Materials and structures of foods

J. Miguel Aguilera

Department of Chemical and Bioprocess Engineering
Pontificia Universidad Católica, Chile

Abstract

Many structural designs of the foods we eat have evolved throughout the centuries based on the properties of raw materials and transformations induced by mankind, mostly by trial-and-error and evolution. Structure in foods is important in that it is directly related to their texture and quality. Some structural elements are recognized by the naked eye while most are discernible only with the aid of microscopes. Typical recognizable elements in food architecture are discussed and illustrated. Although important in themselves the interaction between elements is responsible of the desirable functional properties and textural identity of foods. Application of concepts from materials science and engineering will result in controlled improvement of traditional foods, use of new ingredients and technologies, and design novel foods from molecules to functional structures.

1 Introduction

1.1 Food structure and design

The primary source of structural elements in foods are the tissues of plants and animals (including milk) as produced by nature (Figure 1). Mankind first learned how to preserve the basic foods, and later, how to fractionate them into more pure components, giving birth to the food ingredient industry. Along the way the first forms and textures of traditional foods (breads, cheeses, processed meats, etc) were developed mostly through trial-and-error. In the 20th century food manufacture evolved from an artisan production into the centralized and specialized operation of today where refined ingredients are mixed and assembled into a multitude of products. The end of the past century saw the initiation of food fabrication, whereby new products and analogues are designed and created in a more predictable way. Cooking has provided the opportunity to
Figure 1: The pyramid of food design: from nature to mouth.

Further transform and combine foods to conform to the individual taste and tradition. At the top of the pyramid in Figure 1 is gastronomy, where science and art meet to create the textures and flavors that give the pleasure of good eating.

Structure is an important characteristic of the foods we eat and a subject of extensive research [1, 2, 3]. Most manufactured foods are structurally complex and contain several elements that interact at different levels: droplets, gels, fibers, etc. Although it is possible to have a completely adequate diet in the form of fluid foods, an important part of the pleasure of eating comes from the disintegration of the food structure and the perception of the different elements during mastication. Thus, it is not surprising that food technology has been defined as a controlled effort to preserve, transform or create the desirable structures recognized by a very sophisticated and prejudiced sensor: the mouth.

The aim of this paper is to illustrate how various structural elements present in foods or produced during processing and cooking participate in the formation of their microstructure and contribute to their macroscopical properties.

1.2 Food structure and scale

Before studying the structural elements in foods we must take into account the scale of analysis. A distinction is made between the macrostructure (that
observed by the naked eye) and microstructure (seen with the aid of a microscope) as summarized in Table 1.

Table 1. Levels of structures present in food.

<table>
<thead>
<tr>
<th>Level of structure</th>
<th>Structure (examples)</th>
<th>Scale (μm)</th>
<th>Related property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroscopic +2</td>
<td>Tissue</td>
<td>$10^4$</td>
<td>Food identity</td>
</tr>
<tr>
<td>+1</td>
<td>Particle</td>
<td>$10^3$</td>
<td>Flowability</td>
</tr>
<tr>
<td>Microscopic -1</td>
<td>Cells</td>
<td>$10^2$</td>
<td>Texture</td>
</tr>
<tr>
<td>-2</td>
<td>Starch granule</td>
<td>10</td>
<td>Paste viscosity</td>
</tr>
<tr>
<td>-3</td>
<td>Fat globule</td>
<td>1</td>
<td>Color (milk)</td>
</tr>
<tr>
<td>-4</td>
<td>Cell walls</td>
<td>$10^{-1}$</td>
<td>Toughness</td>
</tr>
<tr>
<td>-5</td>
<td>Casein micelle</td>
<td>$10^{-2}$</td>
<td>Gelation</td>
</tr>
<tr>
<td>-6</td>
<td>Sugars</td>
<td>$10^{-3}$</td>
<td>Amorphous state</td>
</tr>
<tr>
<td>-7</td>
<td>Water</td>
<td>$10^{-4}$</td>
<td>Plastication</td>
</tr>
</tbody>
</table>

Thus, the study of food structures implies bridging lengthscales of the order of $10^9$, from the molecular to the macroscopic level.

