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The science of food structuring[†]

R. G. M. van der Sman* and A. J. van der Goot

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Food structuring is discussed from the viewpoints of soft matter physics and molecular gastronomy. Food is one of the most complex types of soft matter, with multiple dispersed phases and even hierarchical structure. Food structuring seems to be a kind of art, comprising a careful balance between forces driving the system towards equilibrium and arresting forces. A more scientific approach to this complex matter is desirable, using (1) concepts from soft matter physics, *e.g.* free energy and jamming, and (2) complex disperse system (CDS) notation as developed for molecular gastronomy. Combining CDS with state diagrams renders a new tool for the qualitative description of the complex process of making structured foods.

1 Introduction

In physics, food is commonly regarded as a kind of soft condensed matter,^{1,2} but it has been rarely investigated by soft matter physicists, despite encouragement by Donald in 1994.³

Food has been recognized as one of the most complex types of soft matter,⁴⁻⁶ and, contrary to other soft matter, it has taste. The taste of food becomes apparent as it is eaten,⁷ and is perceived *via* both its texture and flavor. Interestingly, texture strongly enhances the flavor and taste.⁸ Hence, in food manufacturing, the formation of exquisite food structure is of great importance. Until now the making of structured foods has been more of an art than a science.⁹

For many years food engineers have successfully used tools from chemical engineering, such as heat and mass balances and unit operation approaches to control the large scale production of manufactured foods, thereby optimizing throughput and ensuring food safety.¹⁰ As chemical products rarely need to be structured, there has been less emphasis on food structuring.

Food Process Engineering, Wageningen University, the Netherlands. E-mail: ruud.vandersman@wur.nl

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An increasing number of food physicists now recognize the potential of soft condensed matter physics to understand and control food structure.^{4,8,11–18} The main paradigm of soft matter is that the governing physics at the level of the mesoscale structures is quite independent of the precise molecular details, but is much more influenced by externally applied fields, such as mechanical stress, as expressed by the softness of the matter. Furthermore, soft matter has a great deal of universality. All soft matter is in principle thermodynamically unstable,⁵ and needs to be stabilized. This can be done *via* modification of the surface properties (interaction potential) or by bringing the soft matter into a kinetically arrested state. Kinetic arrest or jamming occurs in all soft materials if an applied external field crosses a certain threshold.^{19,20}

In molecular gastronomy food is viewed as soft matter with some universality at the level of its structure.^{9,21,22} Consequently, it is thought that similar food texture can be obtained with a variety of different food ingredients.^{8,9} By systematic analysis of the creation of structure during the cooking of food, one can invent new dishes based on similar structure—but with other ingredients. Chemical details do play a role in the taste of food,⁹ but taste is moderated considerably by the texture of the food.^{8,7} The complex dispersed systems (CDS) notation has been formulated for systematic analysis of food structure.⁹ In the spirit



R. G. M. van der Sman

Ruud van der Sman received his MSc in Applied Physics from Delft University of Technology, and his PhD from Wageningen University. Since 2000 he has been an Assistant Professor at Wageningen University. His research focuses on the simulation of food structures (emulsification. fractionation of suspensions) and moisture migration in foods.



Atze Jan van der Goot received his MSc and PhD in Chemical Engineering from Groningen University, Netherlands. Since 1999 he has been Assistant Professor at Wageningen University. His research focuses on structure formation processes in concentrated biopolymer systems.

A. J. van der Goot

of chemistry this notation formally describes transformations in food structure during cooking. We suggest that this formalism has equal potential in analysing the creation of food structure on an industrial scale.

In this paper we discuss the potential from the point of view of soft matter physics and molecular gastronomy for making food structuring a science in its own right. From both viewpoints, we synthesize a new tool for a *qualitative* description of food structuring.

2 Nature of food structure

By and large, foods are dispersed systems,^{6,24,23} like other kinds of soft matter. The dispersed phases are mesoscale particulate structures (colloids) derived from natural food products, or are created artificially *via* food processing.¹⁰ Naturally occurring mesoscale structures are listed in Table 1. These food colloids are constructed by self-assembly. To this toolbox provided by nature, people have added 'artificial' colloids, *e.g.* gas bubbles, oil droplets, ice crystals, fat crystals, and protein aggregates, created by external fields applied by food processing equipment. With these 'artificial' colloids, we adhere to the length scales dictated by our tasting senses, which are sensitive enough to detect structures of millimetre down to micrometre size.⁷

A wide variety of foods can be created using a reasonably limited set of food colloids.¹⁰ Food encompasses most of the dispersions listed in the well-known classification of dispersions used in soft matter physics² (Table 2). This classification is built upon the aggregation state of both the dispersed phase and the continuous phase. The aggregation state is either gas, liquid, or solid. This complex dispersion notation was formulated by deGennes, and builds on the notation used in emulsion science, where O/W indicates an oil-in-water emulsion, and W/O indicates a water-in-oil emulsion. Observe from Table 2 that foods with a gaseous continuous phase are virtually non-existent, as they are not nutritious or not appealing to our taste. Dry food half products can be viewed as a solid-in-gas system.

