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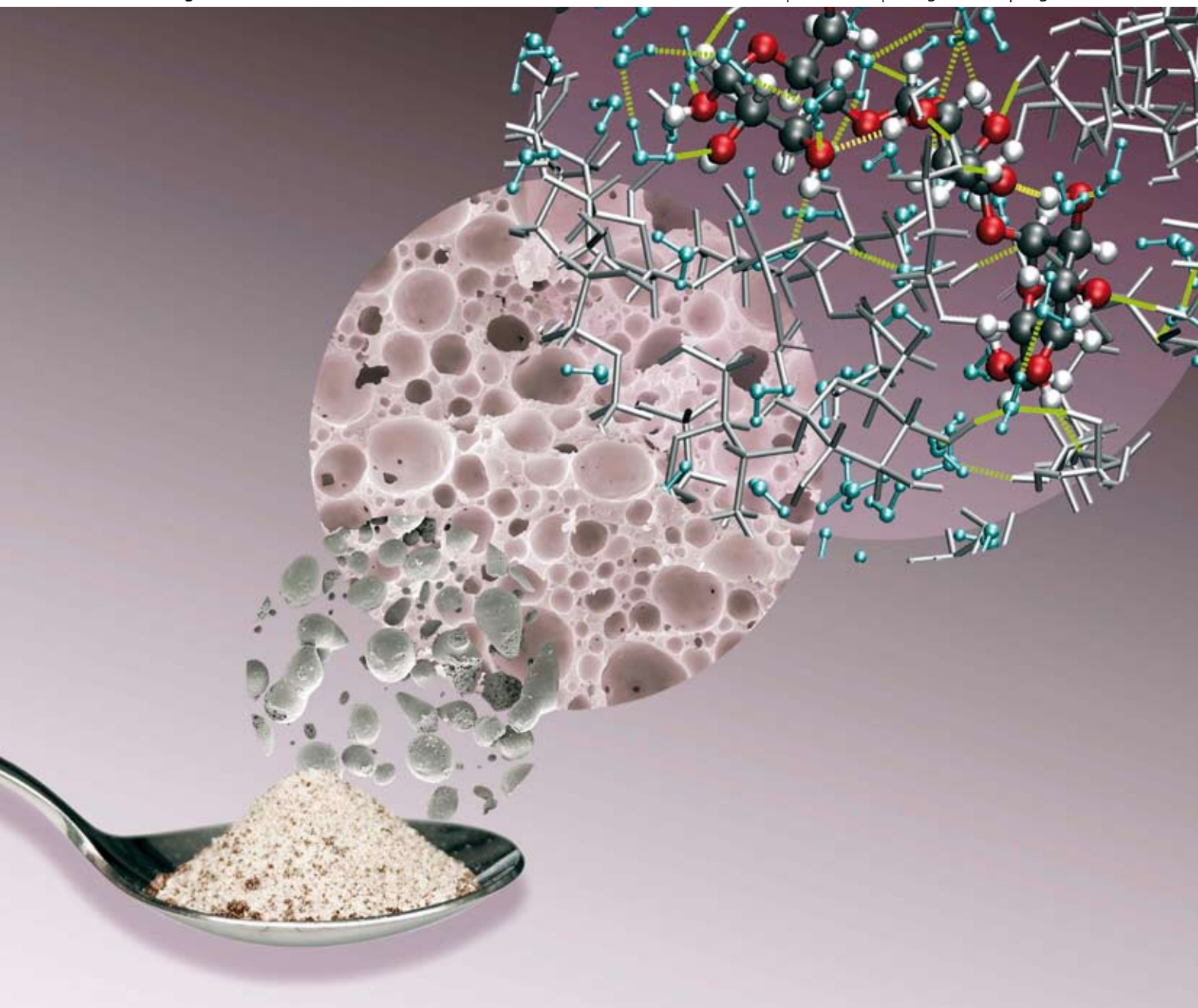
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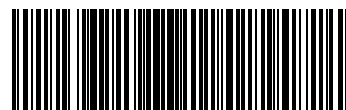
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Food structure and functionality: a soft matter perspective†

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The structure and functionality of foods are described from the perspective of recent advances in soft condensed matter physics. An overview is given of the structure and properties of food materials in terms of the physically relevant length scales. Recent developments in the understanding of the physics of gels, micelles, liquid crystals, biopolymer complexes and amorphous carbohydrates are presented.

1 Introduction

Soft matter is commonly defined as that subset of physical states which are easily deformable by thermal fluctuations, or whose total energy and the corresponding energy minima are of order of kT . Food materials are extremely rich in examples of soft matter since in many cases the basic building blocks are self-assembled structures with complex phase diagrams. By definition this richness of the phase diagram requires that the depth of the small metastable energy wells are of the scale of thermal energy. Larger scale structures, which are also abundant in food systems, are often amorphous systems of varying fragility, which are also a considerable challenge from a physical and thermodynamic perspective. In the following we attempt to outline some applications of soft matter physics to food materials and offer our opinions on where we feel significant progress is being made, and where we believe there are still perspectives for future developments.

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2 Length scales in foods

In a real food product a whole range of length scales will inevitably matter (Fig. 1). At one extreme, a food product is macroscopic, and at the other extreme, it is composed of molecules and atoms characterized by molecular length scales. It depends, however, enormously on the product, its constituents and which of the many length scales are dominant in establishing the product properties. For an emulsion-based food such as mayonnaise, it is the droplet size of around 1 μm which is the relevant length scale, whereas for dairy products it is typically the size of a casein micelle (~ 50 nm) and the size of the individual casein subunits (~ 2 nm) that matter. The relevant length scale of

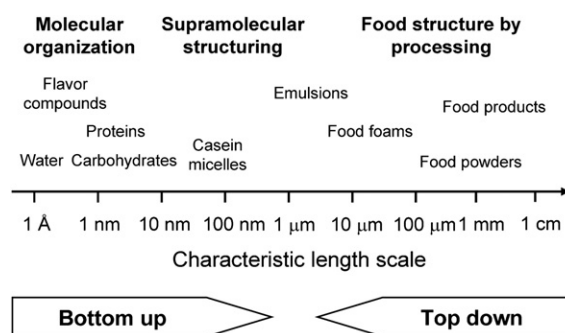
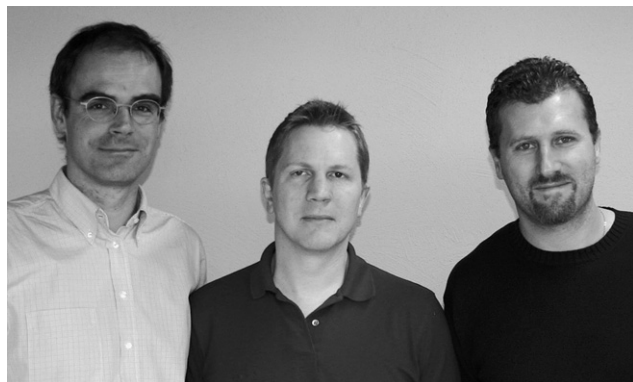


Fig. 1 Characteristic length scales in food and examples of representative food ingredients and food structures.



Job Ubbink, Adam Burbidge and Raffaele Mezzenga

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food powders is typically between 10 and 500 μm , and the structure of starch is described at length scales between the macromolecular (~ 1 nm) and the size of the starch granules (~ 1 mm) (Fig. 2). Even length scales substantially smaller than 1 nm matter in foods. For instance, the interaction of water with amorphous carbohydrates is associated with length scales of a few Ångströms and the diffusion of both water and flavor compounds involves mechanisms at the molecular level. The same applies to the bound water hydrating lipid polar heads in lyotropic liquid crystals or microemulsions.

