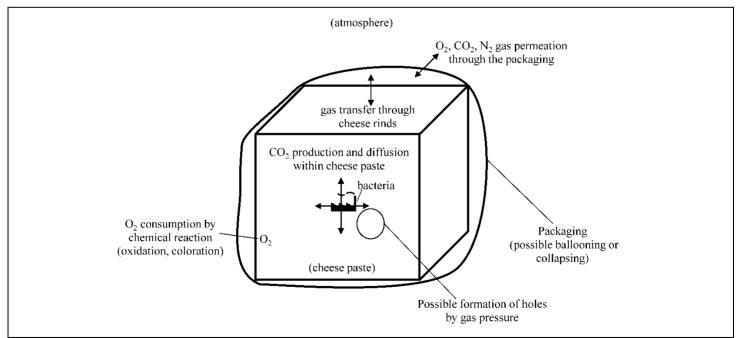
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**RÉSUMÉ.** La dissolution des gaz atmosphériques (oxygène, dioxyde de carbone) dans les fromages sont responsables des modifications physiques et biochimiques (par exemple, évolution de texture ou de couleur) se produisant au cours de l'affinage. Parmi les origines possibles des gaz dissous dans le fromage, on répertorie les gaz produits par des microorganismes volontairement ajoutés au lait ou bien la contamination par des gaz atmosphériques ou encore la production par des microorganismes non désirés. En dépit de l'intérêt de ces gaz dissous dans la conduite de l'affinage des fromages, leurs effets en technologie fromagère sur la qualité du produit ont été peu étudiés. Cette revue répertorie les différentes origines des gaz dissous dans les fromages et leur devenir, en insistant sur les conséquences des transferts de gaz sur les réactions biochimiques et physico-chimiques et la qualité du produit final. Dans cette revue, nous nous efforçons de démontrer que ces transferts impactent significativement la conduite de l'affinage et la durée de vie de nombreuses variétés de fromages. Une meilleure compréhension des mécanismes de transfert (diffusivité, solubilité) dans les pâtes fromagères s'avèrent donc nécessaire pour contrôler la qualité industrielle finale du produit.

ABSTRACT. Contact between atmospheric gases (oxygen, carbon dioxide) and food products like cheese lead to relevant biochemical and physical changes (for example, evolution of texture and colour). Among possible origin of gases in cheese, it could be gases intentionally produced by microorganisms, or voluntarily introduced during cheese preparation or on the contrary unwanted contamination from atmospheric gases, spoilage microflora, etc. In spite of their interest in cheese ripening, the effects of gases during cheese making and storage has been so far under investigated. This review discusses the possible origin and fate of gas in cheese, highlighting the consequences of gas transfer on cheese biochemical and physical properties and quality. We attempt to demonstrate that gas transfer relevantly affects the ripening and shelf life of many cheese varieties. A better understanding of gas transfer properties (diffusivity, solubility) in cheese products during ripening may allow to better control the industrial quality of the final product.

MOTS-CLÉS. Fromage, gaz atmosphériques, diffusivité, solubilité, loi de Henry, loi de Fick.

KEYWORDS. Cheese, atmospheric gases, diffusivity, solubility, Henry's law, Fick's law.



GRAPHICAL ABSTRACT. DIFFUSION - PRODUCTION OF GASES DURING CHEESE RIPENING UNDER FOIL

A BETTER UNDERSTANDING OF GAS TRANSFER PROPERTIES (DIFFUSIVITY, SOLUBILITY) IN CHEESE PRODUCTS DURING RIPENING MAY ALLOW TO BETTER CONTROL THE INDUSTRIAL QUALITY OF THE FINAL PRODUCT. THAT IMPLIES TO CONSIDER THE COUPLING BETWEEN SOLUBILIZATION AND DIFFUSION MECHANISMS WITH THE REACTIONS OCCURRING IN THE FOOD/PACKAGING SYSTEM

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#### 1. Introduction

Cheese ripening is a key step for dairy companies, because it is the longest operation which contributes to the formation of the economic value of the final product. This commercial quality is strongly linked to the development of the desired sensory attributes. The sensory attributes of the ripened cheese, flavor and texture change during shelf life, and the commercial quality needs to remain acceptable within a defined range of variation [1]. Components of the atmosphere (N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub>) may be intentionally or unintentionally incorporated into the cheese milk and further cheese paste during processing, ripening and storage. These components, mainly gases, solubilize and diffuse into the product, triggering some biological and biochemical reactions and providing thus significant evolution of the cheese sensory properties during the whole ripening and shelf life period [2].

Diffusion of oxygen is almost unavoidable due to its occurrence in high concentration in the surrounding atmosphere. Although non-voluntarily added, it may be useful, being consumed by the aerobic micro-flora during initial cheese making operations. On the contrary, other gases such as CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, may be intentionally introduced into the cheese and/or produced by different microorganisms during ripening and storage [3]. For instance, CO<sub>2</sub> may be injected into the cheese milk for improving its renneting-ability via the acidification by formation of carbonic acid. CO<sub>2</sub> could also be produced during ripening by the bacteria and mold metabolism voluntarily added to the cheese paste. This is particularly relevant for cheeses with propionic acid fermentation (Emmental-type and similar cheeses with eye). CO<sub>2</sub> produced by propionic acid bacteria allow the cheese body to open for eyes' growth. This is made possible by wrapping the rindless cheeses into a barrier packaging material and eyes' growth depend therefore on the balance between losses though the packaging film and production by the bacteria [4]. CO<sub>2</sub> could be also injected in the cheese packaging headspace for delaying bacterial growth via its bacteriostatic effects in Modified Atmosphere Packaging (MAP) system [5]. In this last case, modification of internal gas composition during storage relies on the permeation through the packaging material of gases and/or consumption/production of gases for cheese with active metabolism.

The extent of the aforementioned phenomena affect the sensory attributes of the cheese. If the typical "open" texture of Emmental-type and similar cheeses with eyes is sought through the oversaturation of cheese paste with endogenous CO<sub>2</sub> production, such eyes are on the contrary defect in "gasless cheeses" such as Cheddar or Grana Padano. Flavor may also be directly or indirectly affected by transport of gaseous components (CO<sub>2</sub>, NH<sub>3</sub>, and O<sub>2</sub>), leading to quality changes, even after maturation and during storage ([6,7]). These gaseous components, once dissolved in the cheese paste, diffuse and affect cheese flavor mainly by affecting the cheese pH (NH<sub>3</sub>), by affecting bacterial metabolism (CO<sub>2</sub>) [8–10] and by inducing oxidative reactions (O<sub>2</sub>). In addition to product texture and flavor, gas production and transfer occurring in the cheese/packaging system during storage could affect visual aspect of the package leading to package ballooning or collapsing. These phenomena depend on the extend of gases production/consumption, solubility/diffusivity and permeation through the packaging material.

Therefore, the knowledge of the gas transfer properties in the cheese and in the cheese/packaging system is of paramount importance for enabling good decisions concerning ripening, storage and in particular choice of the packaging material [11]. However, study of gas transport in solid food matrices has been widely overlooked by researchers. This may be due to the fact that still nowadays there are no available techniques at a low cost for a non-invasive determination of dissolved gases in solid matrices [12,13]. Information on carbon dioxide solubility and diffusivity in cheese are scarce in the literature, while the information related to oxygen are almost nonexistent.

This review aims to describe the role of gas components during cheese ripening and storage, taking into account the great variety in terms of cheese quality (from soft to hard, mold or mold-free, natural or foil ripened). We aim to highlight that gaseous components (CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>) may affect the

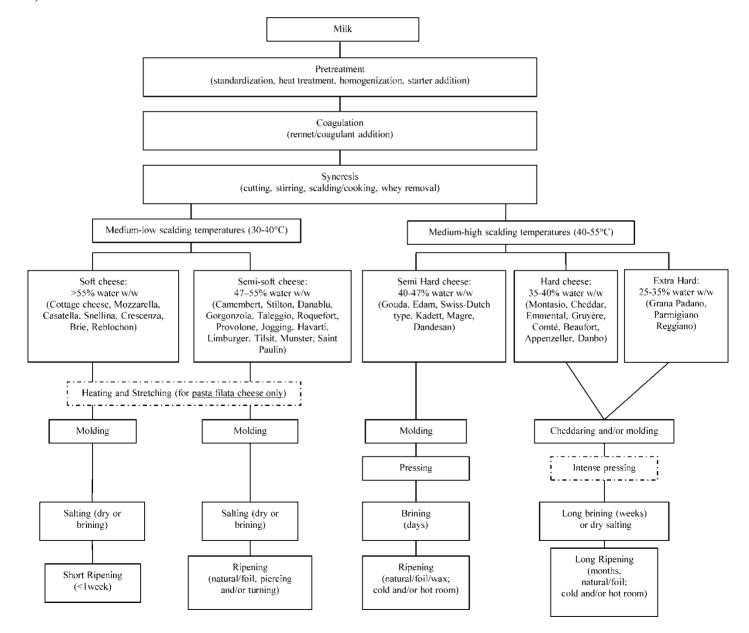
quality of many cheese varieties and that a better knowledge of overall gas transfer properties would help improving control of biochemical phenomena undergoing in cheese making technology.

## 2. Origin of gas in cheese

Along cheese making process, gas species are present. Gas in cheese may be originated from different sources, which may be conveniently divided in four classes: the indigenous gas of the milk, the atmospheric gases, the ones produced by microorganisms (bacteria and fungi) and the ones directly added via the usage of certain technologies (for example, gas injection in cheese milk, gas flushing during packaging).

Cheese making technology can be summarized in few major steps which are common for all cheese types: milk coagulation, syneresis leading to whey expulsion, molding, salting, ripening and then packaging. Description of cheese making process is out of the scope of this review and are not developed further here. However, some complementary information could be found in the <u>Supplementary material</u>.