2 Structural elements in foods

2.1 Air cells and aerated products

Air is a ubiquitous but unreported component of foods. To start, many fruits and some vegetables contain air in the intercellular space and in some cases up to 20% of their tissue is filled with air (e.g., apples). Gaseous structures are part of the architecture of many foods: beverages, cereal and dairy products, and confectionery, among others. The benefits of distributing air (or other gases) have to do mainly with texture: lightness in dairy products, crispness in cereal products, a tingling mouthfeel in carbonated beverages and visual appearance of foam in beer [4].

The most common form in which air and other gases are presented in foods is as bubbles. Aeration is achieved by different mechanisms: beating, steam generation by heating, extrusion, puffing, gas injection, and gas production by fermentation and by chemical means (baking powder).

A liquid foam is a coarse dispersion of small gas bubbles in a liquid separated by thin films or lamellae. Food foams of this sort (e.g., whipped cream) defy common sense in that incorporation of air bubbles (an almost inviscid material) to a liquid results in a structure that stands up against gravity. Stabilization of whipped cream is achieved by the formation of a membrane of liquid fat (and possibly some protein) that seals the air inside cells. Another food foam, highly reputed in gastronomy, is beaten egg whites. As is the case with several liquid foams stabilized by protein, heating denatures egg albumen and dries the matrix producing two notable solid foams: meringue and soufflé.
Wheat is unique among all cereals due to the ability of wheat flour dough to retain gas on expansion, whether produced by fermentation or a chemical reaction. In bread dough the lamella between gas cells consists of a viscoelastic matrix of starch and protein (gluten) plasticized by water. The sponge-like structure of baked products is formed during heating in the oven by changes at the macromolecular level: protein denaturation and starch gelatinization. Extruded and expanded cereal products achieve a high porosity when the hot viscoelastic starch dough exits the die of the extruder and supersaturated steam is released as bubbles into the hot magma. Figure 2A shows a scanning electron photomicrograph of an extruded cereal snack. The porous structure sets in as a
glassy solid foam as a result of rapid release of vapor and the concomitant cooling effect.

The most valuable gas cells in foods are probably those of Emmental cheese, a traditional, unpasteurized, hard cheese made from cow's milk. Emmental cheese (or Swiss cheese) is produced in the form of giant wheels weighing from 150 to 220 pounds each. It is one of the most difficult cheeses to be produced because of its complicated hole-forming fermentation process induced by the bacterium *Propionibacterium shermanii*. High-quality standards demand for uniform sized and distributed walnut size holes (or eyes) with smooth inner walls. Thus, it has been suggested that MRI tomography may be an appropriate way of non-destructively slicing a wheel of cheese to determine the eye condition (and therefore the price) before deciding the final market.

### 2.2 Water and oil droplets

The natural phenomenon that two key liquid components of many foods, water and oil, do not mix has been resolved by dispersing one as discrete small particles (or droplets) in a continuous phase of the other. In technical terms this liquid dispersion is called an emulsion. All emulsions are thermodynamically unstable and tend to break down unless stabilized by some means.

Droplets are important structural elements in emulsion-type food products such as milk, butter, mayonnaise, sauces, etc [5]. Food emulsions can be water-in-oil (W/O) or oil-in-water (O/W) depending on which one is the continuous phase. In either case droplets are stabilized by emulsifiers or surfactants that become located at their interface and avoid coalescence. Nature does its job in milk (which is an O/W emulsion) by coating each fat globule (2-10 μm in diameter) with a complex membrane before it leaves the mammary gland. Figure 2B, shows a fat globule in a complex aerated emulsion: ice cream.

