

Understanding foods as soft materials

Foods make up some of the most complex examples of soft condensed matter (SCM) with which we interact daily. Their complexity arises from several factors: the intricacy of components, the different aggregation states in which foods are encountered, and the multitude of relevant characteristic time and length scales. Because foodstuffs are governed by the rules of SCM physics but with all the complications related to real systems, the experimental and theoretical approaches of SCM physics have deepened our comprehension of their nature and behaviour, but many questions remain. In this review we discuss the current understanding of food science, by considering established SCM methods as well as emerging techniques and theoretical approaches. With their complexity, heterogeneity and multitude of states, foods provide SCM physics with a challenge of remarkable importance.

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When targeting the physics of foods, the intrinsic complexity of the topic represents a challenging problem. One has to capture sufficient detail of the material food components whilst using theoretical tools or experimental methods that are not always entirely adapted to the complexity of these systems. Consequently, food science has been evolving in line with the progress being made in other branches of soft condensed matter (SCM) physics, triggered by a continuously improving insight into the nature of biomaterials and by the development of new experimental techniques¹.

A first great difficulty when dealing with processed foods is that the various components of the food are generally not found in their natural environment and conditions, but in a state far from equilibrium. As a consequence, on external perturbation, such as changes in pH or temperature, the structure of a food will tend to revert towards the equilibrium configuration. An additional degree of complexity is added by the fact that foods structured at different typical length scales normally follow very different kinetics to attain their equilibrium configuration. If correlation length scales are small, very short times are needed to re-organize

molecules to attain equilibrium, whereas if correlation length scales are large, very slow kinetics will be followed. This explains why, to name two extreme cases, foams, where length scales reach the order of millimetres, can be stable for long times despite the high internal energy associated with the presence of very large interfaces, whereas self-assembled liquid crystalline foods, whose typical feature size is a few nanometres, are almost always observed at the equilibrium. Looking at food components at different typical characteristic sizes will also reveal the molecular complexity of these materials. At the smallest feature size, water, the most commonly used solvent in foods, is far more complex than other organic solvents, as it can be viewed as a structured solvent. The presence of hydrogen bonds in water leads to unique aspects, such as the clustering and correlation of molecules at short length scales, which are lost at larger scales², or their ability to hydrate molecules or polymers with hydrogen-bond-accepting sites³. In terms of the solution thermodynamics, these effects greatly decrease the translational entropy of water compared with solvents of comparable molecular size.

At larger length scales, surfactants such as monoglycerides and phospholipids are common molecules in foods because they are used to stabilize interfaces. They can be charged or neutral, but in both cases the enthalpy of mixing of their hydrophilic and the hydrophobic parts is very high, which confers on them their typical amphiphilic nature.

At even larger length scales, two main classes of macromolecules are found: polysaccharides and proteins. Polysaccharides are to foods what polymers are to SCM. They can be neutral or charged, linear or branched. Their molecular mass distribution can be either narrow or broad, but will always differ