Figure 1 provides a technological classification of cheese types, mainly based on the texture of the final product (from soft to extra-hard), which is mostly related to the moisture content (from high to low).

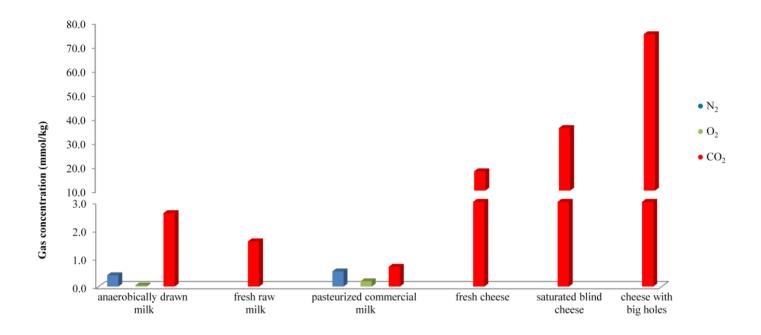


**Figure 1.** Major cheese making operations (actual steps for a particular cheese may vary) from [1]. The most cited cheeses in this publication have been included in the figure.

## 2.1. Atmospheric gases

The earth's atmosphere is a natural source of gases, which are present at a relatively constant percentage (percentage of gas in dry air): about 78.1 for  $N_2$ , 20.9 for  $O_2$ , 0.09 for Ar and 0.03 for  $CO_2$  [14].

Milk in the udder would not be in equilibrium with atmospheric gases as noted by Akkerman et al. [3] who reported that it would be only at 25% and 85% of its saturation in  $O_2$  and  $N_2$  respectively. The concentration of  $O_2$ ,  $N_2$  and  $CO_2$  in anaerobically drawn milk was reported by Noll and Supplee [15] at 0°C and 1 atm: about 0.04, 0.4 and 2.6 mmol/kg respectively, with  $N_2$  being estimated as residual gas. According to this data, anaerobically drawn milk contains high value of dissolved  $CO_2$  compared to fresh or commercial milk in the supermarket (Figure 2). Unfortunately, there is no more recent information about the composition in endogenous gases in milk.



**Figure 2.** Bar chart illustrating typical gas concentration found in milk and cheese during dairy processing. from [3,15–18].

Once exposed to atmospheric air, milk tends to equilibrate its gas composition in order to be saturated according to Henry's law. After contact with the atmosphere, it is expected that milk CO<sub>2</sub> concentration would decrease, while N<sub>2</sub> and O<sub>2</sub> content would increase. For example, Ma et al. [18] reported that CO<sub>2</sub> concentration decreases from 1.6 mmol/kg in fresh raw milk to 0.7 mmol/kg in pasteurized milk (Figure 2). Concentration of O<sub>2</sub> and N<sub>2</sub> in mixed raw milk at room temperature were reported to equal about 0.2 and 0.5 mmol kg<sup>-1</sup> respectively [16], which are slightly higher compared to the values given by Noll and Supplee [15] for anaerobically drawn milk.

The dissolution of atmospheric gases in milk and cheese can be enhanced during some cheese making operations especially stirring and foaming of the cheese milk and cheese curd in the vat [19]. Some other operations could also enhance the contact between the product and atmosphere such as the mixing of curd and salt during cheddaring, specific to Cheddar cheese varieties, the piercing operation in blue cheeses [20,21] or the pressing operation in semi-hard and hard type cheeses [19,22]. In that last case, depending on the pressing conditions, air may be entrapped in the porous curd resulting in the formation of unwanted mechanical openings under rind, when pressing [23]. To avoid these defects, some researchers have thus studied the possibility of eliminating the air present in the curd and whey mixture via vacuum treatment before pressing [24,25].

The extent of the solubilization of atmospheric gases in cheese depends on thermodynamic factors such as temperature and pressure, biochemical factors of the cheese (for example, pH, chemical composition) and, packaging and storage conditions (headspace to volume ratio), similarly to what described for meat products [26]. The influence of fat, salt and moisture content, cheese age and size, temperature, were investigated in relation to the solubility of CO<sub>2</sub> in semi-hard type cheeses [27–29].

## 2.2. Gas produced by microorganisms

Gas (mainly CO<sub>2</sub> and H<sub>2</sub>) can be produced in cheese by a various number of microorganisms such as bacteria and fungi which can be intentionally added into the cheese milk or naturally present in the milk and/or the cheese during manufacturing [30,31]. Intentionally added microorganisms, also called starters, are added for enhance texture and flavor formation. Microorganisms naturally present or coming from milk contamination significantly impact, usually badly, the sensory properties of the final product.

Gas producing microorganisms, which are considered negative if present in high number for certain cheese-makers, may be used as starters by other cheese producers (for example, high counts of Propionic Acid Bacteria are negative for Grana Padano cheese and desired in Emmental type cheeses respectively) [32,33], leading to a difficult technological classification. The same statement is valid for fungi in different cheese varieties [34]. Microorganisms implicating in gas production in cheese have been hereafter classified according to their main role in cheese technology: primary starters (conversion of lactose into lactic acid, with consequent acidification) and secondary flora (production of different metabolites, which directly or indirectly affect cheese texture and/or flavor) [35].

#### 2.2.1. Starters

Primary starters bacteria are lactic acid bacteria (LAB) used in cheese technology for their ability to convert lactose in lactic acid, leading to the acidification of the curd during the first steps of cheese production. They are generally active until the salting and/or cooling operation. They may be divided in mesophilic and thermophilic primary starters, according to their optimum temperature. Mesophilic bacteria are used in semi-hard and soft/semi-soft cheese technologies, where the scalding temperature are between 30 and 40°C. Thermophilic bacteria are used mainly in hard cheese varieties where cooking temperatures may reach 50 – 55°C [35–37]. For more information concerning classification and physiology of lactic acid bacteria (LAB), the reader is referred to [38].

#### 2.2.1.1. Mesophilic Lactic Acid Bacteria

Mesophilic lactic acid bacteria may be classified according to their rate of CO<sub>2</sub> production in cheese, from very slow, slow to fast: O, B, BD starters [39]. B and D refer to the presence of the strains *Leuconostoc* spp. (formerly *Betacoccus*) [40] and citrate-positive strains of *Lactococcus*, previously *Lactococcus lactis lactis* biovar. *diacetylactis* (hereafter Cit<sup>+</sup> Lactococci) respectively in the starter. BD starters contain both type of citrate utilizing organisms, while O-starters lack both types of organisms. While Cit<sup>+</sup> Lactococci are mesophilic homo-fermentative strains, *Leuconostoc* spp. are heterofermentative [41]. The latter are in fact able to produce carbon dioxide from both citrate and glucose, therefore the group BD is used for identifying the most effective producers of CO<sub>2</sub> among the mesophilic starters.

O starters, with slow CO<sub>2</sub> production rate, are for example applied to the production of cheeses where no eyes are desired (for example, Cheddar), while B and BD-starters are used for the production of cheeses where few eyes are desired like in semi-hard Dutch varieties (for example, Edam, Gouda) [37]. BD starters are also used in the production of semi-hard cheeses with intense PAB fermentation (referred as Swiss-Dutch type cheeses in this document and equivalent to Maasdam cheese also found in literature), because of their fast CO<sub>2</sub> production rate contributing to the rapid saturation of milk suitable for the further formation of desired eyes [42]. The usage of either B or BD type of starters is also applied to blue cheese manufacture (semi-soft variety), in order to promote intra curd openings for

the growth of *Penicillium Roqueforti* and to help preventing growth of contaminant molds which are sensitive to high CO<sub>2</sub> concentration [43].

The metabolic pathways used by the aforementioned bacteria are very complex, because they depend on interactions between other microorganisms [44] and environmental condition such as oxygen concentration [45,46], pH, nutrient concentration and their diffusional properties in the cheese [47]. Table 1 summarized the substrates used, major metabolic compounds and corresponding molar ratios for the most known B and BD primary starters.

From the quantity of D-lactic acid<sup>1</sup> produced, the theoretical carbon dioxide produced by the BD primary starters could be calculated, according to the following molar equation [48]:

 $CO_2$  = consumed citrate + D-lactate + 2 x (diacetyle + acetoine + 2.3 butanediol)

Équation 1

#### 2.2.1.2. Thermophilic Lactic Acid Bacteria

Thermophilic (primary starters) LAB (*Lactobacillus helveticus*, *Lb. delbruekii* subsp. *lactis*, *Streptococcus thermophilus*) are commonly used in hard cheese like Emmental-type cheese technology. Among these homofermentative primary starters, *Lb. helveticus* and streptococci are proteolytic and they may lead to production of gas (NH<sub>3</sub>, CO<sub>2</sub>) from decarboxylation and deamination of peptides in the late stages of ripening [42]. Certain strains of *Streptococcus thermophilus* may lead to crack formation in Gouda and Montasio cheeses, due to the decarboxylation of glutamic acid. This characteristic is a defect in the first mentioned Dutch cheeses, while it is desired in the latter mentioned Italian variety [48].

## 2.2.2. Secondary flora

The secondary flora is composed of a mixture of bacteria and/or fungi (molds and yeasts), which can be intentionally added to the cheese milk or on cheese curd surface to form a rind [49,50]. They are in the form of defined cultures and/or composed of adventitious microorganisms coming either from ingredients or the environment [35]. Some adventitious microorganisms may negatively affect cheese quality and they are referred as spoilage microorganisms in this document. The secondary flora, together with the primary starter, is responsible for flavor, texture and rind formation in cheese (Beresford et al., 2001). This flavor and texture formation is systematically related to an aerobic or anaerobic metabolism and gases consumption/production.