Consequently, the physics of a specific foodstuff is governed by length scales which depend on the phenomenon one is interested in. If for such a specific system one is interested in structure-building, the relevant length scale is mesoscopic; if the interest is in understanding the state of water in food matrices it is rather the molecular level which matters. Within the scope of this Review Article, we cannot cover all the relevant phenomena and the associated length scales and we will therefore concentrate on a number of specific cases in which we have an active scientific interest ourselves.

2.1 Gels, micelles and complexes

In heterogeneous colloidal food dispersions, several length scales can be spanned ranging from the nm to the μm . At the smallest length scale, *i.e.* nm, microemulsions, nanoemulsions, and solid lipid nanoparticles have attracted great attention owing to the possibility of formulating high load dispersions whilst maintaining a fully optically transparent system due to the lack of light diffraction in the visible spectrum.^{1–7} More importantly,

when used as delivery vehicles for active ingredients, these types of nm-scaled dispersions have been shown to enhance the delivery efficiency and bioavailability.⁸

Food microemulsions are thermodynamically stable, self-assembled dispersions of typically below 100 nm, in which the oil–water curvature is essentially modulated by the role, type and topology of the surfactant.^{3,9} In a very coarse approximation they are to foods what block copolymer micelles are to polymer solutions in the sense that, above the block copolymer critical micelle concentration (cmc), thermodynamically stable direct micelles, reverse micelles and bicontinuous microemulsions are possible in both systems. Upon concentration or dilution they can be swollen, shrunk, dissolved or inverted, following well established phase diagrams.⁹ Well established theoretical tools to understand microemulsions exist, allowing the prediction of the exact curvature of the surfactant forming the interfaces¹⁰ and the aggregation number, that is the number of surfactant molecules aggregated in the same colloidal entity.¹¹ Nanoemulsions bear many similarities to microemulsions in size and composition, but in this case, although ionic or nonionic surfactants are also used to reduce the interfacial energy, the exact oil–water interface curvature is dictated by the energy supplied during the homogenization or ultrasonification process.¹² Therefore, nanoemulsions are nm-scaled emulsions and, like their larger scale parents, are thermodynamically unstable dispersions which undergo several destabilization processes, such as coalescence, Ostwald ripening and phase separation.¹³ Compared to standard emulsions however, the role of the surfactant becomes crucial, as the amount of interface to stabilize is several orders of magnitude larger. Solid lipid nanoparticles (SLNs) have been proposed as

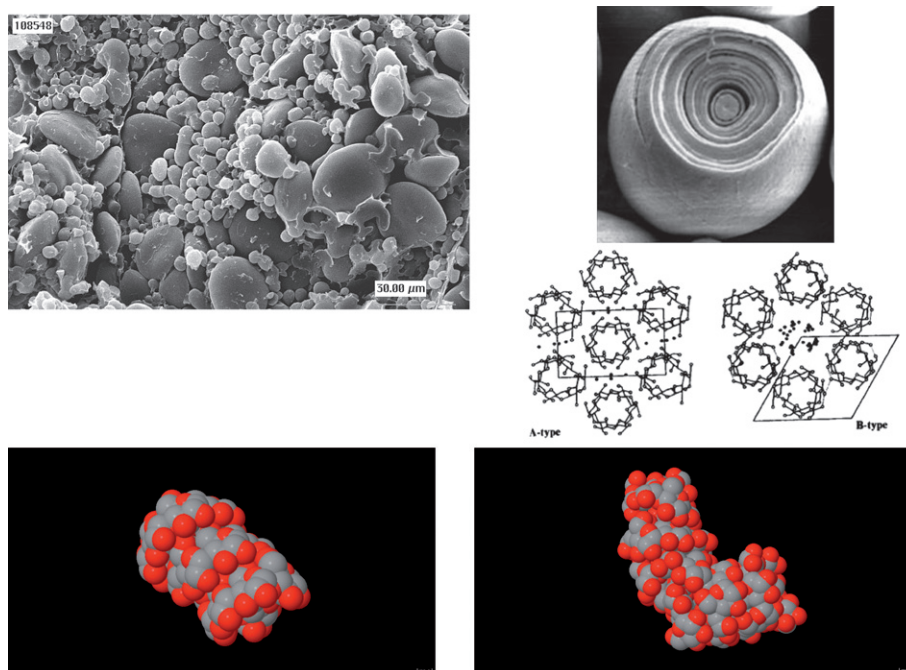


Fig. 2 Montage of images illustrating the naturally occurring hierarchical structuring in starch. Clockwise from top left: (i) SEM micrography of unswelled wheat starch granules (courtesy M.-L. Dillman), (ii) ESEM image of a single starch grain showing the onion-like structure (courtesy N. Nowjee), (iii) schematic crystal structure of amylose in A and B starches (after Imberty¹¹³), (iv) amylopectin, a branched polymer which is usually about 70% of the carbohydrate content of a starch, and (v) amylose, a linear polymer, which forms the balance of the carbohydrate content. Images (iv) and (v) are partially representative structures produced from data available at <http://www.lsbu.ac.uk/water/hystah.html>.

an alternative route to oil-in-water type nanoemulsions in which some of the possible instabilities typical of emulsions are overcome due to the solid nature of the crystallized oil.^{14–16} Practically, SLNs are realized using similar procedures to those used for designing nanoemulsions, but using formulations containing oils capable of crystallizing during the cooling step. In the limit of highly dense surfactant–water mixtures, such as in the case of neutral lipid–water mixtures, the domain of lyotropic liquid crystals is entered. In these systems, which are thermodynamically stable self-assembled complex fluids, the typical length scale is comparable with the contour length of the lipid used, *e.g.* ~ 1 nm.¹⁷ Similarly to their dilute analogues, microemulsions, their structure can be modulated by temperature, composition and guest molecules following precise equilibrium phase diagrams.^{17–19} Lyotropic liquid crystals based on neutral lipids and water will be specifically discussed later.

In electrically neutral polysaccharide-based gels, the typical length scale is somewhat defined by the mesh size of the network. Showing a close analogy to the physics of semi-dilute polymer solutions the mesh size can be expressed as a power function of concentration, resulting in a tunable length scale which affects directly the properties of the gels such as their rheological response to deformation and stress.²⁰ In the slightly more complex case of charged polysaccharide gels, pH and ionic strength provide additional opportunities to modulate the characteristic mesh size of the network, and thus its physical properties.²¹

Another relevant example of tunable length scale in foods comes from self-assembled coacervates which are formed by polyelectrolytes of opposing charge such as those typically observed for protein–polysaccharide mixtures.^{22,23} By varying the ionic strength and pH, for example, the molecular conformation of both the charged protein and polysaccharide can be affected, with profound consequences for the mesh size of their coacervates, both in bulk, and at an adsorbing interface.

2.2 The amorphous state in foods

Very many food products, or parts of food products, consist largely of amorphous carbohydrates in the glassy state. Examples of such products are milk powder, soluble coffee, infant formula, biscuits and cookies, extruded cereals, pasta, beverage mixes and culinary food powders. In addition, amorphous carbohydrates are widely used as matrices for encapsulation of active ingredients in foods, as they combine high physical and chemical stability with very good barrier properties for gases such as oxygen and nitrogen, and organic molecules, coupled with the ability to form particles and films with highly flexible shapes and geometries. The carbohydrates may vary from simple sugars such as glucose or disaccharides such as sucrose and lactose, or may encompass polydisperse carbohydrate oligomers such as maltodextrins and polymers such as starch.