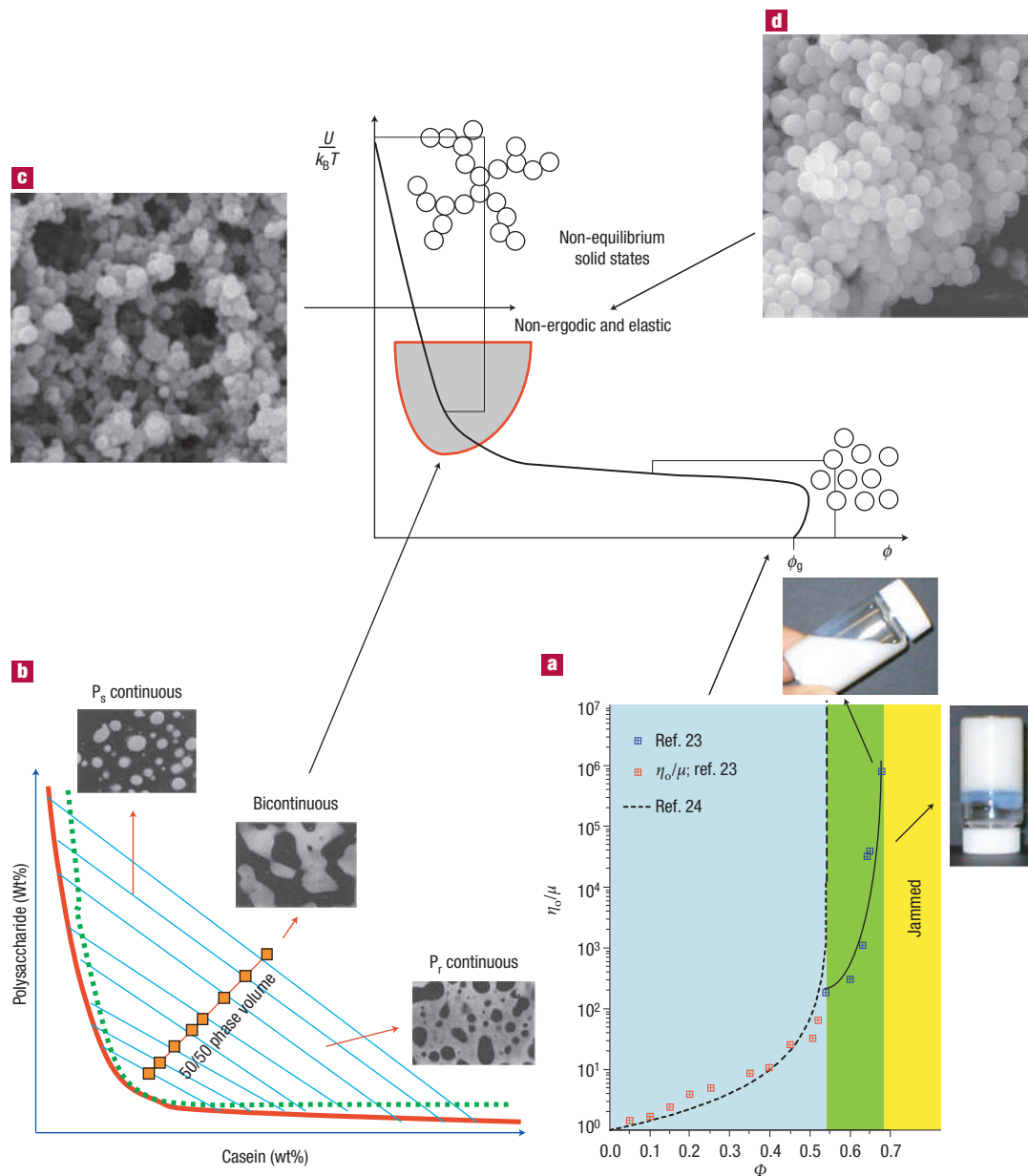


Figure 1 Schematic state diagram of colloidal particles with short-range potentials. (Redrawn after ref. 11, copyright (2004) with permission from Elsevier.) In the main diagram (centre), the solid line of the energy/composition diagram represents the boundary for the formation of disordered solids, the ‘gel’ or ‘glass’ line. At low volume fractions and large interaction potentials U , locally fractal gels are formed, whereas at large volume fractions and low interaction potentials glasses are formed. At intermediate volume fractions and strength of the attraction a coexistence curve is found for a viscoelastic phase separation, where the intersection with the ‘gel line’ leads to the formation of a transient gel¹⁹. Also shown are three different examples from food systems whose properties can directly be linked to this state diagram. **a**, Casein micelles as hard spheres: low shear viscosity, η_0 , normalized by the viscosity of the background, μ , as a function of volume fraction ϕ , for milk-powder suspensions. The dashed line corresponds to the behaviour found for hard-sphere systems^{24,106}, the full line is a guide to the eye indicating the divergence of the viscosity and the transition to a completely arrested state. The pictures show a sample below and above the jamming transition. **b**, Viscoelastic phase separation in mixtures of Xanthan and casein micelles. This is a schematic phase diagram for a colloid–polymer mixture such as casein micelles and Xanthan. The three micrographs from confocal microscopy show the different ways in which phase separation can occur through spinodal decomposition in casein–Xanthan mixtures: formation of either casein- or Xanthan-rich droplets or bicontinuous structures²⁷. **c**, **d**, The third example shows two types of gel formation: the two scanning electron micrographs illustrate the close analogy between the structure of dense colloid gels (**d**, SiO_2 particles, courtesy H. Wyss, see ref. 35 for details) used in sol–gel ceramics production and casein particle gels produced in yoghurt formation (**c**).

substantially from synthetic polymers. Proteins are certainly the most complex macromolecule encountered in foods. This complexity is evident in their secondary structure, which is intrinsically related

to the sequence of amino acids along the backbone. As a consequence, various proteins with different amino-acid sequences will also differ in structure, and thus in their physical properties.

The field of food science is enriched by the range of different aggregation states in which foods are encountered. Although beverages can be viewed as dilute solutions, the great majority of viscous liquid foods are emulsions. Milk, yoghurts and sauces are typical examples of low-volume-fraction emulsions. Butter and margarine are high-volume-fraction emulsions, where the dispersed phase occupies most of the space. Foams are the air-liquid analogue of emulsions, and constitute another big category of foods. Finally, foods can be found in highly viscoelastic forms or even in glassy states. Liquid crystals based on lipids and water are important examples of highly viscoelastic foods where either phase can be loaded with a specific aroma, flavour or active ingredient, whilst preserving the overall rheological properties. Because the structure controls, to varying degrees, the taste, perception and physical properties as well as the dynamics by which different phases of heterogeneous foods are modified and interact with the body, these have to be finely controlled when designing complex heterogeneous products. In what follows we use the perspective of SCM physics to discuss some of the key structural elements found in foods and to highlight the associated scientific challenges.

FROM MODEL COLLOIDS TO COMPLEX FOOD SYSTEMS

Food science and technology have started to profit enormously from parallel developments made in SCM, materials science and nanotechnology. Particularly important recent progress in SCM research is linked to questions of interparticle interactions, particle stability, phase separation, gel and glass formation and the quest for new experimental tools that allow characterization of complex fluids and soft solids over a very large range of length and timescales^{4–6}. These issues are of central relevance for food science and technology. Analogies and differences between the resulting phase diagrams of colloidal suspensions and atomic and molecular systems have already considerably improved our understanding of food materials.

However, colloidal systems often become undercooled, supersaturated or trapped in gel-like states, so the investigation of non-equilibrium properties of soft matter is important for food sciences. Particular attention has recently been given to fluid–solid transitions such as ‘dynamical arrest’, ‘jamming’ or ‘gelation’ frequently encountered in colloidal suspensions^{7–11}. Arrested states of soft matter are often valuable in food research, where yoghurt or cheese manufacture are the food scientist’s analogue of sol–gel processing in modern ceramics formation¹². On the other hand, uncontrolled or unexpected dynamical arrest can have disastrous consequences for materials or food processing.