#### 2.2.2.1. Non-starter lactic acid bacteria

Some strains of <u>hetero-fermentative lactobacilli</u>, also called **non-starter lactic acid bacteria** (<u>NSLAB</u>) or secondary flora, are naturally present in the milk and have been reported to survive heat treatments equal to pasteurization [51]. These bacteria (mainly *Lb. casei* and *Lb. paracasei*) may contribute to gas oversaturation in the curd in aerobic conditions, due to oxidation of pyruvate to carbon dioxide and acetate, or via production of CO<sub>2</sub> from citrate [48,52,53]. Secondary flora NSLAB may include thermoresistant microorganisms which may contaminate the cheese milk and may contribute to carbon dioxide production from citrate such as enterococci [54,55] or the facultative hetero-fermentative *Lb. rhamnosus* and *Lb. casei* types [53] or the hetero-fermentative *Lb. fermentum*, which was described to cause relevant CO<sub>2</sub> production in cooked cheeses [56].

## 2.2.2.2. Propionic Acid Bacteria

Propionic acid bacteria (PAB) are added into the Emmental and Swiss-Dutch cheese milk at high inoculum, to produce high quantity of CO<sub>2</sub> necessary to create the eyes opening in the cheese curd during ripening [33,57]. They are mainly active during hot room ripening (about 20°C). Their metabolism (metabolic pathways number 3, 4, 5 in Table 1) is in fact based on lactate, which needs to

<sup>&</sup>lt;sup>1</sup> Dextrorotatory lactic acid

be converted from lactose by the previously mentioned primary starters. Among the dairy PAB, *Propionibacterium freudenreichii* subsp. *shermanii* and subsp. *freudenreichii* are the most used in cheese technology: they are naturally present in the intestine and rumen of cows and they are classified as Gram +, anaerobic, but aero-tolerant, non-motile, rod-shaped bacteria [42].

PAB are undoubtedly the most important source of CO<sub>2</sub> during hot room ripening of Emmental (and Swiss-Dutch type) cheeses, contributing for about 81.5% of the daily CO<sub>2</sub> production during hot room ripening [58]. About 120 L of CO<sub>2</sub> may be produced in an 80 kg cheese loaf before the cheese is sufficiently aged for consumption, mostly thanks to PAB metabolic pathways under anaerobic conditions [42]. PAB were also found responsible for undesired CO<sub>2</sub> production in Grana Padano cheese [32].

Among all the reported metabolic pathways for PAB (Table 1), the Fitz pathway (number 3 in Table 1) is considered to be the relevant one for semi-hard cheese with intense PAB fermentation (Swiss-Dutch type variety), because the molar ratio between produced propionate and acetate usually obtained in such cheeses is about 2 as in the Fitz pathway [58,59]. The 2<sup>nd</sup> described pathway (number 4 in table 1), so-called CO<sub>2</sub> fixation pathway, is considered of minor importance. The 3<sup>rd</sup> shown pathway (number 5 in table 1) may also take place when aspartase-positive PAB and available aspartate are present. This may be the case if ripening is long enough for relevant proteolysis to take place and if the PAB strain is aspartase-positive which is rather scarce [60]. The type of dairy PAB used strongly influences the quantity of carbon dioxide produced in the cheese (for example, aspartase-positive may produce 3 times more CO<sub>2</sub> than other strains). Wider information concerning the metabolism of lactate and sugars by dairy PAB has been reviewed by Piveteau [61].

CO<sub>2</sub> production by PAB is strongly dependent on cheese composition, especially salt content. Huc et al. [58] demonstrated that the presence of salt in semi-hard cheeses induced a delay in the bacterial development, reducing the CO<sub>2</sub> production and decreasing the eye growth. This relation between salt content and CO<sub>2</sub> production was also observed by Acerbi et al. [62] and was already highlighted in brined Emmental cheese by Pauchard et al [63]. Pauchard et al. (1980) noticed that CO<sub>2</sub> gradients in Emmental wheels were inversely related to the salt gradients (higher CO<sub>2</sub> content in the core and lower at the periphery). In cheddar, a dry salted cheese, with a more homogeneous salt distribution tthan in brined Emmental cheese for instance [64], CO<sub>2</sub> content was found independent from the position [65] confirming the importance of the link between salt gradient and CO<sub>2</sub> production.

## 2.2.2.3. Yeasts

Yeasts may be present in milk at low, insignificant populations, but their natural occurrence in cheese is usually not unexpected for most of cheese types, because of their ability to grow at low pH, moisture content, temperature and water activity [34]. The majority of yeasts found in cheese are located on the cheese surface (for example, the rinds) and required the presence of abundant air supply. Less than 1% of the yeast population found on cheese surface may be also found in the mass [35]. Nevertheless, dedicated yeasts might grow specifically within the cheese mass [66]. Species of *Rhodotorula, Pullularia, Torulopsis, Trichosporon* and *Candida* have been isolated from cream and butter. However, in modern well managed plants the risk of spoilage from these organisms is considered to be relatively small since they are well sensitive to pasteurization [66]. *Torula* and *Candida* yeasts are among the few ones which can grow with LAB and can ferment lactose, carrying out alcoholic fermentation, leading to production of gas (CO<sub>2</sub>). Yeast alcoholic fermentation is reminded in Table 1 [66].

Yeasts play a positive role for flavor and texture development in many cheese varieties [67]. In particular, their role is fundamental in smear surface ripened cheeses, where the "smear" may be defined as a slurry including mainly bacteria (for example, *Brevibacterium linens* etc.) and yeasts (*Candida, Debaromyces, Kluyveromyces, Rhodotorula* amongst others). Although the microbiology of the smear is poorly understood, it is generally believed that yeasts grow during the first few ripening days, oxidizing the lactate completely to CO<sub>2</sub> and water. They also are able to deaminate aminoacids to

the corresponding ketoacids and NH<sub>3</sub> [35]. Smear cheeses are usually semi-soft (Taleggio, Limburger, Tilsit, Munster, Saint Paulin, Havarti amongst others), but hard cheeses (Beaufort, Comte, Gruyère, Appenzeller, Danbo) may also be smeared [35,68]. The significant pH change observable in some cheese due to the smear (production of NH<sub>3</sub>) may probably affect gas solubility, therefore gas transfer in the cheese. Yeasts are considered important not only for smear ripened cheeses, but also some types of blue cheeses: *D. hansenii* is considered to be the dominant yeast species in Danish blue cheese [69], while *G. candidum* in the French cheese Reblochon [70].

#### 2.2.2.4. Molds

The most important mold cheeses (usually semi-soft variety) may be divided in two groups: the ones ripened with *Penicillium roqueforti* forming blue veins (blue cheeses: Roquefort, Gorgonzola, Stilton, Danish blue among all) and the ones with *Penicillium Camemberti* growing on the surface (for example, Camembert, Brie, among others) [35].

Several molds (for example, *Penicillum camemberti* types), similar to what was previously described for yeasts, are able to metabolize lactate, producing carbon dioxide and water, as well as producing NH<sub>3</sub> from deamination of amino acids. Gases produced by the smear on the surface of cheese may dissolve in the headspace or in the atmosphere, depending on the packaging of the cheese.

Gas (especially oxygen) is of paramount importance for the correct growth of that type of molds, because molds need oxygen for their metabolism (respiration). The degree of piercing in blue cheese technology allow to master molds' growth, by controling oxygen diffusion from the atmosphere to the core of the cheese [20,71].

## 2.2.2.5. Spoilage microorganisms

Adventitious microorganisms which may lead to a decrease in quality of the cheese have been classified as spoilage microorganisms. Two main types of spoilage microorganisms were identified which may be considered as having negative effects on the quality of any type of cheese and which can produce gas at early or advanced ripening stage: coliform and clostridia respectively. Other type of microorganisms may be considered spoilage only for some categories of cheeses such as some types of yeasts for certain types of cheeses (see Chapter 2.3.2.3) associated to early gas defects and NSLAB and heterofermentative lactic acid bacteria (for example *Lactobacillus brevis* and *Lactobacillus fermentum*) in Cheddar cheeses, associated to late gas defects [72].

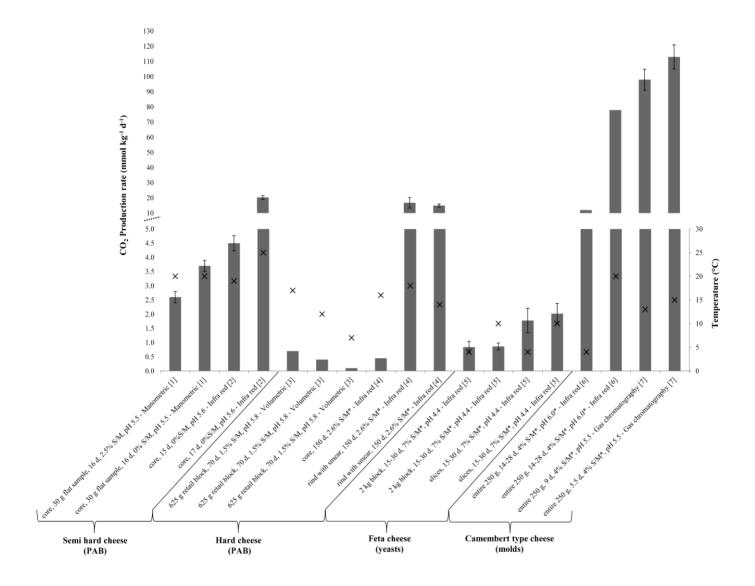
**Coliform**. Coliform bacteria which might contaminate the cheese during processing may also contribute to gas production in cheese, because they can ferment glucose, leading to formation of hydrogen and carbon dioxide [73]. Simplified molar equation describing fermentation of glucose by coliforms to produce gas is summarized in Table 1 (pathway number 7) [74]. Coliform gassy fermentation is known in cheese industry as early gas defect, because loaves of cheeses with coliform fermentation may present defects due to gas production taking place at an early ripening stage [75].