Next to these mesoscale structures, food contains smaller molecular species, like salts, sugars, polyols and phospholipids, which moderate the properties of the continuous or dispersed phases, or their interfaces. These low molecular weight food ingredients serve as surfactants, plasticizers, humectants, for example. In the spirit of mean field theory these moderations can be absorbed in the effective properties of the two phases or the colloidal interaction.^{2,12}

The complexity of foods goes further than the traditional model systems investigated in soft matter physics, which are

 Table 1
 Food colloids derived from natural sources

Source	Mesoscale structure
Potato/wheat	Starch granules
Wheat	Storage proteins as gluten
Milk	Casein micelles
Milk	Globular proteins
Milk	Fat globules
Meat	Protein fibers
Plants/bacteria	Fibers/gums
Fruits/vegetables	Plant cells
Seeds	Oil cells

 Table 2
 Soft matter classification of dispersions with some food examples

Class	Technical Name	Example
S/S	Solid dispersion	Chocolate
L/S	Solid emulsion or gel	Jelly
G/S	Solid foam	Meringue
S/L	Sol or suspension	Fruit juice
L/L	Emulsion	Milk
G/L	Foam	Whipped cream
S/G	Powder	Flour
L/G	Aerosol	



Fig. 1 Examples of food structures, from left to right: ice cream, yogurt and cheese. Pictures were obtained by CSLM, with fluorescent dyes coloring fats (green) and proteins (red). Courtesy of Friesland Foods.

broadly speaking complex fluids with a single type of dispersed phase.⁶ Many foods are mixed dispersed systems. Fig. 1 shows the microstructure of ice cream, yogurt and cheese. Ice cream is an extreme example, with air bubbles and milk fat globules dispersed into a freeze concentrated solution, with the smaller fat globules absorbed at the air/water interface. The frozen continuous phase is again dispersed with ice crystals.³⁰ Yogurt consists of a dispersion of fat droplets in a continuous phase, which is a gel built up from casein aggregates induced by lowering the pH via fermentation with lactic acid bacteria.11 Cheese has a bi-continuous structure consisting of a network of solidified milk fat, and a network of gelled casein aggregates, nowadays induced by rennet enzymes.11 In other foods, such as double emulsions or fresh meat products, the dispersed phase is a hierarchical structure.²⁵⁻²⁷ For double emulsions the complex dispersion notation is expanded with W/O/W and O/W/O, with the latter indicating an (oil-in-water)-in-oil emulsion.

Complex foods like ice cream or bakery products are gels, emulsions, and foams at the same time. Hence, our vocabulary is too limited to encompass the rich complexity of foods. Consequently, the founder of molecular gastronomy, Herve This, has expanded the complex dispersed systems (CDS) notation to capture the structure of culinary creations, especially during production.⁹ This expanded notation is reviewed in a special section, where we propose a further expansion of the notation, better fitted to food structuring. Before we can review the CDS notation, the creation of food structures is discussed in more detail.

3 The making of structured foods

The production of most structured foods, such as bread and cheese, has developed over time in an empirical way. Food

structuring is regarded from a generic point of view in only a selected number of studies.^{11,23,28,29} Aguilera states that the processing of foods is the art of preservation, transformation, creation and destruction of food structure.28 A similar observation is made for dairy gel products by de Kruif *et al.*,¹¹ stating the general steps for their formation: (1) destabilization of the colloidal dispersion via an external field such as temperature, pH, or other colloids; (2) aggregation of proteins; and finally (3) gelation of the dispersion. In step (1) the native colloidal stability of cows' milk undergoes destruction; in step (2) new structures (protein aggregates) are created; and in step (3) the newly formed structures are preserved. Manski et al. have reviewed the making of protein fiber foods.²⁹ They state that the making of these foods with an anisotropic fibrous structure requires a careful balancing of deformation and solidification. 'Solidification' is described as the process that transforms the food from a flowing liquid-like state, to a stable solid-like state. Solidification can be performed via coagulation of proteins (via salt, divalent ions, pH or enzymatic crosslinking, e.g. with transglutaminase). Deformation of coagulated proteins occurs via shear or elongational flows. Fito et al.²³ identify four principle transformations in the processing of structured foods: (1) creation or destruction of a phase (like a bubble or removal of capillary water); (2) phase transition (change in the aggregation state as in freezing); (3) mass and heat transfer; and (4) biochemical transformations as induced by ions, pH, enzymes or fermentation.