Mayonnaise is an O/W emulsion containing a high percentage of oil (ca. 80%). The emulsion is always formed by first mixing egg yolk (stabilizer) and the aqueous phase (e.g., vinegar or lemon juice), and then slowly blending in the oil. The high viscosity of mayonnaise is due to the strong interaction between closely-packed and distorted fat droplets (due to the high fraction of oil).

Butter is a "solid" W/O emulsion containing nearly 80% milk fat. During churning of the cream (which is and O/W emulsion containing ca. 30% milk fat globules) the natural membrane of fat globules is partly broken, liquid fat is released and air bubbles assist in the inversion into a W/O emulsion. Butter has a discontinuous structure of fat globules with limited interaction with the rest of the matrix[5]. If butter is regarded as the natural food, then margarine is the designed analogue. In modern commercial margarine, the continuous fat phase looks as an interconnected network structure of fat crystals or sheet-like crystal aggregates, very different from that of butter. Plasticity of margarine is higher than that of butter as many more bonds are broken in the connected margarine structure[5]. Two interesting conclusions may be derived: First, the original structure of a complex food may not always be a good starting point to develop a
substitute, and second, two different structures may perform similarly on the table.

2.3 Granules and particles

In the context of this paper particles are small discrete portions of matter. Particles are important in foods because many raw materials need to be disintegrated into particles to separate structures in the original tissue (e.g., bran and endosperm in wheat). Size reduction is also required to disperse different solid ingredients into a homogeneous mass and to exploit the large surface area to mass ratio as in wetting, dissolution or melting. Powders are a convenient form of storing, mixing and handling solids. Particulate material in foods is usually produced by grinding solids or after spray drying solutions and suspensions. In this latter case an amorphous metastable state sets in when water is rapidly removed. Amorphous particles (e.g., instant coffee, hydrolyzed proteins, etc) may deform if exposed to moist air undergoing a sintering process known as caking, resulting in large, hard lumps with reduced functionality.

Starch is unique among food carbohydrates because it occurs naturally as discrete granules 5 to 80 μm in size, with unique shapes depending on the source. It provides 70-80% of the calories consumed by humans worldwide. Starch granules are made up of amylose and amylopectin molecules arranged radially in alternating layers of amorphous and crystalline regions. Undamaged starch granules are insoluble in cold water but when heated in excess water they undergo a process called gelatinization, which is characterized by the disruption of molecular order, irreversible swelling of the granule and leaching of soluble components, mainly amylose. Granule swelling and disruption produces a viscous paste, formed by a continuous phase of solubilized amylose or amylopectin and remnants of the starch granule. Cooling of the starch paste usually results in a firm gel and further rearrangement of macromolecules, mainly amylopectin, into ordered structures is called retrogradation. This formation of new crystalline domains is responsible of bread staling.

Cooking of starchy material (e.g., potatoes, beans) confines gelatinization inside the cells. This phenomenon together with the solubilization of the middle lamellae cementing cells in the tissue provides the soft structure of cooked grains and tubers.

2.4 Gels, networks and strands

Many "soft foods" consist of a "solid" network that traps a solvent or liquid phase. A gel is a three-dimensional network constituted of strands connected or linked at specific points to restrain their motion, and swollen by a solvent which is largely the major component (Figure 2C). In food technology, gels are the preferred way of immobilizing water as a solid at ambient temperature (in some cases gels that look "solid" may contain over 98% water!).

Food gels are mostly of two kinds: polymer and particle gels. In polymer gels the flexible molecular strands are linked at a few points by covalent cross-
linking, atomic bridges (normally Ca$^{++}$ or K$^+$) or by formation of ordered zones (microcrystallites). Strands in particle gels are assembled by aggregation of individual globular macromolecules induced by heating or a change in pH or ionic strength. Several globular proteins form irreversible heat-setting gels of particulate nature, for example, egg albumen in boiled eggs. Casein micelles in milk aggregate and form particle gels by the action of acid produced by bacteria, as in yogurt, or after attack with an enzyme (rennet) in the case of cheese.