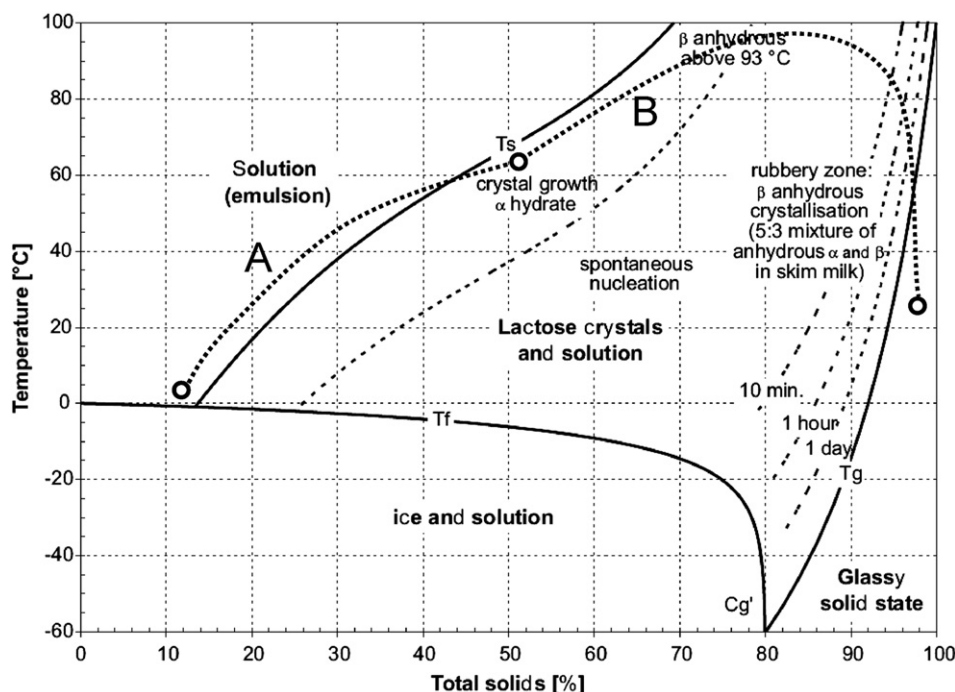


Fig. 3 State diagram of whole milk. The phase transitions shown in the diagram are those of lactose (milk sugar), which as a matrix ‘encapsulates’ the milk proteins and the milk fat. In comparison with the state diagram of pure lactose, the concentration axis (‘Total solids’) is adapted to the composition of whole milk, which includes proteins and fat. Ts: solubility line of lactose; Tg: glass transition line, Tf: freezing line; Cg’: concentration of the maximally freeze-concentrated system. The region in which spontaneous nucleation occurs is indicated as well as the delay of the onset of crystallization close to the glass transition. The processing route for milk powder is schematically indicated in the diagram. The start of the process is milk at a total concentration of ‘solids’ of 13 wt%, stored at 4 °C. The milk is first concentrated by evaporation to a total concentration of ‘solids’ of about 50 wt% (process A) and then spray-dried (process B). During process A, care is taken to avoid spontaneous nucleation of lactose, and by the spraydrying process (B), the system sufficiently rapidly quenched into the glassy state to retain a fully amorphous structure. The final product is milk powder with the lactose in the glassy state. The figure is reproduced with permission from ref. 47.

As for all amorphous materials, the physics of amorphous carbohydrates is primarily governed by the glass transition temperature (T_g). The T_g forms the boundary between the rubbery and the glassy states²⁴ and in the food field is usually measured using differential scanning calorimetry (DSC). The T_g is of importance for both processing and for product stability, as in the rubbery state translational and rotational motion of the matrix molecules is still possible, but in the glassy state large-scale (low frequency) molecular motion of the carbohydrate molecules is effectively inhibited.²⁴

The T_g of an amorphous food matrix depends on the composition, with low molecular weight compounds generally having a lower glass transition temperature than high molecular weight compounds.²⁵ Of major importance is that the glass transition temperature of amorphous carbohydrates decreases rapidly with increasing water content.²⁵ Consequently, by carefully tuning the water content and/or water activity of a food product based on amorphous carbohydrates, the processing and storage stability can be precisely controlled²⁶ (see Fig. 3 for the example of milk powder).

Several aspects of water in amorphous carbohydrates have been addressed using a wide range of techniques including differential scanning calorimetry (DSC),²⁷ dynamic mechanical thermal analysis (DMTA),²⁸ specific volume measurements,^{29,30} infrared spectroscopy,³¹ and neutron scattering.^{32–34} Positron annihilation lifetime spectroscopy (PALS) was introduced as a technique to study the structure and molecular packing of amorphous carbohydrates in both the rubbery and glassy states^{35,36,30} (Fig. 4).

The physics of carbohydrates differs substantially from synthetic polymeric materials in a number of important aspects. In the dry state, carbohydrate polymers have a glass transition temperature which is much higher than virtually all synthetic polymers of similar molecular weight. For example, the T_g of high molecular weight polystyrene and polyethylene are 372 K and 140 K, respectively, whereas the T_g of dry starch is 520 K.²⁶ This clearly demonstrates the relevance of intermolecular interactions in the formation and stabilization of carbohydrate matrices. As a direct consequence of these interactions, the carbohydrate molecules form clusters which behave as pseudo-molecules of higher molecular weight than the individual constituent molecules. These interactions are primarily hydrogen-bonding interactions between the hydroxyl groups of the sugar rings. This also explains the dramatic plasticizing effect of water in amorphous foodstuffs.

Although large-scale motion of the matrix carbohydrates are effectively jammed in the glassy state, small-scale reorganizations within the matrix remain possible, as is evidenced for instance by the diffusion of small molecules such as water,^{37,38} gases^{39,40} and small organic molecules⁴¹ in amorphous carbohydrate glasses. In addition, using spectroscopic techniques such as neutron scattering,³⁴ electron spin resonance (ESR)⁴² and PALS,^{35,36,30} it has been demonstrated that changes in temperature and water content have a profound effect on the local structure and dynamics of a glassy carbohydrate matrix (see Fig. 4 for a summary of recent PALS and thermodynamic results). The sub- T_g structure and dynamics at the molecular level are of major importance for the use of glassy carbohydrates as barrier materials and as bioprotectants and can be influenced by composition,^{36,30} thermal history,^{43,44} and aging.^{45,46}

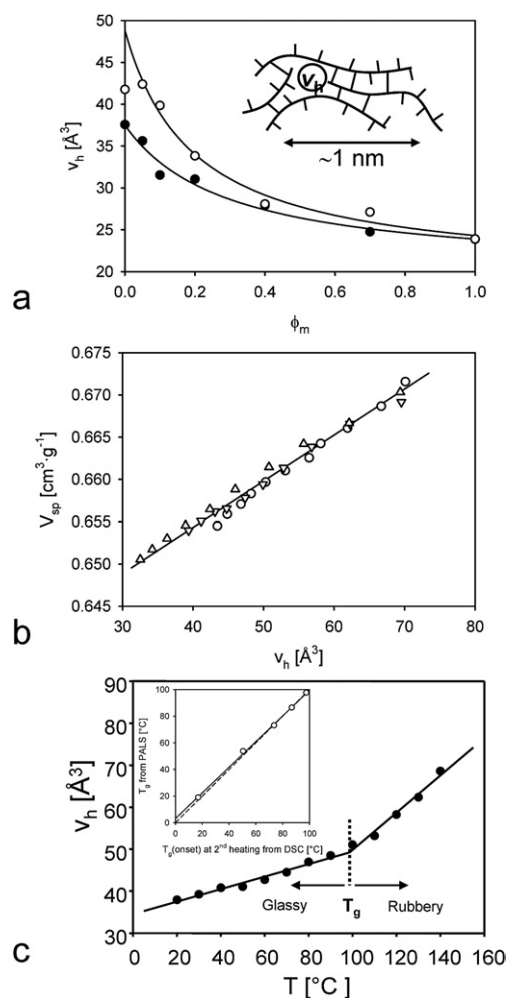


Fig. 4 Molecular structure of amorphous carbohydrates in the glassy state. (a) Hole volume in glassy mixtures of a maltopolymer and the disaccharide maltose in a fully anhydrous system (open circles) and at a water content of 5 wt% (filled circles) as a function of the maltose content. Inset: schematic depiction of a molecular hole in an amorphous carbohydrate matrix. Typically, the number density of holes as detected by PALS is of the order of one hole per ten glucose residues. (b) Correlation between the specific volume and the hole volume for various molecular weight maltooligomers at $a_w = 0.22$ (25 $^\circ\text{C}$) ($R^2 = 0.98$). The data are derived from temperature-dependent hole size and specific volume measurements. Circles: maltodextrin DE-6; triangles (down): maltodextrin DE-12; triangles (up): maltodextrin DE-33. The average molecular weight decreases with increasing DE value. (c) Thermal expansion of the molecular hole volume for a maltooligomer matrix [maltodextrin DE-12 at $a_w = 0.22$ (25 $^\circ\text{C}$)]. The experimental data is fitted with linear functions below and above the glass transition temperature T_g (indicated on the graph). The inset shows the correlation between the T_g as determined from the PALS experiments and from differential scanning calorimetry (the symbols are maltodextrin DE-12 matrices at various water contents).