Clostridia. Spores of Clostridium spp. are resistant to pasteurization and may lead to growth of Clostridia during ripening [76]. If this event occurs, the bacteria, in particular Clostridium tyrobutyricum, is able to convert lactate into butyric acid, carbon dioxide and hydrogen (pathway 6 in Table 1) and it may cause the swelling of the cheese loaf due to the very low solubility of the latter in cheese water phase [77] (H<sub>2</sub> is about 20 times less soluble in water than carbon dioxide) (Fig. 4). This phenomenon was observed in some loaves of Italian [78] and Swiss [79] hard cheese during ripening and it is known as late gas blowing due to the volume increased of the cheese loaves at a later ripening stage, when clostridia spores germinate.

## 2.2.3. Rates of CO<sub>2</sub> production

Examples of CO<sub>2</sub> production rates from different microorganisms are given in Figure 3. It is not possible to precisely compare the production rates, unless they are assessed within the same microorganisms in the same cheese (chemical composition, pH) and same temperature. Information

concerning the count of microorganisms at the moment of the experiment is unfortunately missing and it could have an effect on the total production rate. The CO<sub>2</sub> production rate from aerobic metabolism (mainly yeasts and molds from smear ripened and blue cheese respectively) seems much more important compared to anaerobic fermentation (mainly from propionic acid bacteria in Emmental and Swiss-Dutch type cheeses). Although one may try to associate one source of CO<sub>2</sub> production per one type of cheese, it is more likely that different sources of CO<sub>2</sub> production may be present in a same cheese during ripening. For example, in smear ripened cheeses with some propionic acid fermentation such as Gruyère, Beaufort and Comté, both aerobic metabolism from the microflora of the smear and anaerobic fermentation inside the cheese paste may contribute to the overall CO<sub>2</sub> production of the cheese [80] (Figure 3).



**Figure 3.** CO<sub>2</sub> production rate in cheese types at different temperatures (axis on the right; X-cross on the graph). Main source of CO<sub>2</sub> production is indicated in brackets. Cheese type, position, sample mass, ripening days, salt to moisture ratio (S/M), pH and measurement method are indicated. Asterisk superscripts indicate that values have been calculated from literature and were not given by authors. Standard deviation bars, when available, are reported. Data are gathered from following references: [1] [58]; [2] [62]; [3] [59]; [5] [81]; [6] [82]; [7] [83].

#### 2.3. Gas technologically added in milk and cheese

Gases may be intentionally injected into the cheese milk to improve its quality (for example, milk carbonation) [84] or into the maturation room (controlled atmosphere ripening) [85] or at the moment of packing for shelf life extension purposes (modified atmosphere packaging or MAP) [86–88].

#### 2.3.1. Milk carbonation

The injection of CO<sub>2</sub> in milk under pressure is known as carbonation. It is not a common practice in cheese-making. Quantity of CO<sub>2</sub> added in industrial cheese milk may range from 100 to 1000 ppm according to the desired effect, for example up to a certain pH of the cheese milk, which decreases with increasing formation of carbonic acid in the water phase of the milk [18,85,89]. The CO<sub>2</sub> is usually added (under pressure) to acidify the cheese milk during storage for preservation purposes (especially inhibiting Gram-negative psychrotrophic bacteria) [5] or for decreasing the pH of the milk prior to coagulation, in order to reduce renneting time. CO<sub>2</sub> can be easily removed by de-pressurization of the milk, but its effects are not all reversible. For instance, Nelson et. [90] injected 1600 ppm of CO<sub>2</sub> into cold Cheddar milk, resulting in milk pH of 5.9 at 31°C in the cheese vat. They found that about 13 % of injected CO<sub>2</sub> was kept in the cheese during ripening, resulting in almost three times more CO<sub>2</sub> in the treated cheese compared to the untreated one (337 vs 124 ppm respectively). Left-over CO<sub>2</sub> in cheese from carbonated milk might contribute to open texture in the ripened cheese [77].

## 2.3.2. Controlled/Modified atmosphere during ripening

Usage of controlled/modified atmosphere during cheese ripening is not yet as widespread as is MAP used during storage. However the importance of gas composition in the atmosphere which surrounds the cheese during ripening is well known by dairy technologists. For example during the manufacturing process of blue cheeses such as Stilton, Roquefort, Gorgonzola, the blocks of cheese are pierced with rods to allow oxygen to enter into the curd to facilitate mold growth [91]. Furthermore the usage of a slightly ammoniacal atmosphere during ripening of soft surface ripened cheese like Camembert may be used to reduce bitterness (flavor defect) [92]. The authors related the decreased of bitterness to the decreased of proteolytic activity of Penicillium camemberti caused by the increased pH of the outer cheese layer due to sorption of ammonia from the atmosphere. Mirade & Daudin [93] reported that the presence of carbon dioxide in the indoor atmosphere would increase the opening of the curd of hard cheeses as Emmental, Gruyère (French type) and Comté by stimulating propionic acid fermentation. For these reasons, some authors are developing mathematical models for describing gas transfer during food ripening, including the interactions between cheese and the atmosphere [93,94]. The goal of these models is to optimize gas transfer between food and the surrounding atmosphere via an optimized ventilation system during ripening. Optimized ventilation may be a homogeneous distribution of gases and relative humidity in the ripening room, leading to a homogeneous gas exchange between the food rind and the surrounding atmosphere.

Another way of controlling the gaseous exchange between cheese and the atmosphere and *vice versa* during ripening is by wrapping the cheese with packaging foil (for example, wax, plastic etc.) during ripening. This technology is applied by many industries which ripen their cheeses under foil since the 1920s [95]. Wrapping a food under foil leads to the modification of the kinetics of gas loss and uptake, according to the environmental conditions (temperature, relative humidity, gas composition), permeability of the foil to atmospheric gases and the rate of gases production [2]. The mass transfer properties of the wrapping film have an important effect on the quality of the ripened cheese and this effect varies from one type of cheese to another; especially avoiding high  $O_2$  uptake is important for anaerobic ripened cheeses, avoiding  $CO_2$  losses may be preferable for eyed cheeses [77]. Different quantity of  $O_2$  and  $CO_2$  in contact with mold and yeast ripened cheeses may result in a good or low quality product [87,96–98]. The level of oxygen in contact with the inner part of blue cheeses may be enhanced during ripening thanks to the piercing operation, which, at the same time, allows  $CO_2$  loss.

#### 2.3.3. Modified atmosphere packaging (MAP) during storage

Modification of the natural gas composition of the unfilled volume of packed food products is called modified atmosphere packaging (MAP). It could be active MAP when internal atmosphere is deliberately changed during packing or passive MAP when changes of internal gas composition occur due to the product metabolism (for example, case of respiring soft cheese with molds or blue veined cheese for example). In the first case, barrier packaging films are usually used to maintain the initial

level of injected gases around a threshold value. In the second case, the modified atmosphere is obtained by the interplay of two mechanisms (1)  $O_2/CO_2$  consumption / production by the product and (2) gas permeation through the packaging material, the optimal atmosphere for a given product being achieved only for a given couple of suitable permeability of  $O_2$  and  $CO_2$  for the packaging material [99,100].

In the case of active packaging, the most used gases for extending cheese shelf life during storage are carbon dioxide and nitrogen, often as a mix, at ratios which can greatly vary (from 100 % CO2 to 100% N<sub>2</sub>) depending on the cheese type [86]. Usually CO<sub>2</sub> is used for its bacteriostatic properties, enhanced by its unique high solubility in both hydrophilic and hydrophobic media [5]. Oxygen is often used in low concentrations (1-5%) to limit oxidations. In passive MAP, low  $O_2$  levels are achieved due to the O<sub>2</sub> consumption of the mold ripened cheeses [82,101]. The use of other gases have been investigated by researchers as potential substitutes of the above mentioned ones, but they failed to enter into commercial applications due to safety, regulatory, and cost considerations [102]. The partial pressure in headspace and sometimes also the absolute pressure changes during shelf life due to the activity of microorganisms into the cheese (production and consumption of gases), the permeability of the packaging, the solubilisation and diffusion of gases into the cheese and the environmental conditions (surrounding atmosphere composition, temperature). These phenomena may lead to relevant modifications in the quality of the final product even during storage at the supermarket (for example, contraction or expansion of the cheese package during shelf life) [103]. These gas changes during storage of the packed food can be predicted using appropriate mathematical models coupling mass transfer and respiration models. Such numerical tools are well developed for the field of fresh fruits and vegetable and help to choose the right packaging material for a given product [104,105].

#### 3. Fate of gas in cheese

## 3.1. Basics of gas transfer

In the gaseous state, interactions between molecules are extremely low, when compared with liquid and solid particles. If the interactions between gas particles can be considered negligible (low gas density or diluted gas), the ideal gas law can be applied for describing the behavior of real gases,

$$pV = nRT$$
 Équation 2

where p is pressure, V is volume and n is the quantity of gas, R gas constant and T is absolute temperature.

Considering an ideal gas A at constant temperature T and given total pressure p, diluted into a solvent, low concentration, Henry's law states that the partial pressure of the gas  $p_A$  above the solvent is proportional to the concentration of the component diluted in the solvent,

$$p_A = K_H(T)C_A$$
 Équation 3

where  $K_H$  is the Henry's law constant for a given combination of solute A and solvent and  $C_A$  is the concentration of the solute.

Henry's coefficient  $K_H(T)$  may be expressed in [kg·Pa·mol<sup>-1</sup>] depending on the units for  $C_A$  and  $p_A$ . It should be noted that in some communities Henry's law refers to the reverse expression relating concentration to partial pressure and in this community the  $K_H(T)^{-1}$  is the solubility coefficient  $S_A(T)$  of the component A, which can be expressed [mol·kg<sup>-1</sup>Pa<sup>-1</sup>] for the SI (International System of Units) or [mmol kg<sup>-1</sup> atm<sup>-1</sup>] within this review (conversion factor from mmol kg<sup>-1</sup> atm<sup>-1</sup> to SI units:  $9.86923 \times 10^{-9}$ ). The solubility coefficient represents the equilibrium quantity of gas A that can be dissolved in a material for a given partial pressure of A. Solubility is a thermodynamic property and it reflects the molecular interactions between the solute and the solvent [106].