Interestingly, characteristic macroscopical attributes, e.g., spreadability, mouthfeel, texture, etc., of high-fat foods like margarine, chocolate and peanut butter, depend on the formation of a solid network of fat crystals that entrap the liquid fat fraction. Fats cooled from the melt first form primary crystals (ca. 6 μm) that in turn aggregate or grow into each other to develop clusters (100 μm) which further interact resulting in the formation of a continuous three-dimensional network [6].

2.5 Fibrous foods and fibers

Meat epitomizes a fibrous food and has a special place in the diet of the Western world. Muscle tissue of mammals and birds is made up of long (1-40 mm), thin (10-100 μm) cells or fibers bound together by thin sheets of connective tissue (collagen). Structurally, cooking of meat results in progressive denaturation of myofibrillar proteins leading to hardening, and conversion of tough connective tissue into soft, water soluble gelatin, which allows individual fibers to become apart during chewing.

Structure and chemistry explain the tenderness of cooked fish as compared to meat. Fish muscle consists of segments (myotomes) of rather short fibers that are enclosed by large and thin sheets of weak and very soluble connective tissue (myocommata). While fish contains only about 3% connective tissue, meat has five times more and of different chemical make-up.

The high demand for meat and the inefficiency of the natural process that converts plant material into protein fibers (resulting in high prices), prompted the adoption of fabrication methods used in the plastics industry by food technology. Soybean-based meat analogues that resemble the structure of meat have been produced by dry extrusion (textured vegetable proteins) and wet spinning (soy fibers). However, analogues fail to reproduce nature's ability to retain the juices inside fibers and release them slowly providing succulence and flavor and are perceived as "dry" during mastication.

A certain degree of fibrousness is tolerated (and expected) in a few fruits (e.g., mangoes) and vegetables (e.g., asparagus, celery, broccoli). Structurally, increased fibrousness is a natural response of plant tissue to resist compression forces, and biochemically, a sign of senescence. Fiber reinforcing to improve structural properties is well known in engineering and composite technology. Reinforcement of plant cells walls of long xylem vessels is done with lignin, a high molecular weight, three-dimensional polymer of phenolic subunits. Unfortunately, unlike connective tissue in meat, the lignocellulosic complex is insoluble to all practiced cooking methods and not digestible by our body.
2.6 Crystals and crystalline phases

Single crystals are seldom found as food products. Table salt and sugar are the exemption but they dissolve when added to foods. Calcium oxalate crystals are found in the coat of some seeds, probably to protect them against insects.

To the food technologist, water is the medium in which most undesirable reactions occur and its removal or immobilization is often sought. Freezing provides for simultaneous immobilization of water as ice crystals and temperature reduction that decreases the rate of deleterious reactions. Nevertheless, ice crystallization may induce extensive microstructural changes inside organized tissue.

Although frozen desserts were known to Romans and consumed by French and English royalties, ice cream has only recently evolved into a sophisticated industrial product with a delicate texture very difficult to reproduce at home. Part of the problem is the complex structure imparted to modern ice cream during the freezing process that results in the coexistence of at least four phases: air cells (up to 50% of the total volume), small and uniform ice crystals, a vitreous serum phase containing stabilizers and sugar, and milk fat globules (Figure 2B).

In food materials science the crystalline state (or crystalline phase) is one where at least partial molecular order is attained given the complexity of a multicomponent system. It is often present in foods containing polymers or sugars. The solid crystalline state in foods is normally achieved as a transition from an amorphous state when enough mobility is given to the system, for example, by water plastization or heating. Liquid crystalline phases consisting of lamellar bilayers of monoglycerides are the basis of fat-free margarines.

2.7 Surfaces

Surface topography is one of the most important structural features of foods influencing not only their visual and sensorial aspects but also their behavior during processing, storage and eating. Surface morphology is also related to the specific surface area on which many chemical and physical interactions may occur. For instance, the pleasant sensation that candy and other confectionery products have in the mouth is strongly related to interactions of the tongue and palate with their surface and phenomena such as erosion, melting and solubility.