Recent developments in understanding the physics of carbohydrate matrices in the glassy states have led to a reassessment of the role of the glass transition on the stability of food systems and food processing. For all aspects relating to the food stability and processing in which the rubbery state is relevant, the essential physics is well described by the water- and composition-dependent glass transition, usually in combination with the rheological

properties of the systems in the rubbery state and in solution. An important physical concept in this regime is the fragility parameter introduced by Angell.²⁴ On the process side, this has a significant bearing on the use of technologies such as spray-drying, freeze-drying, extrusion, agglomeration and sintering. Stability issues which relate to the glass transition and which are also dependent on the rheology are for instance powder collapse, stickiness and caking, undesired crystallization and the Maillard reaction in milk powders.^{26,47}

Conversely, stability issues which relate to properties of foods in the glassy state are in fact not related to the glass transition temperature of the matrix, but to the molecular packing and dynamics of the carbohydrate molecules in the glassy state. Such stability issues include the barrier properties for small molecules, in particular oxygen³⁹ (of relevance for the encapsulation of oxidation-sensitive compounds), the stabilization of fragile biological materials (for instance peptides and proteins, but also whole microorganisms such as probiotic bacteria) and surfactant systems (for instance liposomes and vesicles⁴⁸). In addition, the molecular packing in the glassy state strongly influences the sorption of water³⁸ and most likely also the water dynamics. As the T_g generally increases with increasing carbohydrate molecular weight, and as the molecular packing improves with decreasing molecular weight, it is therefore of major importance to determine which stability issue needs to be addressed in a certain food product or encapsulation system before deciding upon the carbohydrate molecular weight distribution. Often, an optimal result will thus be obtained by making a compromise between the T_g and the molecular packing. This compromise is that the content of low molecular weight carbohydrates (in particular disaccharides) is increased to the maximum level at which the glass transition temperature is still sufficiently high to guarantee the physical stability of the food product during heat shocks.

2.3 Higher-order structures: mesoscopic and macroscopic length scales

Despite the traditional emphasis on an analytical chemical description of foods, which is only natural given the origins of food science in chemistry, many of the important properties of foods are determined by structural elements of micro-scale and above. Examples include bubbles, drops, fibres (in the physical and not nutritional sense) and particles. Clearly these structures are large enough that they are almost certainly far from equilibrium and as such are not completely described by the chemical composition because they have significant memory of their process history. Unfortunately, it remains difficult to find well developed techniques that are suited to describing these elements in a meaningful manner, at least partially because it is rarely clear exactly which characteristic features of these structures control their functionality in the final product. It is not controversial to argue that macro-structure has a strong effect on texture, taste and stability of food materials, although exactly what these effects are remains unclear and extremely context dependent. Despite the out of equilibrium state, it would be a mistake to think that food materials are essentially jammed, disordered systems. In some cases, such as glassy materials, this is certainly the case, but, natural materials are in general highly ordered for

good functional reasons, as we discuss at length below. Foods are generally the product of biological evolution and as such strongly driven to optimize for functional effect. For example, plants, which form the core of most food systems, are exquisitely structured on many hierarchical levels in order that the transport system for water is an integral structural part of the plant itself. This structuring has led to highly anisotropic material properties relating to the diffusion of fluids and other molecules and of course mechanical behaviour. Processing of foods, and attempts to optimize them for particular properties, needs to take account of these natural structures and ideally use them to gain an advantage over the brute force approach of the heavy chemicals industry where pressure and temperature are the controllers of reaction rate and hence process efficiency. An additional, and certainly non-trivial, consideration is that raw materials for food processes, *e.g.* milk, wheat and other grains, coffee, cocoa *etc.* depend on the environmental conditions they experience during growth. As such, natural feedstocks vary with the season and climate. A nice, well-known, example of this is the variability in the thickness of the ring in wood depending on the year, which gives a characteristic fingerprint of the trees' environment during growth.

3 Recent advances in techniques, simulations and theory

3.1 Scattering techniques

The structure and dynamics of complex food systems have traditionally been investigated by techniques widely used in experimental soft condensed matter physics. In real space, the structure of foods has been observed by various microscopy techniques (see Section 3.2); some of these techniques also allow monitoring of the dynamics of foods systems. In reciprocal space, both static and dynamic scattering techniques have been used to reveal structure and dynamics.¹⁷ Static Bragg-type diffraction of neutrons and X-rays has been applied to dilute and dense food systems to reveal the structure in the 10–100 nm length scale range. Insight into lipid polymorphism, liquid crystallinity, protein folding, *etc.* can typically be gained by using these techniques. Because most common food properties are, however, directly related to the μm length scale, we will, in what follows, primarily discuss light scattering techniques. The application of dynamic light scattering to foods has greatly benefited from recent theoretical and experimental advances. Indeed, in a typical dynamic light scattering (DLS) experiment, one measures the fluctuation with time of the intensity of singly scattered photons throughout the sample.¹⁷ The time correlation function of this scattered light, yields information on the diffusion coefficient of the scattering objects. Because DLS is limited to single scattering, this technique is only applicable to extremely diluted systems, which is highly incompatible with typical food dispersions. Single scattering information can, however, be obtained in highly concentrated systems, such as real foods, if two scattering experiments are simultaneously carried out on the same scattering volume and the resulting signals cross-correlated.^{49,50} This is the principle of so called cross-correlation light scattering, which has widened the applicability of dynamic light scattering to real food systems as dense as natural milk.⁵¹

A conceptually very different approach to dynamic light scattering, which has found great success and applicability to food systems, is diffusive wave spectroscopy (DWS).^{52,53} This latter technique is applied in the opposite dilution range of DLS, that is, in highly concentrated systems in which the photons are more or less guaranteed to undergo multiple scattering events and are consequently isotropically scattered from the sample. Whilst the angular dependence of scattered light and the structure factor of the scattering objects is lost, the multiple scattering results in random walk, diffusive motion of the photons, from which useful information about the matrix can be extracted. This has led, ultimately, to the application of DWS as a microrheometric technique, in which the diffusion of light by probe colloidal objects suitably inserted in the dispersion, directly reveals the viscoelastic nature of the samples, *e.g.* the complex viscosity or storage and loss moduli.^{53,54} Microrheological measurements using DWS have been demonstrated to correspond closely to more traditional bulk shear rheology experiments assuming that the scatterers are moving in a scale independent manner. The advantage here is the possible application of this method to very small volumes, coupled with the avoidance of inertial effects thus providing access to larger frequency windows and thus more comprehensive relaxation spectra.⁵⁵

3.2 Structural techniques

A number of techniques can be applied to measure the structure of food materials either directly (optical and confocal microscopy, tomography, scanning and electron microscopy) or indirectly from measurements of the mechanical response or from spectroscopy. Tomographic techniques such as magnetic resonance imaging (MRI) and X-ray tomography are extremely powerful since they allow a full 3D reconstruction of the sample structure, but tend to be limited in resolution and/or slow in acquisition times. In general spatial resolution and acquisition times are inversely related due to signal to noise considerations. Dynamical imaging of evolving structural elements is hence even more challenging although great advances have been made in the past decade or so.^{56,57} An additional limitation of X-ray tomography is that the imaging contrast depends strongly on the differences in electron density. Consequently this technique is principally useful for the structural analysis of porous foods, but can still be used in other cases, although the foodstuff might then need to be selectively stained with heavy metals.