The presence of solid-like structures such as particle gels or colloidal glasses has been found under conditions where either repulsive or attractive interactions dominate. In the central part of Fig. 1, we summarize the current state of understanding of dynamical arrest as a function of the strength of the attractive part of the interparticle interaction potential¹¹. For ideal hard-sphere particles, we observe a transition from a liquid to a disordered solid phase

— a glass — at volume fractions of about $\Phi \approx 0.58$ (ref. 13). If a weak and short-ranged attraction is now turned on, this leads to the astonishing observation of a melting of the glass, followed by a ‘re-entrant’ glass or solid formation at even stronger attractions^{7,8,14}.

For colloidal suspensions, such an attraction can, for example, be induced through depletion mechanisms. If a small entity such as a non-adsorbing polymer is added to an otherwise stable suspension of large colloids, the centre of mass of the small species cannot exist within a shell around the colloid. This leads to a gain in the free volume available to the polymer when the colloids approach each other such that their excluded volumes overlap. A net osmotic force is exerted on the large particles and thus there is an effective attraction whose range and strength can be tuned by means of the size and concentration of the added polymer¹⁵.

In the other extreme case of very strong interparticle attraction, we reach the regime of ‘irreversible aggregation’ where one observes the formation of soft fractal gels at very low volume fractions^{16,17}. The analogy between colloidal glasses at high densities and colloidal gels at low volume fractions has stimulated considerable effort into exploring new ways to characterize, understand and use amorphous solid-like soft matter systems¹¹. But we are still far from having developed a general theoretical framework that is capable of unifying the entire range of concentrations and type of interactions that have been investigated.

At intermediate-strength attraction, the situation is even more complicated because phase separation into a dilute (gas-like) and a concentrated (liquid-like) suspension can occur⁵. The position of the corresponding coexistence curve can then intersect with the arrest or gel line, and the phase separation can subsequently lead to the formation of a long-lived ‘interaction network’ (a transient gel) of particles, if the attractive interactions between them are strong enough. The significance of this viscoelastic phase separation in pattern formation in nature and its engineering applications has been pointed out in the past¹⁸.

The resulting schematic state diagram is, however, not only relevant for colloidal model systems, but can now be used to rationalize the behaviour of food systems and provide guidelines for creating tailored food structures and materials. This is illustrated with three examples in Fig. 1. Food colloids such as casein micelles closely follow theoretical descriptions originally developed for colloidal model systems^{19–22}. The analogy between the state diagram for model hard spheres and the behaviour of casein micelles is demonstrated in Fig. 1a, where the zero-shear viscosity, η_0 , normalized by the solvent viscosity, μ , is shown as a function of the volume fraction of casein hard spheres for aqueous suspensions of a milk powder²³. The concentration dependence of η_0 is indeed reminiscent of hard-sphere systems^{13,24}. However, this resemblance only holds over a limited range of concentrations; above some critical concentration we find strong deviations from the hard-sphere behaviour. The viscosity continues to increase and diverges at a concentration significantly larger than the one expected for hard spheres. This behaviour in fact closely resembles