Size reduction in the mouth is normally achieved by mastication. In the case of hard candy, however, solubilization with saliva and erosion between the tongue and palate are the main mechanisms of breakdown. Characteristics that are related to the size, shape and surface roughness of the particle become important for the pleasurable perception before swallowing.

Blooming is a deleterious change in the visual aspect of the surface of chocolate, caused by exposure to fluctuating high temperatures. Technically, it is the result of the migration of cocoa butter and recrystallization on the surface, giving it a grayish appearance. Although a bloomed chocolate is perfectly safe to consume, extensive blooming causes physical changes in chocolate that decrease quality.
3 Liquid foods and suspensions

Only a few foods that flow are homogeneous liquids, like cooking oil, while most are dispersed systems. These complex fluids are said to have (or develop) a “structure” induced by the interactions between the elements they contain (macromolecules, solid particles, liquid droplets and gas bubbles) and with the solvent. Even wine, basically a water/ethanol solution, is said to have “body” and to form “legs” or “tears”, the name for drops of wine that slide down the sides of the glass when it is swirled. In terms of a sommelier “…when thick, plentiful and dense, the legs indicate the wine has big body, richness and thick viscosity”. Scientifically, legs are the result of upward bulk flow induced by surface tension gradients and capillary phenomena, the accumulating liquid returning in the form of drops [7]

The flow behavior of food suspensions like ketchup, jams, stirred yogurt and juice concentrates, among others, depend on the inner structure that develops due to interactions between the different elements dispersed in the solvent. Their flow properties, characterized by the viscosity, do not comply with the linear relationship between stress and shear rate of simple liquids given by Newton’s law. They are said to be non-Newtonian and empirical models have been derived to explain their behavior, but we are still far from predicting their rheological properties from a structural viewpoint [8].

4 Food as composites

At some particular scales all solid foods may be regarded as composites showing different degrees of order and hierarchy in their architecture. For example, among foods produced by nature vegetables and fruits may be regarded as closed-cell, liquid-filled foams, and meat as a fiber-reinforced matrix.

Food composites have been classified into several groups depending on their structure and the failure mechanism when subject to mechanical loading [9]:

- Elasto-viscous fiber composites among which fish an meat are typical of this class. Tissue failure occurs after deformation (flow) with the concomitant liquid and flavor release.
- Liquid-filled foams, like fruits and raw vegetables, which have cell walls pre-stressed by turgor pressure. They show brittle fracture in the mouth and individual cells are broken open, releasing juice.
- Cellular composites with filled cells, most notably cooked starchy vegetables like legumes and tubers, fracture occurs through the cementing material between cells, leaving intact cell walls.
- Particulate composites exhibiting brittle fracture. Biscuits, crackers and fried snacks belong to this category. They show a high modulus and emit a sound that is part of the perception of crispness and crunchiness.

A notable example of composite technology is fried potato strips or French fries. Deep fat frying is unique to food processing and widely used cooking method around the world. Through frying potatoes strips are transformed from a
more or less homogeneous cellular material into a composite having two very distinct structures: A thin outer crust which is dry, rigid and contains most of the oil, and a wet, mealy core or filling almost devoid of any oil. Figure 2D shows how these two structures become neatly distinct when observed by nuclear magnetic resonance imaging (MRI).

5 Conclusions

Nature is the ultimate provider of all food materials but man is the only species on earth that intervene on them to drastically change the original design into desirable forms and textures. The many structures that characterize processed foods have been obtained mostly serendipitously or through trial-and-error. Textural properties of foods are the result of the microstructural arrangement of elements conforming the structure, and the interactions among them. In the last few decades food technologists have approached the study of foods as materials and the concept of food fabrication is developing as an effort to control the structure that imparts the desired properties and functionality.

References