From the different viewpoints discussed above, we deduce that food structuring is a combination of some of the following principal processing steps: (1) the destruction/destabilization of food structure; (2) the creation of new phases (mesoscale structures) by biochemical means or by phase transitions; (3) the deformation and sizing of phases by hydrodynamic means (shear and/or elongational flow); 4) the stabilization of the new (de)formed structure by colloidal means or by taking the food to the jammed state. We focus on these principal steps, and discuss them from the point of view of soft matter physics.

3.1 Destruction and destabilization

During food structuring processes, it happens that deliberate destabilization of the original food structure is required in order to assemble a new structure. This destabilization of food structure is regular practice in the dairy industry, where the native colloidal stability of milk is destroyed in order to produce yogurt, cheese or ice cream.^{11,12,30}

The destabilization of foods can be viewed as an act to impart stabilizing colloidal forces, as mediated by surface active ingredients like surfactants or proteins.¹² This can be done in a variety of ways, for example by displacement of proteins by surfactants (lowering surface energy, but also the energy barrier of the colloidal interaction), by change in pH, ionic strength or temperature (inducing change of colloidal forces or conformation of proteins) or by enzymes (removing part of the protein and thereby changing the steric interaction, or making crosslinks between colloids).

Destabilization is well described by theories from colloidal science.¹² For years there has been an interaction between food science and colloidal science,¹² where the colloidal stability of fluid-like foods (dairy) is one of the main topics. Colloidal

science, now integrated into soft matter physics, has provided the insight that colloidal stability is governed by interparticle forces, like van der Waals and electrostatic forces, steric interactions, depletion forces and so-called structural forces. Colloids are kinetically stabilized (stable for long time scales) if the interparticle potential has an energy barrier large enough compared to thermal fluctuations $(\Delta U \gg kT)$.^{12,31,32} Most colloids are treated theoretically as hard spheres, with some short-range interaction potential—which again is a sign of universality in the behavior of soft matter.

3.2 Creation of new phases

New phases can be created in several ways: *via* aggregation, phase transitions, or biochemically.

Aggregation of food colloids into a new gel phase can happen after destabilization of the dispersion as described above. In front of the energy barrier there can be a secondary minimum in the interaction potential, U_{\min} , making the colloids aggregate in clusters.^{31,33} Aggregation is called flocculation if it is reversible $U_{\min} \approx kT$, and coagulation when it is irreversible $U_{\min} \gg kT$. Aggregation can also be induced by biochemical means. This happens in oriental soy protein products such as tofu and tempeh, where fermentation makes the proteins aggregate. Gels or fibers can be created by enzymatic (transglutaminase) crosslinking of proteins.^{34,35}

Other new phases, such as crystals or bubbles, are created by inducing a phase transition of the water present in the food by a temperature change. Solutes modulate the freezing and boiling points *via* their colligative properties, and even biopolymer can have a significant effect.³⁶

Fats are crystallized during the manufacturing of chocolate, spreads and ice creams. Fat crystals penetrate the interfaces of oil droplets, which are used to destabilize emulsions.³⁰ In chocolate and spreads, aggregation is allowed to continue until a network is formed. This jammed network has a stabilizing function.

In the production of confectionery, low molecular weight carbohydrates such as sucrose also crystallize, forming a stabilizing jammed network.⁵² In other foods, the crystallization of carbohydrates is unwanted as it gives an unappealing, gritty texture, similar to sand in food.¹⁰

Gelatinization of starch granules is frequently used for structuring and involves melting the crystalline structures in the granule and the leaching of amylose. During baking the gelatinized starches will form a gel, thus creating a stabilizing function. Gelatinization is both a function of the amount of solvent and temperature.³⁷ As well as its structuring function, gelatinization also makes the starches available for digestion.

Phase transitions also occur in solutions of surface active ingredients, such as phospholipids, which can self-assemble into liquid-crystals.³⁸ These liquid-crystal phases are frequently used in low-fat spreads. A similar phase transition is the phase separation of biopolymer mixtures (frequently protein/carbohydrate mixtures), forming so-called water-in-water (W/W) emulsions.³⁹ This is quite a novel way of creating food structure.

On occasion, new phases are created by biochemical means. Carbon dioxide is produced by yeast fermentation forming bubbles in beverages (beer and champagne), and bakery products. Thus, for the majority of structured foods the creation of new phases is by phase transition. Phase transitions have been studied intensively in soft matter physics, The thermodynamics of phase transitions are described by free energy functions; free energy is described as a function of composition and the spatial distribution of the phases. These functions also take into account the surface free energy of the interfaces between different phases.^{1,17} The dependency of phase transition on temperature and composition is depicted in phase diagrams.