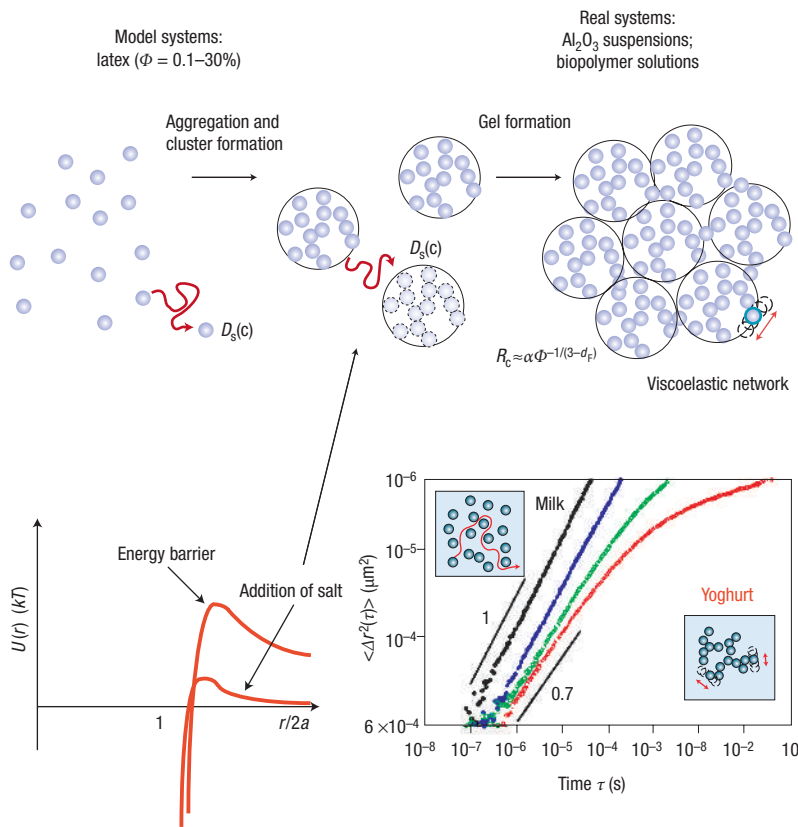


Figure 2 The sol–gel transition, from model systems to yoghurt and ceramics. The figure shows aggregation, formation of large primary clusters with fractal dimension d_f and subsequent secondary aggregation to build a space-filling cluster gel at a critical cluster radius R_c , on salt-induced destabilization of a charge-stabilized particle suspension. Also shown are the subsequent changes in the particle dynamics, characterized by the self-diffusion coefficient $D_s(c)$ from the fast brownian motion of the initial monomers, to cluster diffusion and to locally constrained motion of the individual particles connected to the gel. The reduction of the stabilizing energy barrier in the interaction potential between charge-stabilized colloidal particles on the addition of salt is shown in the lower left corner, where the interaction potential is plotted as a function of the interparticle distance r normalized by the particle diameter $2a$ (for details see ref. 17). This evolution of the local particle dynamics is also demonstrated (inset, lower right) for casein aggregation in the yoghurt formation process as monitored by *in situ* diffusing wave spectroscopy (see Box 1). We see that the average mean square displacement (MSD) $\langle \Delta r^2(\tau) \rangle$ initially shows a linear time dependence typical for classical brownian motion of particles and clusters (black and blue points). After the sol–gel transition this abruptly changes to a stretched exponential and a clear plateau at long times characteristic for the constrained subdiffusive motion of colloids attached to a (locally fractal) particle gel (green and orange points)^{12,32–34,44}.

that found for another class of model colloids, the ‘microgels’, which are soft spherical colloids formed by weakly crosslinked polymers²⁵. We even observe the formation of a jammed state with solid-like properties, a phenomenon of considerable potential importance in the processing of foods. It is clear that the colloid analogy has its limits because of the complex internal subunit structure of casein micelles which may lead to rearrangement and fragmentation under certain conditions, but it provides important guidelines on how the properties of complex food systems can often be analysed (and predicted).

The second example in Fig. 1b illustrates the existence and importance of polymer-induced depletion interactions and the subsequent viscoelastic

phase separation in foods. Most food systems are of complex colloidal and polymeric nature, making their investigation even more difficult. But as we have already seen, in fundamental SCM research it is common knowledge that the addition of a non-adsorbing polymer to a dispersion of colloidal particles induces an effective attraction between the particles^{5,15,26}. Analogous behaviour can thus be expected for food systems, where the balance between different repulsive interparticle interactions and the depletion-induced attraction will determine their long-term stability. This is illustrated with the schematic phase diagram for a colloid–polymer mixture such as casein micelles and Xanthan shown in Fig. 1b. The three micrographs show the different phase-separation scenarios that can be observed in casein–Xanthan mixtures, where phase separation proceeds through spinodal decomposition and we observe the initial formation of either casein- or Xanthan-rich droplets or bicontinuous structures²⁷. At sufficiently high Xanthan and casein concentration this can indeed lead to the formation of an arrested network. Depletion-induced phase separation and gelation thus represent additional complications, but also another opportunity for controlling the stability, microstructure and mechanical properties of food systems.

AGGREGATION AND GEL FORMATION

The third example in Fig. 1 (micrographs c and d) leads us to another area in which fundamental soft matter science has recently produced important findings that are highly relevant to food materials: the influence of attractive interactions on aggregation and gel formation in colloidal systems^{16,17,28–34}. The examples in Fig. 1c and d aim at demonstrating the link between casein aggregation and gelation (used for example in yoghurt or cheese manufacture) and irreversible aggregation through diffusion or reaction-limited cluster–cluster aggregation, which has been intensively investigated in basic colloid research and heavily used in modern ceramics processing^{12,28,35}. The two scanning electron micrographs shown in Fig. 1c and d illustrate the close analogy between the structure of dense colloid gels used in sol–gel ceramics production and casein particle gels produced in yoghurt formation.

More generally speaking, food gels are essential in many technological applications, and are a useful way to modulate texture and sensory perception of foods starting from very dilute solutions. They consist mostly of water with the solid character being provided by a biopolymer-based space-filling network (proteins, polysaccharides) or particles (for example, casein micelles) and mixtures thereof. Various processing routes such as control of ionic strength, change in pH, heating and the use of enzymes are used to produce food gels with desirable mechanical properties. Numerous attempts have been made to profit from the considerable progress made in fundamental soft matter science, and analogies to either polymeric or colloidal gels have commonly been drawn.

Our understanding of biopolymer-based food gels has profited enormously from the analogies drawn

to classical polymer sciences³⁶ combined with the use of new optical techniques that allow non-invasive and time-resolved investigations of complex, soft and fragile food gels^{37,38}. An overview on some recent developments in the characterization of complex colloid and polymer systems with considerable potential in foods is given in Box 1. Here we focus on particle gels, where close analogies have been drawn with irreversible aggregation and gelation in fundamental SCM research. The route towards nanostructured and locally fractal gels is schematically shown in Fig. 2: the addition of salt reduces the stabilizing energy barrier in the interaction potential between charge-stabilized colloidal particles. This salt-induced destabilization leads to aggregation, the formation of large fractal clusters, where the fractal dimension d_f is a measure of the compactness of the individual cluster¹⁶, and finally to the formation of a space-filling cluster gel with solid-like properties¹¹. The aggregation and gelation are also reflected in the particle dynamics, characterized by the particle self-diffusion coefficient D_s . These change from initial fast brownian motion, which slows down because of aggregation and cluster growth, to a locally constrained motion of individual particles incorporated into the gel¹⁷.