Optical microscopy suffers from a similar limitation in resolution, in this case due to the wavelength of visible light, even though structures of the order of 1 μm can still be imaged (in particular using confocal microscopy). A further limitation of optical techniques is that the food sample should be sufficiently transparent. Conversely, a major advantage of optical microscopy is that dynamic processes on time scales larger than about 10 ms can easily be followed, even under highly controlled conditions when special sample stages are used (*e.g.* for monitoring changes upon the cooling of a sample, or upon the mechanical deformation of samples using tensile stages).

Electron microscopy has seen wide use in the analysis of the ultrastructure of foods and food ingredients^{58,59} (in particular using transmission electron microscopy⁶⁰) and in the generation

of microscopic images having a high depth-of-focus (by scanning electron microscopy). In the imaging of samples using transmission electron microscopy (TEM), special staining, embedding and cutting techniques are indispensable,⁶⁰ whereas the use of scanning electron microscopy (SEM) is much more straightforward. An interesting recent development is the progress in so called environmental scanning electron microscopy (ESEM), which allows the analysis of samples at a desired relative humidity and thus avoids artifacts due to the dehydration of foodstuffs.

Over the past decade, scanning probe and single molecule techniques such as atomic force microscopy (AFM) and optical tweezers have become of enormous importance in soft condensed matter physics, biophysics and physical chemistry. AFM in particular has become a central technique in many fields as it allows not only the high-resolution mapping of the three-dimensional surface structure of soft matter, but also the determination of the elastic properties and interaction forces of surfaces. In food-related fields, AFM has been applied to image the structure and functional properties of biopolymers,⁶¹ emulsion systems⁶² and biological systems such as (probiotic) microorganisms.^{60,63} Single molecule techniques are technically often more demanding and are applicable only for highly specific systems and have therefore seen no significant use in the food field. They remain important, however, as they allow very precise measurement of the stretching forces of biomacromolecules. In this way, the persistence length of biomacromolecules can be determined and for carbohydrates, the chair–boat conformational transition has been detected.⁶⁴

An alternative to direct imaging is to measure the stochastic structural response of the material to perturbations in stress, strain or other fields. Generally speaking this is termed rheometry and can be either macro or microscopic. In the former case a small stress or strain perturbation is applied by the instrument at the material boundary (*e.g.* a moving surface such as a cone and plate geometry) and the response (either deformation or force) measured. Linear response theory together with some assumptions about the material constitutive law then allows the extraction of a spectrum of material relaxation times, which gives some information about the physics of the structure.⁶⁵ An alternative set of microrheometric techniques have more recently been developed⁶⁶ which measure the random walk of marker particles and invoke a generalized fluctuation–dissipation theory to derive the linear viscoelastic response of the sample (see Section 3.1). A nice feature of these techniques is that the perturbation is by definition in the linear regime, since it is essentially the thermal noise in the sample. This is not necessarily the case for macroscopic rheometry and in that case care must be taken not to violate this assumption of linearity in the system. In practice this means that measurements are often limited to extremely small strains. An additional potential problem with macroscopic rheometry is that of sample slip at the instrument–sample contact. It is generally fairly simple to detect the presence of sample slip, but avoiding it can be fraught with difficulties. Finally, the frequency range to which microrheology is applicable extends to larger frequencies compared to macroscopic rheometry, which can represent a substantial advantage when fast relaxation mechanisms have to be captured. Nevertheless, in the linear viscoelastic regime, and for the same frequency range,

good correspondence has been found between micro- and macrorheological measurements for general soft materials and food systems.^{53,54} One of the most successful applications of microrheology to foods has been the investigation of acid induced gel formation in milk and milk based products.^{67–69} Diffusion MRI can also be used to provide stochastic structural information for food materials.^{70–72}

Recently, positron annihilation lifetime spectroscopy (PALS) was introduced as a technique to study the molecular structure of amorphous and crystalline carbohydrate matrices.^{35,73} Even though PALS does not directly image topological detail, we nevertheless rank it as a structural technique since it provides stochastic quantitative information about the molecular holes and voids between the molecules in dense matrices.⁷⁴ This includes the average hole size and the hole size distribution, and, in special cases, information on the anisotropy of molecular holes (for instance in stretched fibres).⁷⁵

3.3 Statistical mechanics of food systems

Although rarely at equilibrium, those examples of foods whose structure can be considered thermodynamically stable can be understood and modelled using statistical mechanical concepts. Essentially, a model suitable to describe the essential physical features of the food system under investigation has to be constructed first. Successively, the partition function of the system is formulated and the corresponding free energy is derived. The absolute minimum of the free energy corresponds to the equilibrium configuration, while local minima capture metastable configurations. The major difficulty in following this approach is to be able to actually minimize the free energy. Coarse-grained field theoretic simulations solved within the mean-field approximation, also called self-consistent field theory (SCFT), represent

an elegant solution to this problem, since the particle-based partition function (and Hamiltonian) is mathematically transformed into a field-based partition function *via* a Hubbard–Stratonovich transformation.⁷⁶ In the resulting partition function and Hamiltonian, the system is described by fluctuating chemical potential and density fields, which allows the detection of minima by simple finite differences or finite element methods.⁷⁶ SCFT has been applied successfully to complex soft matter systems such as block copolymer melts, homopolymer–block copolymer blends and colloidal dispersions. More recently, Schick *et al.* have proposed the use of this method also for complex food systems at equilibrium such as lyotropic liquid crystals formed by lipids and water.^{77,78} Mezzenga *et al.* have extended the SCFT formalism to model solvent/lipid systems to capture most of the possible liquid crystalline phases encountered in foods.⁷⁹ Examples of these liquid crystalline phases are reported in Fig. 5.

Finally, by treating with a statistical mechanics approach the reversible hydrogen-bonding occurring between water and the lipid hydrophilic heads, Lee and co-workers have further improved SCFT applicability to lipid–water systems, leading to remarkable quantitative agreement between theoretical and experimental phase diagrams.^{80,81} An example of phase diagrams predicted by this approach is reproduced in Fig. 6.

Unfortunately many food materials are solid or semi-solid in their physical state, for example sluggish systems such as rubbery and glassy materials with very long relaxation times. In these cases, we are often not interested in the equilibrium properties of the material, but instead would like to know something about the system evolution. In this case we can consider using direct molecular dynamics (MD) simulation techniques. MD simulations are also extremely useful to investigate the structure and dynamics of complex food systems at the molecular level, as they

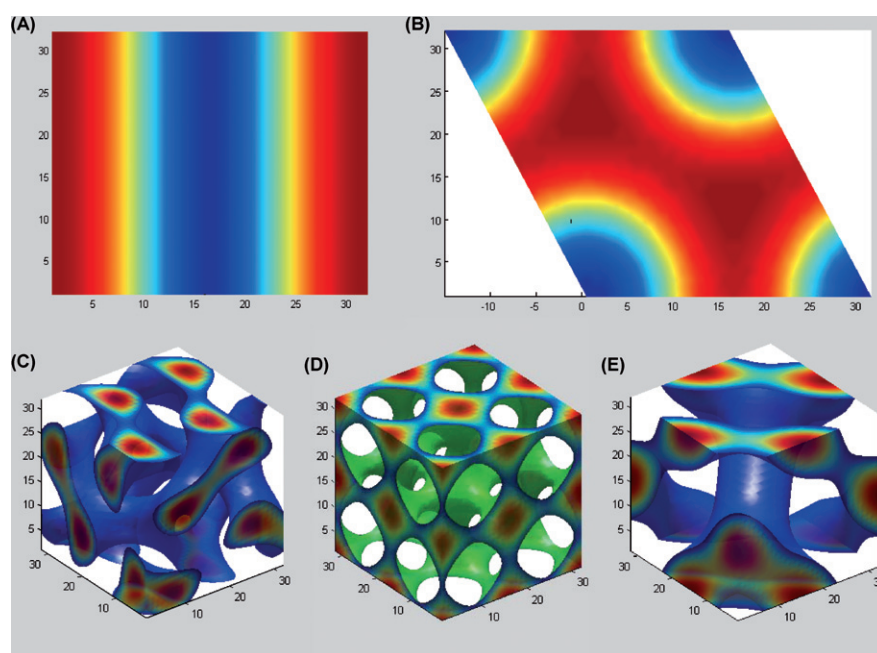


Fig. 5 Liquid crystalline phases observable in lipid–water mixtures obtained by SCFT simulations by modelling lipids as block copolymers and water as a homopolymer-like solvent. (A) Lamellar, (B) hexagonal, (C) Ia3d double gyroid, (D) Pn3m double diamond, (E) primitive. Reproduced with permission from ref. 79.