A good starting point for the thermodynamics of food is the Flory-Huggins theory. A select number of papers have reported that the Flory-Huggins theory and its extensions apply to the cooking of meat,¹⁶ surfactant stabilized emulsion droplets,¹⁷ cooking rice or pasta,^{45,46} potatoes,⁴⁷ fat (triglycerides),^{49,50} gels,⁴⁸ and W/W emulsions.⁴⁰ In our opinion, the Flory-Huggins theory has not yet been fully exploited in food science.

3.3 Deformation

The size distribution of the dispersed phases is important for the sensory appreciation of foods. The sizing in newly formed phases is predominantly performed by the deforming and dispersing action of fluid flow.⁵³ In order for the dispersed phases to be deformed, they need to be in the fluid state.²⁹ This may require destabilization, unjamming, or melting of crystalline dispersed phases such as starch granules and fat globules. The deforming action of fluid flow is frequently performed simultaneously with the creation of new phases.^{31,39,54,55}

The theory for sizing of dispersions is well developed in emulsion science, which began with the seminal work of Taylor.⁵⁶ Of key importance is the work of Grace,⁵⁷ who generated a curve of the critical capillary number as a function of the viscosity ratio. Beyond the critical capillary number, droplets will breakup. The Grace curve has become one of the work horses for food emulsions.^{53,58} The Grace curve holds evenly for concentrated emulsions, if the effect of surrounding droplets is absorbed in an effective viscosity, following mean field theory.^{53,59}

In a concentrated emulsion the resulting droplet size is the result of a balance between breakup and coalescence. This coalescence occurs if for two colliding droplets the hydrodynamic forces overcome the particle interaction force. Deformation of emulsion droplets is moderated by dynamic interfacial tension effects and the viscoelasticity of the continuous or droplet phase.^{17,53}

In addition to sizing, deformation is also used to obtain anisotropy in the shape of the dispersed phases of foods.^{29,55,61,62} The competition between deformation and viscoelasticity plays an important role in creating anisotropy in structures.^{34,60}

Emulsion science is absorbed in soft matter physics; droplet deformation theories not only hold for the traditional emulsions of oil and water, but also for foams,^{63,64} polymer blends⁶⁵ and water-in-water emulsions (i.e. phase separated biopolymer mixtures).³⁹ This is again evidence of the universality of soft matter.

3.4 Jamming

After (de)forming new food structures, they have to be preserved until the moment of consumption. This preservation is achieved *via* either colloidal stabilization for liquid-type foods, or by bringing solid-type foods to a gel or glassy state.^{5,10,34}

In soft matter, glassy and gel states are viewed as manifestations of a kind of universal state, namely the jammed state.^{19,20,66} Weeks⁶⁶ gives a list of jammed soft matter, which encompasses most structured foods: colloidal suspensions in the glassy state, gels, emulsions and foams at high volume fractions, and granular material.

Liu and Nagel¹⁹ have introduced the concept of the jamming state transition in a state diagram, as shown in Fig. 2. The jamming state transition depends on the strength of the particle interaction (compared to thermal energy, kT), the volume fraction ϕ , and the ratio of mechanical stress/yield stress σ/Σ . Their picture is far from complete, as jamming depends on the quenching speed, shear rate, polydispersity and particle shape.⁶⁶ However, it offers a powerful universal view of stabilization of food structures, and of course the reverse process, destabilization (unjamming). This universal view states that unjamming can be achieved by the application of one or more of the following measures: temperature increase (above glass transition T_g), application of mechanical stress (*via* shear or high hydrostatic pressures) crossing the limit of the yield stress Σ , and change in the volume fraction $\phi < \phi_{max}$ by dilution with solvent.

3.5 A multiscale picture

From the above discussion, it follows that food structuring implies the use of external fields, which act directly at the mesoscale *via* the deformation and (un)jamming of the structural elements, or indirectly *via* the molecular level, inducing the creation of new structural elements by phase transitions or biochemistry, and the stabilization thereof. External fields are generally applied by macroscopically (metre) sized processing equipment. Hence, food structuring is a *multiscale* problem (Fig. 3).

Full understanding of the *multiscale* problem of food structuring is a formidable task.¹⁸ In our opinion, this can only be achieved *via* multiscale computer models. Consequently, a decade ago we began this task by developing mesoscale



Fig. 2 Jamming state diagram.



Fig. 3 Food structuring is a multiscale problem, with micro- and macroscale forces working on the mesoscale food colloids induced by the external fields applied by the processing equipment.

simulation models for emulsions and suspensions,^{17,41,71} which is still quite unique to the field of food science. The mesoscale models are incorporated in a multiscale simulation methodology. From the mesoscale models, closure relations for effective parameters are derived, and used as input for macroscale models. For these macroscale models, we follow the volume-averaged/ porous media approach pioneered by Quintard and Whitaker,⁷⁰ and promoted for food applications by Datta and coworkers.⁶⁹ Such macroscale models have been developed for food suspensions in microfiltration,⁷² and the cooking of meat.^{16,73} However, the multiscale methodology for food structuring needs further development, as much of the rich physics of food structuring needs to be incorporated.