An important technological challenge in materials sciences and food technology is to optimize the mechanical properties by controlling interparticle interactions from net repulsive (stable) to net attractive (unstable)^{28–31}. Considerable efforts have been made to obtain a detailed understanding of the relation between microscopic and macroscopic properties. For gels formed at low particle concentrations this has been successfully accomplished using fractal concepts³². But it is only recently that attempts have been made to understand aggregation and gelation at high particle concentrations and under conditions relevant for food systems^{12,17,29,33,34,37,39}. The progress is due to the availability of new experimental methods such as diffusing wave spectroscopy (DWS; for details see Box 1), and the use of much more refined computer simulations that include reversibility and restructuring events. Nevertheless, understanding the relationships between interparticle forces, structure and rheology of particle gels remains a difficult problem²⁹.

Gel formation in milk represents an essential step in the manufacture of various dairy products. In unheated milk at its natural pH (pH 6.7), dispersed casein micelles are stabilized by a 'hairy' layer of κ -casein molecules that acts like a polyelectrolyte brush on synthetic colloidal particles. They can subsequently be destabilized by slow acidification through lactic acid bacteria (for example, yoghurt), by enzymatic action of chymosin (cheese), or by combinations thereof (for example, quark; significant acidification and minor enzymatic action). Once destabilized, the casein particles start to aggregate and finally form a three-dimensional network entrapping the serum phase^{12,19–22}.

Over the past 15 years, acid-induced gel formation in milk has attracted growing interest from research groups all over the world. Methods such as oscillatory rheometry^{40–43}, DWS^{12,44–49} and

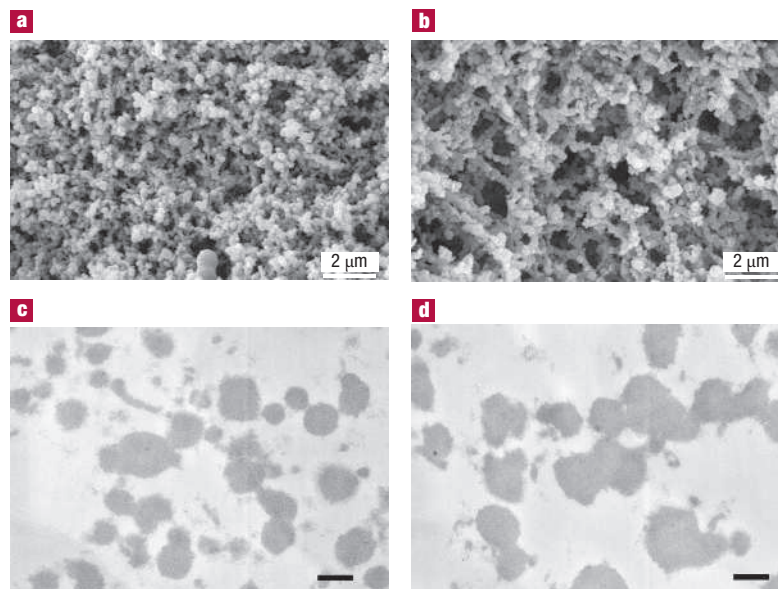


Figure 3 Gel network structure obtained by SEM (a, b) and TEM (c, d) of gels fermented with *Streptococcus thermophilus* under different conditions. a, c, Fermentation at 30 °C without chymosin representing slow acidification, and b, d, 40 °C with chymosin representing a fast acidification. In the purely acid-induced gel the casein micelles tend to form filament-shaped aggregates (a, c), whereas in the case of the combined acid- and chymosin-induced gel (b, d), the micelles tend to arrange themselves into more compact aggregates allowing the formation of junctions with several neighbouring micelles. The structure indicates that the faster the colloidal dispersion of casein micelles is destabilized, the coarser is the resulting gel network. In c and d, scale bars represent 0.2 μm ; reprinted from ref. 107, copyright (2003) with permission from Elsevier.

ultrasonic spectroscopy^{45,50,51} have been used to investigate various aspects of the dynamics of gel formation. Protein network microstructure in acid milk gels has also been investigated over a range of length scales by transmission and scanning electron microscopy (TEM, SEM)⁵² and confocal laser scanning microscopy (CLSM)^{41,43,49,53}. Examples are given in Fig. 3 and illustrate once again the close analogy between food particle gels and those obtained in sol-gel ceramics processing. Microscopic analysis has also been carried out to visualize structural organization during the process of gel formation, on the length scales both of casein particles (TEM)^{54,55} and of the network (CLSM)⁵⁶.

Despite recent progress, we still seem to be far from a full understanding of the mechanisms and kinetics of acid milk gelation. Although theoretical approaches such as the adhesive sphere, percolation or fractal model applied to acid-induced gel formation in milk may successfully explain specific aspects of the process, none of these can rationalize its kinetics⁵⁷. The challenge for future research lies in developing a theory that links particle interactions, internal micellar changes, structure formation (particle aggregation and network assembly) and rheological properties into a model that explains the kinetics of gel formation and the physical properties of the resulting gels, including the effects of processing parameters such as temperature and acidification kinetics.

Box 1 New light scattering techniques for turbid suspensions

Dynamic light scattering (DLS) or photon correlation spectroscopy (PCS) is one of the most popular experimental techniques in the investigation of colloidal suspensions, and it has played an important role in recent developments where it has helped to gain invaluable data on the dynamic properties of colloidal systems (Fig. B1a). However, its application to many systems of industrial relevance has often been considered to be too complicated because of the very strong multiple scattering in undiluted solutions. There are two recent solutions to this problem, which have now also started to play a major role in the characterization of complex food systems³⁷.