Henry's law has been used by several researchers for representing the concentration of gases as a function of their equilibrium partial pressure in numerous solutions and foods [107]. Although this law is universally accepted for describing behavior of low concentrations of solutes, the range of its actual validity should be subjected to experimental test when applied to real systems like food [12]. Tables collecting solubility coefficients of several gases in water have been reported in the literature [12,108], but coefficients in complex matrix like food are difficult to find. Henry's law has been so far validated for some gases in few foods and beverages: CO<sub>2</sub> in meat [109], O<sub>2</sub> in microbial culture media [110] or O<sub>2</sub> in various organic liquids such as acetone or ethanol [111]. To the best of our knowledge, the only studies reporting validation of Henry's law in cheese products are the ones of Fava and Piergiovanni [109] in Emmental type cheese, Jakobsen et al [103] in semi-hard cheese, Acerbi et al [29] in Maasdam type cheese and Chaix and others (2015) in processed cheese.

Considering a steady state, the diffusion of a component in a diluted solution, with negligible electrical charges, can be quantified by making use of Fick's first law [112] which states that the diffusional flow rate per unit area  $J [kg \cdot s^{-1}]$  of a compound transported in the direction of x [m], through a cross section of surface  $A [m^2]$  perpendicular to x, in a unit time t [s], is proportional to the concentration gradient dc/dx,

$$J = \frac{dC}{dt} = DA \frac{dC}{dx}$$
 Équation 4

where C [kg·m $^{-3}$ ] is the concentration of the studied compound and D [m $^{2}$ ·s $^{-1}$ ] is the diffusion coefficient or diffusivity.

By combining Eq. 4 and Henry's law (Eq. 3), Fick's first law can be transformed into relationship of permeation.

$$J = PA \frac{\Delta p}{\Delta x}$$
 Équation 5

where J is the flux of permeating gas through a plane sheet of thickness  $\Delta x$ , P is the permeability coefficient (product of D and S of the permeating gas in the material), and  $\Delta p$  is the difference of partial pressure between on both sides of the plane sheet. This law states that the rate of steady permeation through a thin slap of material (i.e. a packaging film or a slap of food) is proportional to the difference between partial pressure on each side of the film/slap. Eq. 4 is particularly relevant for packaging, to characterize gas and vapor permeation through the packaging and thus the exchange with the surrounding atmosphere. Indeed the concentration of the gas or vapor which surrounds the packaging material is usually better known and quantifiable than the corresponding concentration in the material and, in thin membranes as packaging material the steady state is generally reached very quickly therefore first Fick's law applies.

For non-steady-state systems, second Fick's law describes the change in concentration (c) with time at any place as a function of the local concentration gradient:

$$\left(\frac{\partial c}{\partial t}\right) = D\left(\frac{\partial^2 c}{\partial x^2}\right)$$
 Équation 6

The value of D depends on the migrant and the matter in which the migrant diffuses. The knowledge of D remains the main bottlenecks in the use of Fick's law to predict diffusional transport and the value of D is often derived from diffusions experiments [12]. For a detailed mathematical treatment of second Fick law, the reader may refer to [113]. Mathematical solutions of Eq. 6 have been widely used by food researchers for describing total mass transport and concentration profiles as a function of time within food where non steady state conditions are usually encountered (for example, during drying, remoistening, brining, etc.). These mathematical solutions of Eq. 6 are fundamental prerequisite for determining diffusivity coefficient which is identified by fitting mathematical solution to experimental data.

Second Fick law is usually used in food science to describe overall mass transport within the material without considering the different mechanisms of mass transport that prevail in the studied food (which are probably not only molecular diffusion as stated in Fick's laws). Foods are often inhomogeneous and have multiple phases. Some of these phases are barriers to diffusion (fat crystals). Therefore the overall diffusivity identified is then an apparent or effective diffusion coefficient,  $D_{\text{eff}}$ . Although this  $D_{\text{eff}}$  has no physical meaning in relation to the food structure,  $D_{\text{eff}}$  is still very useful to predict mass transfer in food systems.

## 3.2. Solubility of gas in cheese

Gas in cheese may be found either dissolved in the cheese paste (water or fat fraction) or under its gaseous form (inside eyes of eyed cheeses or other eventually present micro-cavities).  $CO_2$  is the most soluble atmopsheric gases in water with solubility 20 to 50 times greater than the other gases (at  $20^{\circ}C$  and atmospheric pressure, Figure 4). Solubility of  $CO_2$  in dairy fat at the same temperature is even greater (Figure 4). Since all cheese varieties include high amount of water and fat, significant quantity of  $CO_2$  may be found dissolved in both the water and fat phases of the cheese.

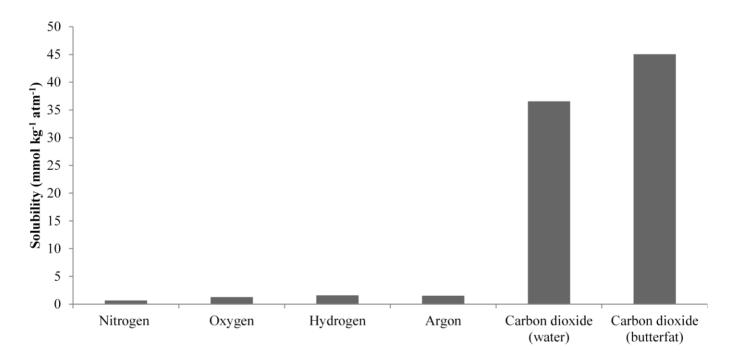
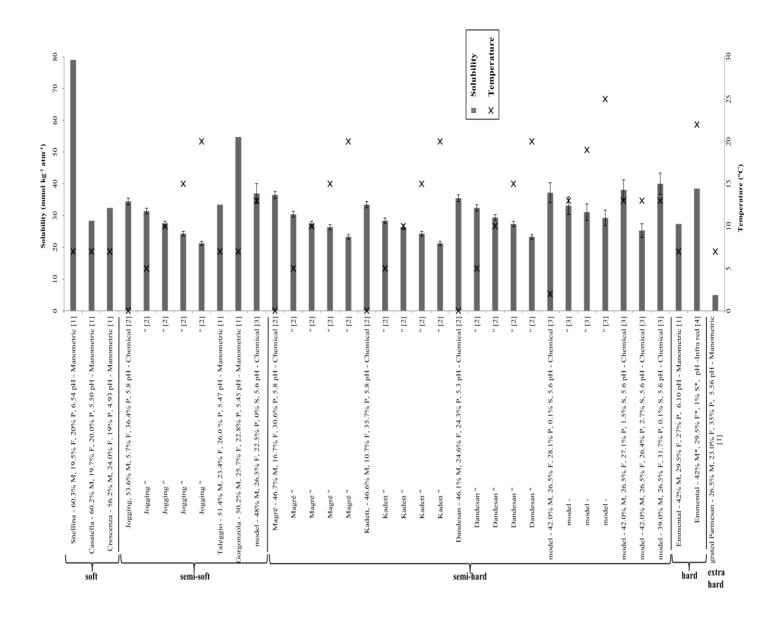


Figure 4. Solubility of atmospheric gases in water [114] and in butterfat [103] at 20°C.

The actual concentration of dissolved gas in cheese depends on several factors such as the cheese composition (especially moisture, protein, fat, salt content, pH), temperature, presence of an impermeable packaging or natural rind, area of cheese in contact with the atmosphere (etc.). These technological and physico-chemical parameters are affected by the cheese making technology used which vary according to the different cheese types (Figure 1).

Values of carbon dioxide solubility in cheese have been collected from literature and listed by temperature and by cheese type (Figure 5).



**Figure 5.** Solubility of CO2 in cheese at different temperatures. Cheese type and composition (when available) is reported as M, F, P, S for moisture, fat, protein and salt (% w/w) respectively. pH is also indicated. Asterisk superscripts indicate that values have been calculated from literature and were not given by authors. Standard deviation bars, when available, are reported. Data are gathered from following references: [1] [109]; [2] [103]; [3] [115]; [4] [63].

Solubility values shown in Figure 5 have been assessed by dairy researchers by making use of Henry's law (Eq. 3). This law has been experimentally validated by Fava & Piergiovanni [109] and Jakobsen et al. [103] via manometry and chemical based method respectively. In both cases a linear correlation was identified, but with an offset. Fava & Piergiovanni [109] found negative intercept with y-axes, meaning that at zero partial pressure of carbon dioxide a negative amount of carbon dioxide is found in the cheese. They explained this peculiar phenomenon with the fact that disturbances due to eventual production of CO<sub>2</sub> were not accounted for during the manometric measurement. In fact, with the manometric method developed by Fava & Piergiovanni [109], the solubility of the gas in the cheese was calculated from the total gas pressure drop registered in the system upon solubilization of carbon dioxide and the drop of pressure can be disturbed by CO<sub>2</sub> production from the cheese. On the contrary, Jakobsen et al. [11] found a positive intercept and explained it by the fact that all forms of CO<sub>2</sub> were extracted by acid when using chemical titration. Consequently CO<sub>2</sub> such carbonated and carbamates bound to the product, independent of the partial pressure of CO<sub>2</sub> were also extracted. Acerbi et al. [29] also checked the validity of Henry's law for semi-hard cheese. The authors found no disturbances at the beginning of the curve with an offset at zero partial pressure. Contrary to Jakobsen et al. [11], the

solubility coefficient assessed by Acerbi et al. [29] was free from non-gaseous CO<sub>2</sub> species, because the authors carefully assayed the "blank sample" (that is, cheese sample that did not received the CO<sub>2</sub> adsorption step treatment, equilibrated at zero CO<sub>2</sub> pressure, via N<sub>2</sub> absorption step) in order to subtract the residual CO<sub>2</sub> content in the cheese due to presence of non-gaseous CO<sub>2</sub> form in the cheese at zero CO<sub>2</sub> partial pressure (for example, carbamates, carbonates). The methodology is detailed in Acerbi et al. [29] and a similar methodology is detailed in Chaix et al. [116] where intercept at 0 was also obtained for processed cheese.