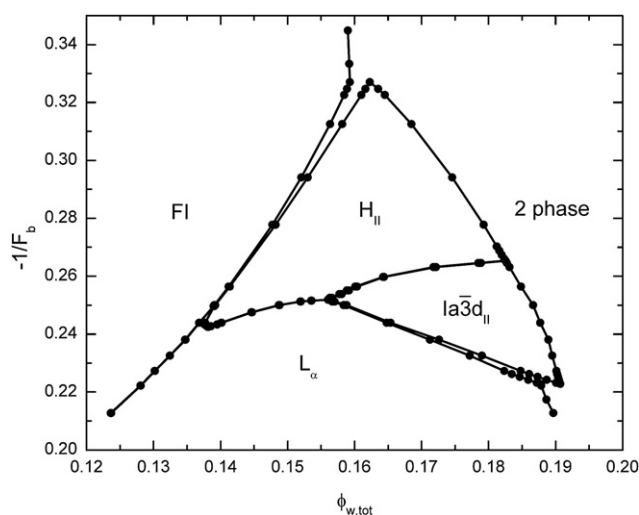


Fig. 6 Phase diagram predicted by SCFT for a lipid–water mixture, by implementing reversible hydrogen-bonds between water molecules and the polar lipid head in the overall energy of the system. The $-1/F_b$ vertical axis reports an ‘effective’ temperature, while the Φ horizontal axis gives the volume fraction of water molecules. Regions corresponding to isotropic fluid (FI), lamellar (L_{α}), hexagonal (H_{II}), and bicontinuous double gyroid cubic phase (Ia3d) are correctly predicted. Reproduced with permission from ref. 80.

allow the incorporation of molecular structure, physical properties and interactions in a highly detailed manner unattainable in analytical statistical mechanics. Such MD simulations can be either based on all-atom models or use coarse-graining procedures to reduce the level of molecular detail and thus the required computer power. Recent advances in computing performance and in force fields and simulation methods now enable the simulation of systems of a complexity which is sufficiently high to be directly relevant for the food field. Simulations can currently typically include of the order 1×10^4 particles, for which simulation times up to 10–100 ns are feasible. This allows the accurate simulation of the behaviour of liquids and even fairly viscous systems. MD simulations have been carried out for a variety of food systems. The food-related systems which have been most thoroughly investigated are carbohydrate–water systems.^{82–86} Detailed mechanisms for the diffusion of water in such systems and for the hydrogen-bonding between the carbohydrate and water molecules have been derived from such simulations.

3.4 Fluid dynamics and non-equilibrium processes

The science of continuum mechanics is extremely advanced for solids, liquids and semi-solid materials, and there has been much progress over the past century or so in describing the macroscopic behaviour of materials. Much of this science base can be directly applied to the description of food materials, although we would argue that this is not necessarily always the best course of action! Consider what we might need to know about the rheology of food materials? One can imagine two distinct perspectives: firstly process engineering, and secondly sensory science.

We often wish to design food processes and need some physical parameters to use in our design equations, that is to say classical process engineering. In this case, non-Newtonian

models of varying complexity have been used for a long time in the design of food process equipment. Here, continuum mechanics often do a very good job of solving our problem, and rheological measurements can be directly used to feed computational fluid dynamics (CFD) and other continuum simulations. However, in the case of non-equilibrium processes, this approach doesn’t work well since our constitutive models, which are dynamical equations of state, are inadequate. Unfortunately, as we have already noted, food processes are almost invariably far from equilibrium, which leads to a strong link between specific process history and product state. Although there is a vast literature available describing the effects of processing on structure *e.g.* ref. 87–90, it is almost always difficult to interpret, since the workers generally make little effort to distinguish between the effects of geometry (*i.e.* path dependent memory) and shear and temperature fields. The second perspective, in which rheology is used as an indicator for the textural, or more generally, organoleptic properties of food, will be addressed in the subsequent discussion.

4 Structuring of foods at multiple length scales

4.1 Assembly and structuring of foods in nature

Foods of a simple structure do not exist in nature; in fact all matter considered as foods by humans and of a natural origin displays a highly complex organization *e.g.* starch (Fig. 2). However, foods and food ingredients in nature have these highly complex and diverse structures for numerous, divergent reasons. Interestingly, only two of the common foods have evolved with the primary purpose of being eaten, namely milk and fruits. The importance of milk in the weaning of newborn mammals is obvious, and both the composition and structure of milk are highly adapted to this purpose. Fruits have evolved to be eaten by animals as a way to distribute seeds and so maximize the spreading of plants and trees. For this reason, fruits are attractive to animals including humans when ripe, with a high content of low molecular weight sugars (conveying sweetness), an attractive color and a delicate, soft texture. Conversely, when unripe, fruits tend to be unattractive, with the sugar stored in the form of non-sweet starch, with generally an inconspicuous greenish color and a hard, unpleasant texture and astringency.⁹¹

All other foods and food ingredients from nature with a complex structure have evolved for reasons having nothing to do with their use as a food. For instance, meat, being one of the most valued foods by humans,⁹¹ is nothing more than the muscle tissue enabling animals to move and perform various functions. The structure of meat is therefore determined by the requirement that it can convert chemical energy from nutrients into mechanical energy by a contractive mechanism. This in the first place necessitates a fibrous and anisotropic structure. In the second place, muscle fibres are extensible (and thus soft) as they need to contract and relax. The structure and the softness of meat gives rise to a texture which is highly appreciated by humans, for particularly tender meats, even when raw. Tendons, in contrast, are to transmit the muscle force to the bone, and, in order to be effective, need to be highly inextensible. Tendons are thus composed of very tough and dense connective tissue almost indigestible in the digestive tract and they are texture-wise also

very unattractive. Also from a compositional point of view, meat is valued by many animals, as it is highly nutritive and tasty at the same time as it contains large amounts of amino acids and proteins, minerals, nucleotides and nucleic acids and sugars and their degradation products. In particular after roasting and searing, the complex mixture of reducing sugars, proteins and amino acids present in meat gives rise, *via* the Maillard reaction, to a wide range of aroma and taste compounds.^{92,93}

Most plants have also not evolved to serve as a food, and many plants have developed chemical deterrents to discourage animals from eating them. In addition, the cell wall of plants generally consists largely of cellulose which is indigestible by humans (but which may be hydrolysed by prolonged heating). It is therefore not a surprise that the first parts of plants to be eaten on a large-scale are seeds (nuts and grains), tubers and bulbs which contain high amounts of human-digestible starches. The original purpose of the starch in these plant parts was however not to stimulate the consumption by animals, but to allow the reproduction of the plant itself.