A very interesting approach aims at efficiently suppressing contributions from multiple scattering from the measured photon correlation data. The general idea is to isolate singly scattered light by performing two scattering experiments simultaneously on the same scattering volume and to cross-correlate the signals obtained¹¹⁰. A particularly interesting scheme is the ‘3D cross-correlation’ experiment (3D-DLS) schematically shown in Fig. B1b. Several research groups^{110,111} have demonstrated the feasibility of such an experiment and clearly shown that dynamic light scattering need not be restricted to dilute suspensions of small particles, but that it can be used successfully to characterize extremely turbid soft matter such as undiluted skim milk or turbid heat-set protein gels^{112,113}.

A second approach, known as diffusing wave spectroscopy (DWS), is based on a completely different principle. Whereas DLS relies on the suppression of multiple scattering, DWS works in the limit of very strong multiple scattering, where a diffusion model can be used to describe the propagation of light across the sample (see Fig. B1c for a schematic description)^{114,115}. It is thus still possible to study the dynamics of a colloidal suspension by measuring the intensity fluctuations of the diffusing light observed either in transmission or backscattering geometry. Although DWS does not yield explicit information on angular dependence of the scattered intensity and thus on particle size, shape and polydispersity, it is capable of providing unique information on particle motion such as the time dependence of the particle mean-square displacement on very short time and length scales.

A particularly interesting application of DLS or DWS in fundamental soft matter research as well as in food science and technology has been ‘optical microrheology’^{37,116}. The underlying idea is to study the thermal response of small (colloidal) particles embedded in the system under study. By analysing the thermal motion of the particle it is possible to obtain quantitative information about the loss and storage moduli, $G'(\omega)$ and $G''(\omega)$, over an extended range of frequencies^{37,117}. As DWS allows access to a broad range of timescales, this results in an unprecedented large frequency range covered by DWS-based optical microrheology (Fig. B1d).