## 3.2.1. pH effect on CO<sub>2</sub> solubility in cheese

Different "species" of CO<sub>2</sub> may be present in water as a function of pH [8]. CO<sub>2</sub> can hydrate and dissociate in water and the reaction scheme may be written as:

$$CO_2 + H_2O \xrightarrow{pK=2.59} H_2CO_3 \xrightarrow{pK=6.37} HCO_3^- + H^+ \xrightarrow{pK=10.25} CO_3^{2-} + 2H^+$$
 Équation 7

Yagi and Yoshida [117] pointed out that at pH values lower than 8, the concentration of carbonate ions may be neglected (pKa =10.25), leading to the possibility to consider only the following simplified hydration reaction which may happen in cheese products (pH lower than 8):

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+$$
 Équation 8

The formation of carbonic acid can be neglected during ripening of acid-coagulated cheese varieties because their pH is generally lower than 5 and the pKa of carbonic acid equal 6.37. On the other hand, this form of CO<sub>2</sub> cannot be neglected during shelf life of some Italian fresh cheeses such as Burrata and Mascarpone, as well as mold ripened semi-soft cheese varieties such as Camembert, Munster and Roquefort, where the pH may range from 6 to 7 [118]. Semi-hard and hard cheese varieties such as Swiss-Dutch and Emmental-type cheeses have pH between 5 and 6, therefore the majority of carbon dioxide species dissolved in those products shall be in the form of dissolved CO<sub>2</sub>. It is generally agreed that the rate of CO<sub>2</sub> solubilization in water increases with pH. The CO<sub>2</sub> absorption rate of water solutions was studied by Livansky [119]. The author noticed a marked increase in CO<sub>2</sub> absorption rate for NaHCO<sub>3</sub> (1, 5, 25, 100 mM) solutions at pH > 8, probably because of the increased transformation rate of CO<sub>2</sub> into HCO<sub>3</sub> (hydration reaction) [119]. Akkerman et al. [3] estimated that the slightly higher pH in Emmental cheese (0.1 – 0.2 units) compared to Gouda may lead to about 3% higher solubility in the first cheese compared with Gouda. The author explained this behavior with the fact that a higher fraction of CO<sub>2</sub> is converted into HCO<sub>3</sub> at higher pH. Furthermore, the very low solubility of gaseous  $CO_2$  in acidic media (pH 1 – 2) has been exploited by numerous researchers for extracting and quantifying dissolved CO<sub>2</sub> in solid food products [11,120–123].

Although the solubility of CO<sub>2</sub> is influenced by the pH of the cheese, the effect of pH changes in cheese in relation to gas transfer (including solubility) properties have never been investigated to the best of our knowledge. This has been scarcely investigated in meat, where controversy results are present: no relevant difference was found for 0.6 change in pH units in cooked meat from Sivertsvik and Jensen [124], while relevant difference was found in fresh meat by Gill [120] (30% CO<sub>2</sub> solubility increase for 0.6 change in pH units in fresh meat). One reason for the lack of research carried out on the subject may be the difficulty of studying the pH as a variable in food, keeping all the other variables constant (usually pH gradients in cheese are due to different chemical composition and bacterial metabolic activity).

## 3.2.2. Repartition of gas in cheese with eyes

Some studies carried out on natural ripened Emmental cheese have highlighted that about 52% of CO<sub>2</sub> is dissolved in the continuous cheese paste, 32% is lost from diffusion outside the cheese and 15% is stored inside the eyes [63,125]. Similar results have been described by Seuvre and Mathlouthi [126]

who analyzed a 70 kg Emmental wheel and found 42% gas dissolved in the cheese paste, 41% diffused out from the cheese and 17% in the eyes. Although these values were affected by high deviations (gas in the eyes was estimated from the other two values and its standard deviation equaled 30% of the mean value), they give a rough idea of the repartition of gas in Emmental like ripened cheeses. Akkerman et al. [3] measured the gas composition into eyes of Gouda and Maasdam (Swiss-Dutch) cheeses by inserting a needle into the eye and analyzing via gas chromatography. The oxygen detected was assumed to be a contaminant from the atmosphere during the analysis, therefore it was subtracted from the results, together with atmospheric  $N_2$  (3.72 times  $O_2$ ). The researchers found corrected ratios  $N_2/CO_2$  of about 1 to 3 for 6 and 35 weeks ripened Gouda respectively, while ratio 0.17 was found for purchased Swiss-Dutch of about 13 weeks.

## 3.3. Consumption by microorganisms

Oxygen is an important external electron acceptor for many homo and hetero-fermentative LAB, because its usage lead to a more efficient energetic balance for the bacteria cells [127]. It is in fact reported by several researchers that the oxygen dissolved in cheese curd shall be consumed by the primary starters during the first days of cheese production [3,128].

Among the microorganisms found in cheese, molds are probably the most important oxygen consumer, because of their metabolism (see § 2.2.2.4). They grow in fact on the surface of cheeses (for example, surface ripened cheese such as Camembert and Taleggio) or close to the fissures created during piercing in blue vein cheeses (for example, Stilton, Roquefort, Gorgonzola).

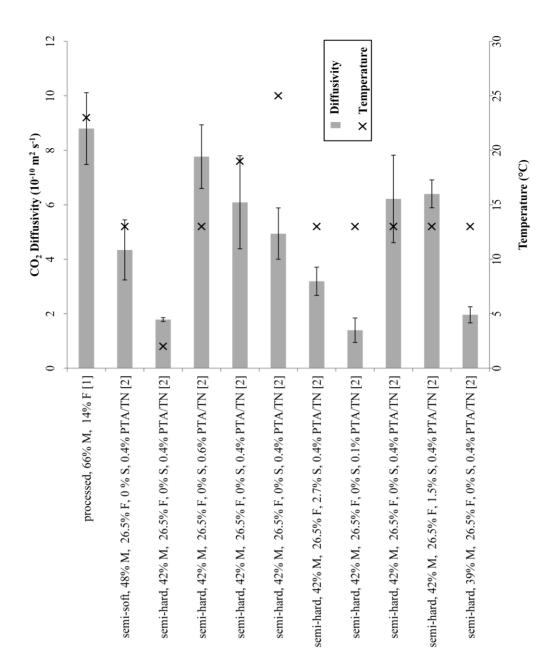
Nitrogen (and Argon) are not consumed by the microorganisms typically found in cheese and nor is carbon dioxide, with a few exceptions [86]. Therefore these gases may be found dissolved in cheese water and/or fat phase for longer period. Whenever they are present at concentrations higher than their solubility in the cheese paste, they may also diffuse into cheese porosity creating eyes (for example, Emmental, Swiss-Dutch and some Dutch cheese varieties) [3,77].

## 3.4. Consumption by chemical reactions

Oxygen is involved in many biochemical reactions such as oxidations often light induced, which are probably taking place at the cheese surface when transparent packaging are used [6,7]. There are many compounds in cheese which could react purely chemically to form flavor compounds [129], but nature of this reaction is poorly understood.

#### 3.5. Gas loss to the atmosphere

Depending on the diffusivity of the gas inside the cheese paste, the permeability of the packaging/cheese rind and the partial pressure gradients, the gas present in cheese may be lost in the atmosphere [86]. Mostly water vapor, CO<sub>2</sub> and NH<sub>3</sub> would diffuse in the atmosphere during cheese ripening, especially for PAB ripened cheeses and mold ripened cheeses for CO<sub>2</sub> and NH<sub>3</sub> respectively. Literature values for gas diffusivity in cheese are scarce. Chaix et al. [130] reviewed O<sub>2</sub> and CO<sub>2</sub> solubility and diffusivity in solid food matrices, but the authors did not report any value for gas diffusivity in cheese. More recently, CO<sub>2</sub> effective diffusivity in processed cheese and semi-hard cheese was experimentally assessed by Chaix et al. [131] and Acerbi et al. [132] respectively (Figure 6). These mass diffusion coefficients are extremely useful when used as input parameters in mathematical models for the prediction of gradients of gas formed in different positions of the cheese during processing. However little information is available to explain the physical meaning of the effective diffusivity coefficients and a more throughout investigation of cheese micro and nano-structure should be addressed to face this lack in literature.



**Figure 6.** CO<sub>2</sub> diffusivity in cheese at different temperatures. Cheese type and composition (when available) is reported as M, F, PTA/TN, S for moisture, fat, ratio of phosphotungistic acid soluble nitrogen on total nitrogen and salt (% w/w) respectively. pH equaled 5.60 in all cheeses. Standard deviation bars, when available, are reported. Data are gathered from following references: [1] [131]; [2] [132]

## 4. Effects of gas in cheese

The presence of gases in cheese during ripening and further storage has been related to quality parameters such as structure and texture and flavor formation. For instance, CO<sub>2</sub> production has been related to the open texture in eyed cheeses such as Emmental, Swiss-Dutch and some Dutch varieties [77]. Gas plays also relevant role during ripening and shelf life of semi-soft cheeses such as blue and surface ripened ones, where the production of NH<sub>3</sub> and CO<sub>2</sub> gas lead to relevant pH changes in the cheese matrix [133]. Effects of gas on cheese ripening and shelf life are hereafter presented.