Recently, more qualitative methods have been developed, which are also helpful in shedding some light on the complexity of food structuring: the CDS method by Herve This,⁹ the SAFES method of Fito *et al.*,²³ and state diagrams with process trajectories.^{75,76} These qualitative methods are reviewed in more detail below, and we synthesize a new tool by combining the CDS and state diagram approach.

4 Qualitative descriptions

4.1 SAFES

The systematic approach to food engineering systems (SAFES) method states that food structure can be characterized by three dimensions: (a) the composition; (b) the different phases; and (c) the aggregation state. Food processing imparts changes in these three dimensions. As discussed above, SAFES recognizes three general processes: (a) phase transitions; (b) mass transfer; and (c) biochemical reactions. The interactions between the three dimensions of food structure and processing is shown in Fig. 4. SAFES indicates the changes in phase, state and composition due to processing *via* a large matrix (about 20×10), which is a 2D projection of the SAFES cube shown in Fig. 4. However, the matrix is difficult to interpret due to its large size and the fact that it is a projection of a 3D data structure.

In both the soft matter classification of dispersions, as given in Table 2, and the SAFES method, dispersions are classified by their phases and their aggregation states. In SAFES, the rubbery state and the glassy state of food are seen as aggregation states. Furthermore, SAFES interprets bound water and free (capillary) water as different phases. However, SAFES lacks a means to denote hierarchy in the food structure.



Fig. 4 Three dimensions of food structuring based on the SAFES methodology.

4.2 CDS

A much more flexible method to denote the complex, hierarchical structure of food is the complex disperse system formalism. CDS was developed by Herve This for defining the structure and the production of culinary creations.⁹ The CDS formalism is an extension of the notation of soft matter dispersions as shown in Table 2. The CDS formalism is extended by including the steps in the processing of the food, written in the form of a kind of reaction. Hence, whipping a cream is defined as:

$$O/W + G \to (G + O)/W \tag{1}$$

Here O/W is the cream, an oil-in-water emulsion, and G is the gas phase (i.e. air). By whipping, the gas is dispersed into the emulsion, but the oil droplets absorb at the interface—which might be viewed as the new dispersed phase. Hence, the symbol '/' = 'dispersed into', and '+' = 'mixed with'. With parentheses and brackets the hierarchy of the structure can be indicated. Other symbols used in the CDS formalism are: '@' = 'included in', and \subset = 'superposed upon', which are useful for describing foods with a distinct macroscopic structure, such as French fries or a cereal product with a distinct crust and crumb/core region.

We view the CDS formalism as a very elegant way to define the 'phase' dimension of food structures, and their related processing steps. Compared to SAFES, CDS only partly recognizes the 'composition' dimension, and lacks the 'state' dimension. CDS distinguishes the different compositions of oil and water, as in the notation of the emulsion O/W.

4.3 State diagrams

The usefulness of the state diagram for indicating the glassy state has been recognized for some time by food scientists.^{77–79} The state diagram is often combined with the phase diagram indicating first order phase transitions such as freezing or boiling.

Recently, the state/phase diagram has been used by a selected number of food scientists to depict the processing of complex foods such as bakery products.^{74–76} In the state diagram the trajectory of the food material is depicted in a temperaturemoisture content diagram, and is viewed as a powerful tool for a more fundamental and quantitative understanding of the processing of structured foods.^{18,74,80,81} Vuataz has used the state diagram of milk, indicating ice and lactose crystallization and glass transition, to optimize spray drying.⁸¹

For multiphasic materials such as foods, the theory of glass transition has to be applied carefully. A number of papers in food science indicate that in multiphasic material there are multiple glass transitions, as observed for starch/inulin mixtures,⁸² for starch/sucrose mixtures,⁸³ and for bread and cereal products.⁷⁹ It has been reported that some phase separation probably also occurs.

For a multiphasic material, the common representation of a state diagram as a temperature/moisture content diagram is not correct in a thermodynamic sense. In multiphasic materials there will be different partitioning of water between the phases,^{75,84} but they will have the same water activity. Hence, state diagrams should be depicted as a temperature/water activity diagram.⁷⁴

4.4 Synthesis

All three methods reviewed here have their pros and cons, but by combining their strong points a more comprehensive method for the qualitative description of food structure can be synthesized. The strong point of SAFES is the description of food structure in terms of dimensions (phase, state and composition), and that food processing acts on these dimensions. For soft matter other than food, composition is not that important (as the mesoscale structure is largely independent of composition), but for food the composition dimension is important due to its link with taste, texture and health. Hence, we take the composition dimension into account.