4.2 Food processing: top-down structuring

As we have already noted, processed food products are rarely at equilibrium and as such they retain memory of their process history.⁹⁴ One way to think about this is in terms of order–disorder transitions which can occur at particular length scales which are determined by ambient process conditions and material relaxation times. For example in the shearing of an emulsion the thermodynamics will drive the system to phase separate into lipophilic and hydrophilic phases, although the advective motion inherent in the shear will in turn break up the system into smaller droplets. The critical size of the droplets is generally determined (at least for the simplest cases) by the capillary number, which, although traditionally seen as the ratio between viscous and surface forces, could also be viewed as a ratio between a characteristic phase separation time which coarsens the droplets (related to the chemical potential and hence the surface tension) and a characteristic break up time driven by the local shearing in the fluid. A similar situation applies in the case of self-assembling amphiphilic systems where the size of the dispersed mesophase is determined by the ambient process conditions⁹⁵ (see also Section 2.1).

Consequently, almost identical recipes (that is to say materials which are in some sense close together in formulation space) can result in vastly different products based on their trajectories in process space. A good example of this phenomenon can be found in the vast variety of dough/bread products available, all of which are essentially variations on flour, water and yeast mixtures (*e.g.* Fig. 7). Paper, wood and cardboard are good non-food examples of the same kind of argument. The logical consequence of this essential process dependence is that the traditional chemical industry paradigm in which chemists develop products on a bench and then ask chemical engineers to scale them up to a factory is unlikely to be optimal for food production. Product and process development therefore need to be coupled at an early stage in order to assure success. Furthermore, as previously noted, food is generally even more complex than synthetic systems due to the presence of large residual biological structures in the feedstocks, such as plant cell

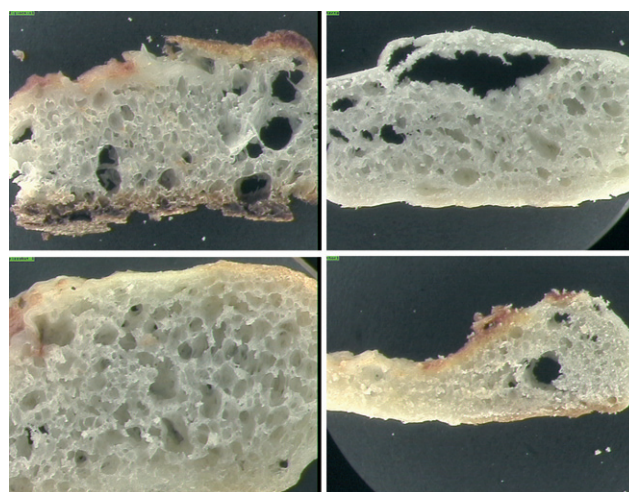


Fig. 7 Images of identically baked pizza bases showing the variation in structure that results from changing the mixing parameters at constant composition. Images courtesy of Roberto King.

fragments, milk fat globule membrane and animal tissue, which exist due to the living origin of the source ingredients. In the synthetic case, we can usually specify pure components, even if, for example, the polydispersity of polymer chain lengths is relatively uncontrolled.

All of this of course begs the question of what level of model/understanding do we require in order to really ‘engineer’ better processes and products by design rather than predominantly trail and error, black art and past experience? Although the answer to this is almost certainly context dependent, it is clear that we can build models of varying complexity depending on the design questions that we need to answer. In some cases one could imagine that a little physical insight and some dimensional analysis could be enough *e.g.* one could make an argument that the characteristic length scale of a phase separating mixture quenched into a glassy region of the phase diagram should be of the order of the square root of the product of the diffusivity and some characteristic time related to the quench rate purely on dimensional grounds. Since this, as we have noted previously, is a non-equilibrium process, we would expect that the governing dimensionless quantities be formed from combinations of transport (kinetic), rather than equilibrium properties. Of course, this is an enormous simplification, which neglects a lot of the subtlety inherent in the process, so in many cases we might expect that this estimate is hopelessly incorrect. Two alternative levels of description for the same problem are those of SCFT and molecular dynamics, both of which take into account the detailed description of the physical chemistry inherent in the problem. Of course, the ‘cost’ associated with these latter techniques is significantly greater than that of a scaling argument, but the return is also likely to be significantly more detailed information. Once again, the real skill is to pose the appropriate question. On a more concrete note, knowledge of the phase diagram of milk (Fig. 3) allows us to choose a process path (the dotted line) which minimizes the risk of lactose crystallization during the production of milk powder. Lactose crystals are undesirable in a milk powder, since they are poorly soluble and can lead to quality issues.

4.3 Self-assembly and mesoscopic processing

Self-assembly of food components at the mesoscale ($\sim 0\text{--}100\text{ nm}$) gives rise to many of the rare cases of food structures at equilibrium. Indeed, in this case, three important requirements for observing truly thermodynamically controlled structures are gathered together: (i) the short length scales allow local rearrangement of molecules *via* short mean displacements, (ii) the minimization of high free energy drives the system towards equilibrium with little effect of thermal and compositional fluctuations (which are damped by diffusion) (iii) typically short relaxation times allow reaching equilibrium configurations within observable time scales.⁹⁴

A typical case is that of lyotropic liquid crystals such as those based on water and monoglycerides. Various structures can be observed depending on the water/lipid weight ratio and the temperature, the most commonly observed being lamellar, reversed columnar hexagonal, reverse double gyroid (Ia3d), reverse double diamond (Pn3m) and reverse primitive (Im3m).¹⁹ The role of parameters influencing the specific curvature of the lipid water interface driving order–order and order–disorder phase transitions has been the object of intensive research studies during the past thirty years, and has been tackled by various topological, geometric, and thermodynamic approaches. Interestingly, different curvatures of the interface and topology of the liquid crystals impart very different rheological properties to these materials, and virtually the full viscoelastic spectrum can be covered: from purely plastic materials (lamellar), to viscoelastic fluids (reverse hexagonal) or very rigid structures (bicontinuous cubic), in which the storage moduli can reach $\sim 1 \times 10^6\text{ Pa}$.¹⁸

Consequently, the effect of guest molecules in either the hydrophilic or hydrophobic domains has profound consequences on the final viscoelastic properties, as order–order transition temperatures can be accurately adjusted.^{96,97} Ultimately, this can also affect the rates at which compounds may be released *via* water–lipid interfaces, when lyotropic liquid crystals are used as delivery vehicles for active compounds.⁹⁸

5 Physical approaches to controlling food functionality

5.1 Stability

Historically, one of the main objectives of food technology is the preservation and stabilization of foods. As the main factor influencing food stability is microbial spoilage, the main emphasis in the food preservation field has been on high temperature treatment of food, on dehydration and on osmotic stress. Of these approaches, the one based on food dehydration is of most relevance to us from the perspective of soft condensed matter physics, as the removal of water and the concomitant lowering of the water activity not only limits microbial growth, but also influences the physical state and the molecular mobility within the food matrix. For example, dehydration of a foodstuff may bring its amorphous constituents into a glassy state in which significant molecular reorganizations and molecular mobility are inhibited, and in which, next to an improved microbial stability, the physical stability of the product is enhanced.

Approaches towards food stability based on a control of the physical state of the food matrix or specific constituents of the

food matrix have seen major developments over the past decades. The increasing awareness of the relation between the phase diagram of a food product or constituent and the stability of the food product has led to a strong stimulus of soft condensed matter research in the food field. One important example is, as mentioned, the control of the physical state of an amorphous food matrix by tuning water activity (or water content) and storage temperature. By keeping amorphous food products in the glassy state, undesired effects such as crystallization of one or more of the food matrix constituents may be avoided (for instance the crystallization of lactose in milk powders).

Apart from for amorphous foodstuffs, phase diagram based analysis of the stability of food products is applied for food lipids and for surfactant-based systems such as microemulsions and liquid crystalline phases. The stability of a lipid-based food product such as chocolate is essentially determined by the thermal treatment applied to induce a certain crystal structure and shape. In addition, apart from conveying an acceptably high stability to chocolate, the state and structure of the lipid crystals also influences the sensory properties of chocolate. Similar stability-related issues with surfactant-based systems have been discussed above (see Section 2.1).