#### 5.1. Texture

Gas is fundamental for the open texture of many cheeses, from the spherical big eyes found in Emmental and Swiss-Dutch type cheeses to the smaller and plentiful openings of Havarti cheese and the typical fissures enlarged by CO<sub>2</sub> produced by Lactic Acid Bacteria (LAB) in pierced blue cheese which enable growth of certain molds [21,77,134].

Practically, the gaseous components which may be responsible for open texture in cheese are CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> [77]. CO<sub>2</sub> is quantitatively the most relevant gaseous component formed during propionic fermentation (Table 1) in Swiss and Swiss-Dutch type cheese. The most important consequence of CO<sub>2</sub> production in such cheeses is represented by the eye growth: when carbon dioxide is not soluble in the curd anymore, it diffuses towards the existing nuclei and contributes to their growth [3,135], assuming that cheese paste allows deformation [23]. It implies that the equilibrium CO<sub>2</sub> pressure is far surpassed in such cheese to obtain holes. In Gouda cheese, CO<sub>2</sub> production is far below saturation, however this type of cheese commonly show some small eyes which formation has been ascribed to the (over)saturation of the cheese milk by atmosphere and especially N<sub>2</sub> followed by fairly slow CO<sub>2</sub> production by staters [3]. Nitrogen plays thus a paramount role in the texture opening of such Dutchtype cheese varieties.

Oxygen is also present in cheese, but its contribution to open texture is not considered to be relevant, because it is usually consumed by the starter bacteria during the first days from renneting [3]. Presence of hydrogen in cheese is mainly related to the metabolic pathways of spoilage bacteria such as coliforms and clostridia [77]. Martley and Crow [77] reported that hydrogen may be responsible for formation of texture defects (defective openness, for example, cracks or slits) in raw milk cheeses where nitrates and lysozyme are not allowed or not used (for example, Parmigiano Reggiano, farmer's Gouda, Emmentaler cheese).

Ammonia gas, produced by molds from the catabolism of protein in surface of mold ripened cheeses (for example, French Camembert and Brie, Italian Taleggio), is responsible for the typical pH gradient of such cheeses. Because of its direct effect on cheese pH, ammonia does have an important indirect effect on texture of mold ripened cheese. Such cheeses are often considered to mature from the outside toward the core (higher to lower pH respectively) due to contributions by the external flora to texture-producing biochemical reactions [133]. The high pH in the outer layers of such cheese leads to the creation of a calcium ion gradient due to the precipitation of calcium phosphate at the surface [136–138]. Calcium ions then migrate from the interior outwards, and this contributes to the softening of the cheese by reducing the extent of casein crosslinking. The overall increase in pH in Camembert during the maturation period increases the rate of plasmin-induced proteolysis that also contributes to cheese softening [133]. Thus, the maturation process is driven by the development of pH and calcium gradients in the cheese, which are related to the ammonia produced by the surface micro-flora of such cheeses [136–138].

#### 5.2. Flavor formation

Carbon dioxide, oxygen and ammonia shall be considered relevant for flavor formation in cheese. Carbon dioxide is a food additive recognized by the European Union with number E 290 (EU, 2011) and it can be used in food formulations as acidulant (among all its functions), with the principle of "quantum satis". The perception of carbonation in the mouth of mammals (mice) was reported by Chandrashekar et al. [139]. The authors studied the electrophysiological responses of taste receptor sour cells to CO<sub>2</sub> and the responses were evident for carbonated drinks (for example, club soda), CO<sub>2</sub> dissolved in buffer and even direct stimulation of the tongue with gaseous CO<sub>2</sub>.

Urbach [129] included CO<sub>2</sub> in the list of flavor compounds of Cheddar cheese. However it is not possible to make clear conclusions concerning the flavor impact of indigenous CO<sub>2</sub> in cheese, because of it is not possible to isolate the production of gas from the other metabolites originated during the metabolism of microorganisms in such a complex matrix like cheese. Some researchers have studied the effects of CO<sub>2</sub> enriched modified atmosphere packaging on cheese flavor formation. In particular, Juric et al. [140] found that 100% CO<sub>2</sub> atmosphere resulted in undesirable flavor and texture of sliced Samso cheese (Danish semi-hard cheese) stored under light. These results have been confirmed by other authors in other cheese varieties such as Cameros cheese [141] or Graviera cheese [142].

Ammonia (originating from deamination of free amino acids) is an important constituent in many cheeses such as Camembert (soft and surface mold ripened), Gruyère and Comté (semi-hard cheeses) [143]. Ammonia production affects taste development since it neutralizes acidity and increases pH.

Light-induced degradation of lipids, proteins and vitamins in cheeses causes both the formation of off-flavors and color changes, which rapidly impair product quality and marketability and eventually may lead to loss of nutritional value and formation of toxic products (for example, cholesterol oxides) [144]. Light-induced oxidation requires oxygen, a light source and a photosensitizer [145]. Riboflavin (vitamin B2) in cheeses is an efficient photosensitizer, and, on absorbing light, is excited to a higher energy level [145]. Reverting to its ground state, the photosensitizer may react with fatty acids or oxygen, producing either free radicals or reactive oxygen species. Both of these pathways may lead to formation of lipid free radicals, which, once formed, result in autocatalytic oxidative processes. The off-flavors associated with light-induced oxidation, including metallic, oily, fishy, tallowy, rancid and oxidized, become apparent when the lipid hydroperoxides decompose to alkanes, alkenes, alcohols, aldehydes, esters, ketones and acids [6,145]. Pro-oxidants such as copper and iron may enter the product via processing equipment. Chlorophyll may be added with herbs and fruit to cream cheese, initiating immediate oxidation of the unsaturated lipids of the herbs or fruit, and leading to oxidation of milk lipids [6]. Limiting the availability of oxygen in the package and reducing light penetration with the use of innovative packaging will minimize light-induced oxidation.

Cheese produced from non-pasteurized milk may be more prone to oxidative and hydrolytic rancidity, because indigenous lipoprotein lipase will give rise to hydrolytic rancidity and the eventual oxidation of these lipids will lead to oxidative rancidity [146].

#### 5.4. Coloration

Defective coloration was noticed in cheese packed with modified atmosphere and exposed to light. Colchin et al. [88] reported color bleaching in red Cheddar (colored using annatto) slices packaged under CO<sub>2</sub> and exposed to light. The shift in color was proposed to be due to an interaction between CO<sub>2</sub> and high-intensity light, leading to the oxidation of the pigment molecule, bixin [88]. However the interpretation of the discoloration given by the authors is questionable, because of the different residual oxygen concentrations found in the different packs used in the experiment (2.69% and 0.02% residual O<sub>2</sub> found in packs which were initially targeted with 100% CO<sub>2</sub> and 100% N<sub>2</sub> respectively). Therefore, the discoloration found in the cheese packed with target 100% CO<sub>2</sub> may have been due to the relatively high presence of oxygen in the pack, instead of the high CO<sub>2</sub> concentration.

Formation of a pinkish color was reported in several different cheeses, from soft mold ripened (Gorgonzola, Camembert, Brie) to hard cheese varieties (Cheddar cheese) [30], Grana cheese [147] and Emmental [148]. Oxygen is mentioned among the possible causes of this pink discoloration defect, which have been reviewed by Daly et al. [148]. The authors concluded that pink discoloration may be due to a set of conditions, rather than one single factor. Furthermore they suggested more research to be undertaken concerning the role of oxygen content and oxidation reduction potential among all for a better understanding of the causes of the defect.

#### 5.5. Anti-microbial effects

Among the gases discussed in this review, CO<sub>2</sub> is surely the most important and studied within the dairy industry, because of its inhibition effects on numerous microorganisms. CO<sub>2</sub> has a symmetrical structure with a zero dipole moment, which makes it highly soluble in both the fat and liquid phase of cheese. The high solubility of this molecule in a wide range of food makes it a very good bacteriostatic compound, because of its dissolved concentration in food determined the growth inhibition of certain microorganisms (especially Gram- spoilage bacteria) in a modified atmosphere [149]. Dixon and Kell [150] reviewed the inhibition by CO<sub>2</sub> of the growth of microorganisms: they pointed out that a single, unitary mechanism of CO<sub>2</sub> inhibition seems out of questions and CO<sub>2</sub> possibly exerts an effect both on metabolism and on energetics of cell synthesis. But the mechanism still remains unclear. Singh et al.

[5] summarized the main mechanisms for bacteria inhibition by CO<sub>2</sub> as oxygen displacement, pH lowering, cellular penetration and their interactions.

In the study of Mannheim & Soffer [151] headspace flushed with pure CO<sub>2</sub>, extended shelf-life of cottage cheese at 8 °C by about 150% without altering sensory properties or causing any other negative effect. In the study of Temi [152], a 100% CO<sub>2</sub> atmosphere guaranteed the best microbiological stabilization and sensorial properties of the fresh cheeses (Kashar cheese). Their study determined also that 40 and 100% CO<sub>2</sub> can be used to extend the shelf life of fresh Kashar cheese. However, the benefit of enriched CO<sub>2</sub> atmosphere for increasing cheese shelf life must be put into balance with sensory aspects, since some authors also noted that 100% CO<sub>2</sub> atmosphere resulted in undesirable flavor (see § 5.2). Hence, a compromise between bacteriostatic effect and negative effect on sensory quality should be found. Gonzalez-fandos et al. [141] recommended thus packaging in 50% CO<sub>2</sub>/50% N<sub>2</sub> and 40% CO<sub>2</sub>/60% N<sub>2</sub> for extending shelf life of Cameros cheese while retaining good sensory characteristics, although the best microbiological quality was obtained with the 100% CO<sub>2</sub> atmosphere but with a very negative effect on sensory quality.

## Conclusion

Exchange of gaseous components (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, NH<sub>3</sub>) between cheese products and the surrounding environment may cause several biochemical and microbiological changes in the cheese matrix, leading to different quality (texture, color, flavor) of the commercial product.