Food processing is classified based on the direction of the process in the SAFES cube (Fig. 4), and this classification has much in common with the other classifications discussed in Section 3. However, SAFES is missing the class of deformation and sizing processes, and consequently it is also missing the dimension 'size', which is of course an important attribute of food structure.⁵ However, we argue that size is a quantitative trait of food structure, and can be excluded from a qualitative description of food structure, as proposed below.

The strong point of CDS is its compact representation of phases (and hierarchy), and how processing affects them. It can easily be extended with the full description of the 'composition' dimension, by indicating the phases with letters referring to their composition. Following Aguilera and Stanley,¹⁰ food can be viewed as composed of proteins (P), carbohydrates (C), oil and fats (O), air (A), and water (W). However, by referring to the composition of the phase, one loses the reference to the aggregation state of the phase. We suggest two remedies: (1) indication of the aggregation state using subindices, or (2) introducing new letters for components in different aggregation states. In (1) the aggregation states of water are represented as W_S , W_L , W_G , with the indices following the notation of soft matter classification (see Table 2). In (2) the aggregation states of water are

represented by V for vapor, W for liquid water, and I for ice crystals. Solid fats can be represented by F. Biopolymers in foods hardly change the aggregation state, with the exception of starch, whose native form is a crystalline granule. The starch granule gelatinizes or melts at high moisture content or high temperature. In practically all cases, after gelatinization the starch will form a gel. Hence, gelatinization can also be represented as a kind of reaction $W + S \rightarrow W/S$, with S representing starch, and W/S the starch gel, which is viewed as water dispersed in the starch gel network. In the synthesized method, we follow remedy (2) to indicate the different aggregation states. W is used for free and capillary water, and bound water is thought to be part of the biopolymer.

We propose some modifications for the description of the hierarchy of food structure: (1) '@' ('included in') describes only a dispersed phase, which has a very distinct or stabilizing interfacial layer; and (2) | ('parallel to') described foods with a bi-continuous structure, such as cheese.

The @ symbol can be used for example to indicate vegetable cells, which are seen as a water phase encapsulated by a cell wall of pectin/cellulose, and denoted as W@C. Another use of that symbol is for protein or surfactant stabilized O/W emulsions, denoted as (O@P)/W or (O@Z)/W, with Z derived from the Dutch word 'zeep' for soap. It is known that surfactants can drive proteins from the interface, as happens in ice cream manufacturing.³⁰ In the CDS formalism the process is described as (with the proteins dissolved again in the aqueous phase):

$$(O@P)/W + Z \to (O@Z)/(W + P)$$
⁽²⁾

The strong point of state diagrams is that it is a well-known and widely used method in food science and soft matter physics to indicate the aggregation states together with the jammed states (the gel or glassy state). However, for multiphasic materials such as foods they must be properly represented as water activity/ temperature diagrams.

Processing steps such as destabilization, creation and jamming can be conveniently represented by trajectories in the state diagram. In general these processing steps will cross the phase and state transition lines. Consequently, regions bound by the lines of phase and state transitions can be represented by the CDS formalism. In a way, state diagrams can be viewed as a cross section of the SAFES cube displayed in Fig. 4.

In the synthesized method, food structuring is represented in state diagrams, with the state of the food structure indicated by the modified CDS formalism as proposed above. These state diagrams combined with the CDS formalism and processing trajectories are named food structuring diagrams (FSD).

5 Construction of food structuring diagrams

The construction of food structuring diagrams requires some quantitative knowledge of glass and phase transitions, as well as knowledge of the water activity as a function of composition and temperature. There is already a large body of knowledge and data on the glass transition of food materials.⁸⁵ The glass transitions are often well described by the Coachman-Karas relation.⁹² There is also a reasonable amount of understanding of phase transitions of food components. Freezing of the aqueous

phase can easily be computed from composition data.³⁶ Understanding of the thermodynamics of binary mixtures of fats is quite extensive;⁵¹ from this phase diagrams can be computed. Starch melting and gelatinization can be described by the Flory theory of melting point depression.^{37,93} Theories for protein denaturation are less well developed. Several researchers have remarked that protein denaturation has many similarities to polymer melting.^{93–95} The denaturation temperature is highly dependent on moisture content, and must be preceded by a glass transition.^{94,95} For denaturation of collagen, the Flory theory of melting point depression is frequently applied.⁹⁶

There is a large body of experimental data on the water activity of foods, described by the semi-empirical GAB-model.⁹⁷ Some recent studies indicate that there is good potential for the freevolume Flory-Huggins theory,⁹⁹ which has been shown to apply to low and high molecular weight carbohydrates,^{43,44,98} and to proteins.⁴² The free-volume theory has the attractive property of applying to the entire water activity range ($0 \le a_w \le 1$), that should be covered by the FSD. The commonly used GAB theory fails in this, as it is only valid for $a_w < 0.9$.