One highly interesting aspect of food stability is the relation between the physical state of a food system and the rate and mechanism of chemical reactions. A case of special importance for foods is the Maillard reaction,^{92,93} which shows an interesting dependence on the water content of the system.^{99,26} It is well established that the Maillard reaction in milk powders only proceeds at appreciable rates in the rubbery state,⁴⁷ which can be induced by water absorption or by temperature increases or by both. When in the rubbery state at fairly high water contents, the lactose which was originally in an amorphous state will crystallize into anhydrous lactose, forcing all water into the remaining amorphous lactose fraction, which thereby becomes further plasticized. This additional plasticization increases the molecular mobility in the amorphous matrix and thereby speeds up the rate of the Maillard reaction.⁴⁷

The physical state of the matrix is not only important for the Maillard reaction, but also influences various reactions such as oxidation (which is enhanced in the rubbery state because of the higher diffusivity of oxygen) and reactions between incompatible food matrix constituents. This however leads us into the field of encapsulation which we will discuss below (see Section 5.4).

5.2 Texture

What is texture? A generally accepted working definition is that ‘texture is the sensory and functional manifestation of the structural, mechanical and surface properties of foods detected through the senses of vision, hearing, touch and kinesthetics’.¹⁰⁰ This actually has some quite important implications, since it is immediately clear that a material has no inherent texture, despite apparently endless attempts in the literature to measure so called sensory–instrumental correlations. Surprisingly, these studies are often quite successful in relating things like viscosity and density to ‘smoothness’ and ‘thickness’ for example^{101,102} (and thus have a role), although this is not always the case, particularly for complex materials. An alternative approach to the problem is to try and imagine the human instrument and analyze the sensitivity

of sensory structures found in the mouth. Some recent studies have attempted this and suggest that often the brain's interpretation of texture is a complex multi-modal synthesis of all available data.¹⁰³ Physical data available on the human sensory system is quite patchy, but there is a lot of physiological data of variable quality in the medical literature.^{104–109} This approach seems promising as a means of reverse-engineering food structure for desired sensory effect, although it is currently in its infancy. One thing that is abundantly clear is that measuring effective bulk properties of food matrices (*e.g.* viscosity or another continuum rheological function) is not enough and that many of the more interesting textural attributes can be attributed to inhomogeneity (as expected given the enormous variety in differently structured foods available). In the future we will need to better understand how to characterize these inhomogeneous structural elements and relate their characteristics to effects.

5.3 Appearance

Consumer acceptance, or ideally preference, is driven by all of the sensory data available to the brain, and as such visual properties of a food product cannot be neglected. These effects can be either macroscopic or microscopic manifestations of the material structure. In the former case, the structural elements of the material are directly observable *e.g.* bubbles in bread, whereas, in the latter, only their ensemble statistical effects are manifest to the consumer *e.g.* fat droplets in milk. In both cases these are strong preference drivers which need to be controlled. In the macroscopic case, all of the bubbles will probably need to be controlled to lie within a reasonably narrow range or the product is likely to be perceived as defective, for instance a large cavity in an aerated chocolate bar. In the latter case, only the ensemble properties of the size distribution need to be maintained, and large deviations of the size of individual elements are acceptable. For example, fat droplets in milk determine the optical properties of the milk by multiple light scattering, which is unaffected by single large or small droplets (unless the droplet is large enough that it is macroscopically visible), although skimmed and semi-skimmed milk tend to exhibit a blue tinge when compared with full cream milk. Colloid science provides us with a toolkit to engineer these responses.

5.4 Encapsulation, stabilization and release of micronutrients

The creation of novel functionalities of active ingredients in complex food matrices is of major importance for the food industry. One important motivation for this development is the continuous demand for food products which satisfy ever-increasing consumer requirements for the appeal, organoleptic performance and convenience of a food product and thus require for instance better and more natural flavor release. Another motivation is the current emphasis on the nutritional value of foods and the corresponding interest in introducing bioactive ingredients in foods.

It is usually not straightforward to introduce active ingredients into foods, because of an incompatibility between the active ingredient and the food matrix, or because of the often severe conditions during food processing. Active ingredients are often sensitive compounds which are difficult to maintain in

a functional form in a food system. This sensitivity may be of a physical or chemical nature.¹¹⁰ Physical factors influencing the functionality of active ingredients are volatility, in the case of flavor compounds, which may lead to premature release from the food matrix, and, in the case of bioactive compounds, transitions between various polymorphs which influence the bioavailability. Many active ingredients in foods are also chemically sensitive. Because of chemical reactions, such as oxidation by atmospheric oxygen, or because of chemical reactions between the active ingredient and the food matrix, the active ingredient degrades, either during food processing or during the shelf life of the food product.

Delivery systems are increasingly employed to facilitate the introduction of active ingredients in foods.¹¹⁰ Following their functionality in a food matrix, such systems are conveniently known as encapsulation systems (protection of the active ingredient) or controlled release systems (modulation of the bioavailability or release of the active ingredient). Given the large variety of active ingredients, and the variability of conditions in the food system, a significant range of delivery systems has been developed.¹¹⁰ Food-grade materials which are used in delivery systems include glassy carbohydrates,¹¹⁰ lipids,¹¹¹ biopolymer complexes¹¹² and surfactants.⁹⁸

Although the expectations for the use of delivery systems in food are very high, this is not always born out in practice.¹¹⁰ One reason is the intrinsic complexity of the situation, with numerous factors often playing in opposite directions. For instance, flavor compounds need to be easily released during the consumption of a food product, as otherwise they are not perceived and are thus effectively lost. However, they should not escape the same food matrix before consumption. Another, probably even more important, reason is that whereas the development of encapsulation and delivery systems has received extensive scientific and technological attention, much less attention has been devoted to the study of the interaction of active ingredients and the delivery systems and even less systematic and scientific knowledge is available on the performance of delivery systems in actual food applications.¹¹⁰ Consequently, significantly more effort should in the future be spent on improving the understanding of the factors governing the functionality of the combination food—bioactive ingredient—delivery systems than on the (isolated) development of delivery systems.

6 Perspectives

We conclude with a few observations regarding the future of soft condensed matter research in the food field.

Advanced techniques for the analysis of structure and dynamics of condensed matter are still becoming better and, in addition, more adapted to the analysis of complex systems such as foods. This will generate an enormous amount of raw data on which to draw conclusions. As we have demonstrated in this paper, foods are natural materials which possess an enormous amount of complexity from both a physical, chemical and structural perspective, and as such it will become increasingly easy to get lost in the mass of available data. Consequently, theories and models are needed to help organize and interpret the available information on the structure and dynamics of foods and food materials. This encompasses both statistical mechanical

theories, non-equilibrium thermodynamics, and bioinformatics. Undoubtedly the rapidly increasing computational power will allow us to calculate, simulate or search in a faster and more effective manner, but we believe that asking the correct question and designing an elegant experiment to answer it will become critical if further progress is to be made.

What will be the consumer drivers of the future that will drive the evolution of the food industry? Current wisdom suggests that consumers want to have natural food which is low in fat, sugar and salt, but which still tastes good, is convenient to prepare and has an unlimited shelf life! It is not difficult to see that there are considerable challenges ahead if we are to engineer these products. It is however dangerous to extrapolate current trends to the future: perhaps the future consumer will return to more traditional foods, albeit of significantly enlarged variety and available in a range of qualities including the very best. The best guess for the moment is that various consumption styles will be present at the same time.

The days of food science as a research field with a limited appeal beyond the domain of industrially prepared foods is drawing to a close. The past years have seen the science of food emerge as a multidisciplinary research area, with some challenging problems to solve for physicists, chemists, engineers, biologists, physiologists and psychologists, and with an increasing impact on society.

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