The gas transfer properties and their interactions with cheese products may represent key information for understanding the phenomena undergoing between them and better controlling their use in cheese technology (milk carbonation, modified atmosphere during ripening or during storage). However, values for gas consumption, production, solubility and diffusivity in cheese found in literature are scarce. We highlight the need for a deeper investigation between these values of solubility and cheese characteristics (notably composition) and interactions between the mentioned gases and the cheese products.

Table 1. Main metabolic pathways including production of gas in cheese.

Pathway	Microorganisms involved	Substrate used (mol)	Metabolites produced (mol)		
	CO <sub>2</sub> production from lact	ose (hetero-fermentative strains or B	-starter), anaerobic conditions [37,153]		
1	Leuconostoc spp.	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> + H <sub>2</sub> O	2 C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> + 2 C <sub>2</sub> H <sub>5</sub> OH + 2 CO <sub>2</sub>		
		lactose + water	2 D-lactate + 2 ethanol + 2 carbon dioxide		
	CO <sub>2</sub> production from citrate (BD-starters), aerobic conditions [37,73,153]				
2	Leuconostoc spp. and Lactococcus lactis subsp.	2 C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	2 C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> + C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> + 4 CO <sub>2</sub>		
	lactis biovar. diacetylactis (+ various NSLAB)	2 citrate	2 acetate + acetoin + 4 carbon dioxide		
	Propio	nic Acid Bacteria Classical Pathway (Fi	itz equation) [42,154]		
3	РАВ	3 C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	2 C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> + CO <sub>2</sub> + H <sub>2</sub> O		
		3 lactate	2 propionate + acetate + carbon dioxide + water		
	Propionic Acid Bacteria Wood-Werkman Pathway (CO <sub>2</sub> fixation pathway) [42]				
4	РАВ	3 C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	$(2-x) C_3H_6O_2 + C_2H_4O_2 + (1-x) CO_2 + (x) C_4H_6O_4$		
		3 lactate	(2-x) propionate + acetate + (1-x) carbon dioxide		
			+ (x) succinate		
	Propion	ic Acid Bacteria Fermentation of aspa	rtate to succinate [42]		
5	Aspartase-positive PAB	3 C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> + 6 C <sub>4</sub> H <sub>7</sub> NO <sub>4</sub> + 3H <sub>2</sub> O	3 C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> + 3 CO <sub>2</sub> + 6 C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> + 6 NH <sub>3</sub>		
		3 lactate + 6 aspartate + 3 water	3 acetate + 3 carbon dioxide + 6 succinate + 6 ammonia		
		Butyric fermentation from Clost	ridia [37]		
6	Clostridium tyrobutyricum	2 C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> + 2 CO <sub>2</sub> + 2 H <sub>2</sub>		
		2 lactate	butyrate + 2 carbon dioxide + 2 hydrogen		

	Coliforms gassy fermentation [73,155]			
7	Coliform bacteria	2 C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> + H <sub>2</sub> O	2 C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> + C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> + C <sub>2</sub> H <sub>6</sub> O + 2 CO <sub>2</sub> + 2 H <sub>2</sub>	
		2 glucose + water	2 lactate + acetate + ethyl alcohol + 2 carbon dioxide + 2 hydrogen	
	Y	easts and molds gassy fermenta	ation [20,66,71,77]	
8	Various yeasts (sp. of Rhodotorula, Pullularia, Torulopsis, Trichosporon, Candida, Debaromyces,	$C_6H_{12}O_6$	2 C <sub>2</sub> H <sub>6</sub> O + 2 CO <sub>2</sub>	
	Kluyveromyces among all) and molds (Penicillium Roqueforti and Camemberti amongst others)	glucose	2 ethyl alcohol + 2 carbon dioxide	
		Hydrolization of urea	[73,156]	
9	Streptococcus thermophilus	$CH_4N_2O + H_2O$	2 NH <sub>3</sub> + CO <sub>2</sub>	
		urea + water	2 ammonia + carbon dioxide	
10	Decarboxylation of amino acids [73]			
	Lactococcus lactis subsp. lactis, Streptococcus	R-CH(NH₂)COOH	$R-CH_2(NH_2) + CO_2$	
	thermophilus, various NSLAB, PAB,	amino acids (arginine, aspartate, glutamate)	Amine + carbon dioxide	
	Deamination of amino acids [143,157]			
11	P. Camemberti, G. Candidum, Br. Linens	R-CH(NH <sub>2</sub> )COOH	R-CH <sub>3</sub> CH <sub>2</sub> OCOOH + NH <sub>4</sub>	
		amino acids (arginine, tryptophan, tyrosine)	α-ketoacid + ammonia	

## Supplementary material: Basics of cheese technology

A basic overview of the cheese production steps is necessary for understanding the difference in material properties (mainly flavor and texture) of the cheese types, because this is greatly affected by the cheese production procedures used. For example, for cheese types characterized by presence of eyes and open structure, the shape, size and distribution of eyes is dramatically influenced by the detailed technology in terms of starter cultures, adjunct cultures, milk manipulation and thermal processing, pH of the curd, cooking temperature, salting, ripening temperature etc. [158].

Cheese making technology can be summarized in few major steps which are common for all cheese types: milk coagulation, syneresis leading to whey expulsion, molding, salting and ripening. Figure 1 is a technological classification of cheese types, mainly based on the texture of the final product (from soft to extra-hard), which is mostly related to the moisture content (from high to low).

## 1. Pre-treatments on milk and milk coagulation

After milk is collected from the farms and delivered to the cheese-making facilities, it usually undergoes some physical treatments (pre-treatments in Figure 1). These may include centrifugation (for example, for many semi-hard cheese varieties) or natural creaming (for example, for Grana Padano and Parmigiano Reggiano cheese) for standardizing the quality of milk in terms of fat to protein ratio for a certain cheese recipe, heat treatment (for example, thermization and/or pasteurization) to decrease risks of spoilage from microorganisms and homogenization in case a certain color or texture of the final product is desired [133]. Different starter microorganisms are added to the cheese milk according to the desired flavor and texture formation in the final cheese. After rennet is added, milk coagulation takes place, leading to the formation of a milk gel.

## 2. Syneresis, molding and salting

The milk gel is cut, stirred, heated and whey is partially removed from the whey-curd mixture in order to obtain an optimal liquid (mainly whey) loss during the syneresis. Syneresis may in this context be defined as the rearrangement of casein molecules, resulting in a tightening of the casein network [134]. The temperature used for heating the whey-curd mixture after coagulation may be divided in medium-low and medium-high (Figure 1), resulting in the production of soft to semi-soft and semihard to extra-hard cheeses respectively. At this step of cheese-making, the majority of the whey has been removed from the whey-curd mixture and the whey-curd mixture is going to achieve a more defined shape (molding operation). Before molding, the curd of Cheddar and pasta-filata cheese varieties only is submitted to the so called heating and stretching, and cheddaring operation respectively. The heating and stretching operation includes kneading and stretching of the curd in hot water (curd reaches temperature of about 55°C) in order to obtain the typical fibrous texture and stretchability of pasta filata cheeses (for example, Mozzarella, Provolone). The cheddaring operation includes the cutting of the curd into large strips that are piled up and turned several times. These steps are repeated to allow acidification by starter microorganisms and the formation of a typical curd texture, similar to that of cooked chicken breast meat [57]. Furthermore Cheddar type cheeses and few other varieties (for example, Stilton) are characterized by a peculiar salting operation which includes the mixing of dry salt with milled curd just after the cheddaring operation and before pressing. The pressing operation is common for semi-hard and harder cheese varieties, being more intense for harder cheeses. This operation allows to expulse more liquid (mainly whey) from the curd, which becomes more compact and achieves a shape which is very similar to the final cheese shape. It follows the salting operation mainly via brining (immersion of the cheese inside a salt solution) for some cheese varieties (mainly semi-hard and harder cheese varieties) or via dry salting (application of dry salt on the cheese surfaces) mainly for softer cheese varieties (for example Roquefort, amongst others).

#### 3. Ripening

Ripening may be defined as the operation of storing the cheese at controlled environmental conditions (temperature and/or relative humidity and/or gas composition) for the time which enables the cheese microflora to transform the salted curd into a product with the desired flavor and texture (cheese). The cheese may be ripened as it is (natural ripening) or wrapped into a plastic foil (foil ripening) or wax which have the function of limiting the gas and vapor exchange with the surrounding atmosphere (water loss or accumulation of gas inside cheese for eyed varieties). Some important steps may take place during ripening depending on the cheese variety. For example, cheeses with propionic acid fermentation (Emmental and Swiss-Dutch) are moved into a warm room (about 18-25°C) for some time (days or weeks) in order to allow the propionic acid bacteria to produce high quantity of CO<sub>2</sub> closer to their optimum temperature (see § 2.3.2.2). The piercing operation is typical for blue cheeses (for example, Roquefort, Gorgonzola, Danablu, Stilton) and it consists in perforating the cheese with metal needles during ripening for creating fissures inside the cheese. The created fissures enable oxygen to diffuse inside the cheese paste with consequent desired growth of the molds (for example, Penicillium roqueforti). Generally, all cheese varieties, apart for the very short ripened ones, are turned during ripening. Cheese turning is needed for enable cleaning for avoiding excessive growth of molds on the rind of certain natural ripened cheeses (for example the very long ripened Grana Padano and Parmigiano Reggiano cheeses), but it may be less frequent to allow development of desired molds in mold ripened cheeses such as Camembert and Brie, where mold spores are added in the cheese milk. The smearing operation is also carried out for enabling growth of certain microorganisms on the surface of surface ripened cheeses (for example, Taleggio, Comté, Beaufort, Appenzeller, Montasio, Gruyère, Limburger, Tilsit, Munster, Saint Paulin, amongst others), where a solution of microorganisms is smeared on the cheese surfaces during ripening.

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