In the examples below we examine the food structuring of cereal based products (pasta and bread), with starch and gluten as the main structuring components. For both starch and gluten, it is shown that Couchman-Karasz applies for their glass transitions.^{86,87} The onset of gelatinization and the melting line can be computed using the Flory theory of melting point depression, where one has to take into account that native starch is only partly crystalline.⁸⁸ Above the melting line the starch is fully molten, and is in the rubbery state. For gluten there is no clear evidence that the Flory theory for melting point depression holds. However, as it is known that gluten denaturation (thermosetting) is also strongly dependent on moisture content,⁸⁰ and the Flory-Huggins theory is assumed to hold for the solubility of gluten,⁶⁸ it is quite probable that the Flory theory holds. The thermosetting of gluten coincides with the regime of starch gelatinization, as indicated in the state diagrams of ref. 75 and 89. Therefore we will not draw this line explicitly in the state diagram in Fig. 5. We have displayed the melting, onset of gelatinization, boiling and freezing lines of starch, together with the glass transitions of starch and gluten-which are also quite near to each other. Experimental data is taken from ref. 90 and 91.

6 Examples

6.1 Dried pasta

As a first example we consider the manufacture of dried pasta.^{80,100} Pasta is made from mixing durum wheat flour and water (W). Durum wheat contains mainly starch (S) and gluten (P), and is richer in gluten than other wheat cultivars. After mixing flour with water, and kneading, the gluten proteins develop into a (gel) network, where the starch granules are embedded in the network as fillers.

During the cooking of fresh pasta at T > 70 °C, the proteins denature and coagulate; the starch granules gelatinize more or less simultaneously. However, for dried pasta products it is desired that the starch does not gelatinize completely, but that the gluten proteins do denature. Denaturation makes the gluten network very rigid, such that upon final cooking the starch is



Fig. 5 State diagram of cereal products, displayed as a temperature/ moisture content diagram. Symbols indicate experimental data from ref. 90.

restricted in its swelling, and amylose leaching is reduced. This results in a firmer pasta with reduced stickiness. Hence, processing of the dried pasta requires careful balancing of the temperature between protein denaturation and starch melting. Hence, the dried pasta is heated and dried at moderate temperatures $T_{\rm gel} < T < T_{\rm m, \ s}$. For example a dough of 30% moisture content is dried at 90 °C.¹⁰⁰

From a food structuring point of view, the making of dried pasta has the following steps: (a) destabilization of the wheat flour *via* dispersion in a solvent (water); (b) formation of the gluten network *via* shear during kneading; (c) stabilization of the gluten network *via* denaturation; (d) stabilization of the whole product *via* solvent removal (drying), thereby bringing it to the glassy state. These steps can be formulated in CDS, where we assume that wheat flour is composed of native starch granules embedded in a gluten matrix (S + P), with a low moisture content, being in the glassy state. The water bound to biopolymer is not represented explicitly.

The mixing and kneading is given by:

$$(S+P) + W \to S/(W/P) \tag{3}$$

Starch granules remain in the native state, and added water is absorbed by the proteins, enabling them to deform and aggregate, and form a network (W/P). The starch granules are fillers in the gel network. After mixing, the pasta is heated until the drying temperature. At the end of the heating step the starch is only partly gelatinized, but the gluten is denatured:

$$S/(W/P) \rightarrow S/(W/S)/P_d$$
 (4)

Subsequently the pasta is dried to remove the solvent, and bring the pasta in the glassy state, and dried, thereby denaturing the proteins $(P \rightarrow P_d)$ and removing the solvent $(W \rightarrow V)$:

$$S/(W/S)/P_d \to S/P_d + V$$
 (5)

After attaining the glassy state the pasta is cooled.

During the final cooking of the dried pasta by the consumer, water is added, and the pasta is heated to boiling temperature whereby the starch granules gelatinize and absorb water:

$$S/P_{\rm d} + W \to (W/S)/P_{\rm d}$$
 (6)

The processing of the dried pasta is indicated in the FSD in Fig. 6, where we have used as a starting point the kneaded dough at 30 $^{\circ}$ C and 30% moisture content. We have followed the process trajectories given in the state diagram of ref. 80. The transition lines demark different structures of the processed pasta, and are indicated using CDS.

6.2 Bread baking

The process of bread making is comprehensively described by Cuq and coworkers,⁷⁵ and has already been illustrated by means of a trajectory in a state diagram, which we reformulate as an FSD.

The baking starts with a dough, which is made from a mixture of wheat flour (S@P), yeast and water (W). During mixing the proteins are hydrated, and tiny air bubbles (A) are included in the dough. Subsequently, the mix is kneaded, where gluten particles deform, entangle and make crosslinks *via* covalent disulfide bonds. Hereby a gluten network is formed. Note the similarity of this first processing step (dough making) with that of pasta making.