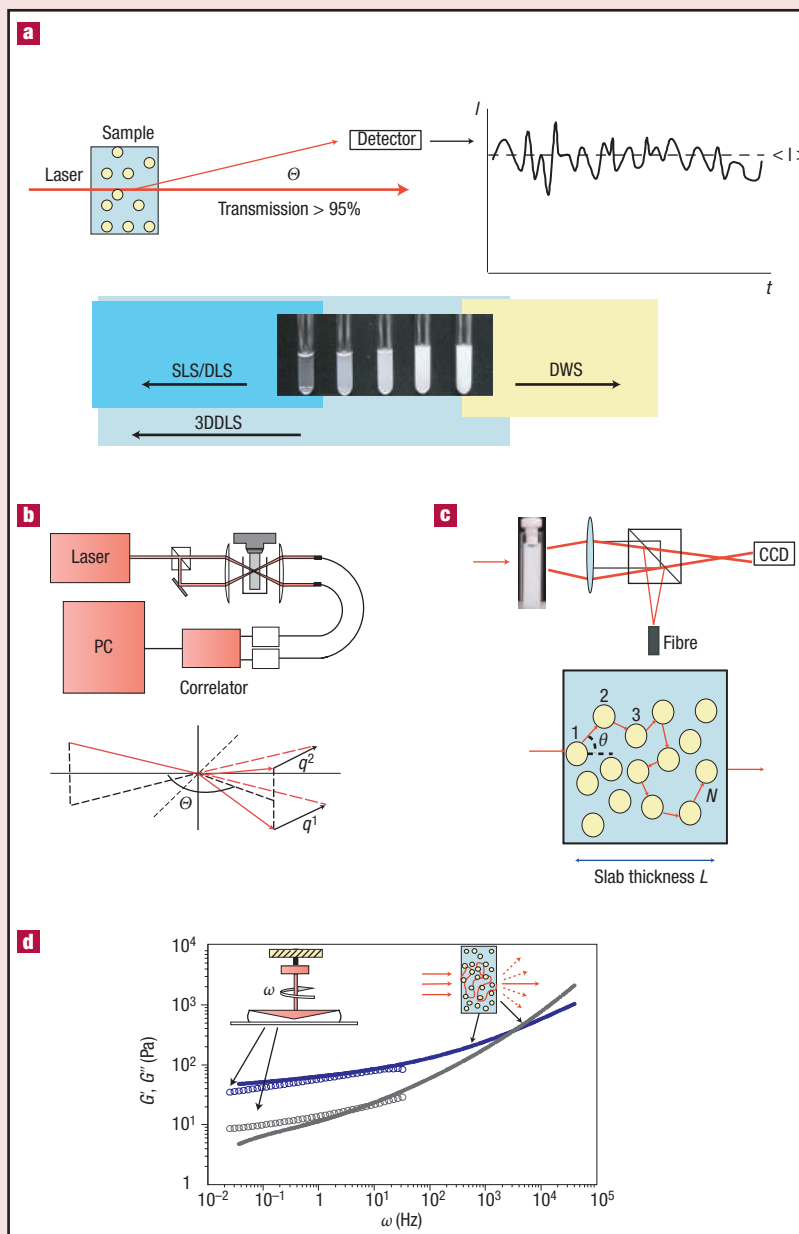


Figure B1 Range of applicability of classical DLS, 3D-DLS and DWS. **a**, Schematic representation of a standard SLS/DLS experiment in the single scattering limit and the temporal fluctuations caused by the brownian motion of the colloidal particles that are analysed in a DLS experiment³⁷. **b**, A 3D-DLS experiment, showing how the 3D arrangement of the two individual scattering experiments that are then cross-correlated results in exactly the same scattering vector q (refs 37,111,112). **c**, Schematic view of a DWS experiment in transmission, where a single mode fibre detection system and a charge-coupled device (CCD) camera are combined to yield a very broad range of accessible timescales, and a description of the succession of scattering events resulting in a diffusive transport of light in a turbid sample^{37,114–116}. **d**, The result of a DWS-based optical microrheology experiment with a casein gel obtained with acidified skim milk, and a comparison with a classical rheological measurement using a standard rheometer with the sample^{12,44}.

FOAMS AND BUBBLY LIQUIDS

Foams are metastable inclusions of gas in a fluid phase which are ubiquitous in foods owing to their ability to generate a sensation of lightness and creaminess, both of which are powerful drivers of preference. Some typical examples of food foams are cappuccino, beer 'head', ice cream, dessert mousses, bread, cakes, wafers and whipped cream. At present, the exact sensory stimuli responsible for this perception remain unclear, although there is general agreement that the origin is probably largely rheological. The metastability is from at least two perspectives. First, draining is caused by the large density difference between the internal gas and continuous fluid phase and results in creaming phenomena similar to, but much faster than, that observed in emulsions such as milk. Second, Ostwald ripening or disproportionation is the dynamic change in bubble size distribution caused by the Laplace pressures of the bubbles and modulated by the gas solubility in the continuous phase. Because the Laplace pressure is inversely proportional to the bubble radius, the large bubbles grow at the expense of the small ones, which will eventually disappear. Experiments on disproportionation kinetics have recently been carried out⁵⁸. Figure 4 illustrates Ostwald ripening through a sequence of optical micrographs.

As a consequence of metastability, foams used in food products require stabilization, which is broadly achieved by tailoring either the bulk or interfacial rheology. Often we need to have a foam stabilized at relatively low volume fraction in something like a chocolate mousse, in which case the matrix is usually gelled by hydrocolloids in the continuous phase. Assuming that the matrix is then 'solid', the material is stable for as long as desired. Frequently, the change of matrix state is achieved by temperature swing, an extreme case of this being ice cream, in which the matrix is actually frozen. The second approach to stabilization is to use a surfactant, which may be either short-chain or a longer polymer such as a protein. Generally, short-chain surfactants are added to reduce the surface tension of bubbles, which in turn increases the capillary number. It then becomes easier to entrain gas into a fluid, making initial manufacture easier. In the long term, a short-chain surfactant has a negligible effect on drainage, but reduces the Laplace pressure and hence the theoretical rate of Ostwald ripening. Effects with respect to coalescence are less clear, although it is likely that Marangoni stresses, which are caused by gradients in surfactant concentration, couple to the local hydrodynamics to reduce the rate of bubble 'collisions' and presumably the rate of coalescence. These kinds of issues are more relevant to beverage foams, which are generally dry foams (called so when bubbles are no longer spherical), although in practice proteins usually play an important role (for example the 'head' on a pint of beer).

An important consequence of the metastability of foams is that they are, by definition, far from their equilibrium state and so their 'stability' is a poorly defined concept. In most cases 'stability' loosely refers to the rate of the coarsening of the bubble size distribution, or in some cases the lifetime of the foam volume. Both of these are kinetic and not

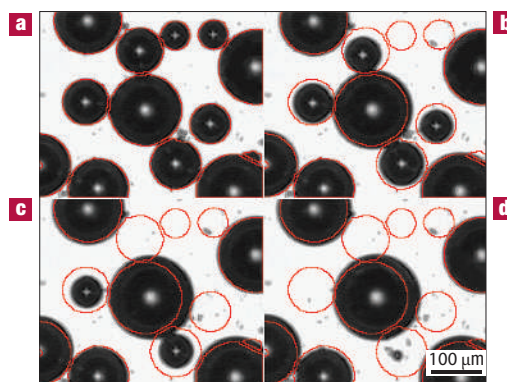


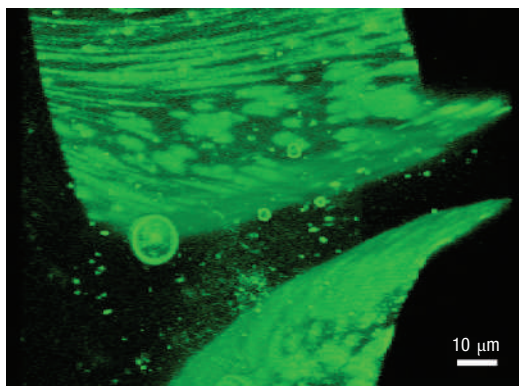
Figure 4 Time-lapse sequence (extracted from a video) illustrating Ostwald ripening. Bubble circumferences are drawn in red **a**, at the beginning of the experiment, and **b-d**, after 25, 50 and 75 minutes, respectively, showing the progressive loss of small bubbles due to gas diffusion towards big bubbles which progressively enlarge. Courtesy of G. Mayor.