The second processing step is fermentation, where the temperature is raised to about 40 °C, making the yeast convert some of the starch into CO_2 (G), which diffuses into the air bubbles, expanding the dough.

Further expansion is obtained during the final processing step: the baking. Baking occurs in ovens with air heated to a high temperature of about T = 220 °C. The hot air makes the dough



Fig. 6 Food structuring diagram for cooking dried pasta, with the transition lines copied from state diagram in Fig. 5.

surface dry and dense, which then acts as a barrier for transport of water vapor. This water vapor is generated as the rising temperature of the dough elevates the vapor pressure. As the water vapor cannot escape easily, it fills the gas bubbles already formed during fermentation. The internal evaporation makes the gas bubbles and thus the dough expand further. Expansion is retarded by the strain hardening property of the gluten network.⁶⁷ Eventually the gluten proteins denature (thermoset) and the starch gelatinizes. The denatured gluten does not hold much water, but this water is readily absorbed by the gelatinizing starch.

Several walls of the expanding gas bubbles collapse, leading to a co-continuous network of the gas phase, letting the water vapor escape. The collapse of the whole bread is prevented as the crust enters the glassy state. After cooling the crumb remains in the rubbery state.

The basic processing steps are written in CDS format below. The mixing and kneading creates a gluten network (W/P) in which native starch granules (S) and tiny air bubbles are trapped:

$$W + A + (S + P) \rightarrow A/(S/(W/P)) \tag{7}$$

During fermentation, the structure does not change; only CO_2 (G) is added to the gas bubble. $A/(S/(W/P)) \rightarrow (G + A)/(S/(W/P))$. During baking we have the phase changes of water (evaporation), gluten and starch:

$$(G+A)/(S/(W/P)) \to (G+A+V)/((W/S)/P_d)$$
 (8)

The bread structure is stabilized as the crust enters the glassy state (indicated by the absence of free water (W)):

$$(G + A + V)/((W/S)/P) \to A|(S/P_d) \tag{9}$$

The complete process we write in more general form, without distinguishing between the various gases (all indicated as a gas G), and the biopolymer (all indicated as a solid S):

$$G + W + S \to G/(W/S) \to (G/S) \subset G|(W/S)$$
(10)

The ⊂ indicates that bread is also structured at the macrosale, namely in crust and crumb, with the crust being a solid foam, and the crumb a foamed gel. The food structuring diagram of the baking process is indicated in Fig. 7. The starting point of the process trajectory is the fermented dough at 40 °C. The dough is heated up to boiling point, while crossing the onset of gelatinization and melting lines. During baking moisture is removed, whereby the baking dough will follow the boiling line.⁷⁶ Due to the large size of bread, temperature gradients will develop inside the bread, which means that the crumb is still in the rubbery state when the crust enters the glassy state. If the crust is in the glassy state, the bread is removed from the oven and is cooled.

Observe the similarities with pasta making. For both products flour is mixed with water and is sheared leading to a gluten network (gel), which stabilizes the dough. Subsequently, the dough is heated and new phases/structures are created *via* phase transitions. Finally, the newly structured food is stabilized *via* a glass transition.



Fig. 7 Food structuring diagram for baking bread, with the transition lines copied from the state diagram in Fig. 5.

7 Conclusions

Food structuring is a complex (*multiscale*) problem, which can benefit much from developments in soft matter physics and molecular gastronomy. From soft matter physics we have learned that the evolution of the food structure is independent of the details at the molecular level, and displays a certain degree of *universalism* in: (1) thermodynamics, as this is largely described by (extensions) of the Flory-Huggins theory; and (2) jamming behavior. From the thermodynamic and jamming properties, we can construct state diagrams, which should be properly presented as a water activity/temperature diagram.

We have suggested combining state diagrams with the *complex disperse system* notation from molecular gastronomy and processing trajectories into so-called food structuring diagrams (FSD). We view these diagrams as a powerful *qualitative* method for describing the dynamics of food structuring in all its three dimensions: components, phases and aggregation states. We have analysed the cooking of pasta and baking of bread with FSD, and have observed some similarities, indicating there is some *universalism* in food structuring.

As food structuring is a careful balancing act between various forces, time and length scales, a more *quantitative precision* is required. This is the area where soft matter physicists can contribute greatly to food science. More precise quantification of food structure development can be obtained *via* mesoscale experiments, for example using microfluidic devices, or multiscale simulations, requiring coupling between macroscale simulations (*cf.* ref. 69) and mesoscale simulations (*cf.* ref. 17,41).

The proposed tools for investigating food structuring are also thought to be useful for other food structure-related disciplines: food destruction during consumption and digestion, and conceptual food product/process design.^{76,101,102}

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