thermodynamically determined quantities and as such can be considered as structural relaxation times. Clearly, the larger a structural entity becomes, the less it is likely to be controlled by local molecular-scale details and more by the far-field, mean-field or coarse-grained interactions. Nonetheless, throughout food technology, the effects of processing on the creation and stability of the foam structure have been systematically underestimated in favour of formulation science. Perhaps one reason for this is that it is extremely difficult to measure the dynamics of bubble size distributions in a dynamic and non-invasive manner. Optical methods are generally difficult owing to the inherent multiple scattering of visible light, but conductive and ultrasonic tomographic techniques can give an indirect indication of bubble size, whereas other techniques are becoming available to study 'wet' foams⁵⁹. Another problem specific to foams and bubbly liquid foods is the difficulty in finding short-chain food-grade surfactants⁶⁰. In fact very few exist other than non-ionic mono-glycerols and tweens (polyoxyethylene sorbitan mono-oleate), and 'zwitterionic' (simultaneously positively and negatively charged) phospholipids. Presumably this is because surfactants tend to have detrimental effects on cell membranes, and as a consequence most natural foods, and indeed biological structures, are stabilized by other means such as proteins. Proteins are interesting surface-active macromolecules, which exist naturally in either globular (tightly structured and particle-like, for example β -lactoglobulin) or near-random coil (β -casein) configurations. Because proteins have both hydrophilic and hydrophobic regions they can be thought of as long-chain, multiblock copolymers, although the folded structures are intricate and complex. This structuring endows proteins with a complex behaviour at an interface, because the protein conformation changes after adsorption⁶¹. In turn the stepwise unfolding of the structure creates an extremely large activation energy for the desorption process, which makes protein adsorption appear to be an irreversible process. As a result of this unfolding it is possible to create multilayer protein membranes, which act as extremely effective structural stabilizers, mostly by means of viscoelasticity⁶².

Interfacial rheometry of protein layers is a fairly new science, owing to the complexity of instrument design and the inherent bulk hydrodynamic coupling with the interface. Illustrative work in this area

Figure 5 Three-dimensional reconstruction of foam interface consisting of biopolymers using confocal microscopy.

Clearly the interface is not homogeneously covered with proteins (labelled with a green fluorescent dye). The protein distribution is believed to be strongly influenced by the hydrodynamics of the continuous phase during the bubble formation. This is shown by the elongated zones of proteins at the interface adjacent to the lamellae, whereas the protein-rich regions are circular in proximity to the plateau borders. Courtesy of E. Kolodziejczyk.



has been carried out using a dilatational bubble apparatus⁶³, and Fuller and co-workers have pioneered the development of a floating needle shearing device powered by a Helmholtz coil⁶⁴.

Given the apparent irreversibility of protein adsorption to an interface, it is initially surprising to find that short-chain surfactants such as tweens can quickly displace proteins from interfaces. Presumably this is because the adsorbed smaller molecules crowd the proteins and force them to refold, which lowers the energy barrier and hence raises the probability for a protein molecule to desorb. Recent thermodynamic models consistent with protein desorption driven by short-chain surfactants are perfectly capable of predicting this behaviour in a qualitative and to some extent quantitative manner, and are in line with experimental evidence^{65,66}. Attempts have been made⁶⁷ to compare brownian dynamics simulations of competitive protein and short-chain surfactants with experimental measurements made by atomic force microscopy on real films, and these seem to suggest some correlation between the two. Figure 5 illustrates, by means of CLSM, the complex and inhomogeneous distribution of proteins at the liquid–air interface of a protein-stabilized foam.

In the past couple of years, the idea of using particles to stabilize interfaces (often called Pickering stabilization) has resurfaced. Essentially, a small particle can be adsorbed to an interface, with a free energy change of the order of 100 kT or more. Clearly these particles are well anchored to the interface and as such can have a strong stabilizing influence, which for food is a big advantage, as potentially many food-grade particles are available. But there appear to be many subtle effects at work, as particles are often also used to destabilize interfaces. Seemingly there is a balance to be made between the particle surface properties, particle size, interfacial curvature and film thickness^{68,69}. It seems extremely unlikely that Marangoni effects occur for adsorbed proteins, although they may be present with adsorbed particle systems.

Foams have an interesting and rich rheological behaviour⁷⁰. At dilute volume fraction of gas and constant pressure, they seem to behave in a broadly similar manner to emulsions and suspensions, as the effects of bubble interactions are second order and above with respect to the volume fraction. But this is a generalization, because the local hydrodynamics close to a bubble are controlled to a large extent by

the mobility of the interface and the internal phase, which in turn is intimately coupled with the surfactant. Nevertheless, in the far field the two materials are essentially identical. For this reason, coupled with the reduced rates of drainage and Ostwald ripening, a fair amount of research that purports to relate to foam is actually based on experiments with emulsions⁷¹. As the volume fraction is further increased, depending on the polydispersity of the bubble radii, the critical packing fraction is reached so that the spherical bubbles must become deformed in order to fill the required space. Once the bubbles become deformed, the structure becomes cellular in nature and can support small strains with a shear modulus, G , scaling with the Laplace pressure difference across the air–liquid interface according to the ‘Stamenovic estimate’⁷². Naturally these disordered ‘glassy’ materials (or ordered ‘crystalline’ for monodisperse bubbles) support a finite yield stress, beyond which they will plastically deform and bear a structural resemblance in some ways to a macroscopic version of an amorphous metal. Most rheological models for foams are based on a more or less cellular, unit cell structure and range in complexity from early, somewhat simplistic, two-dimensional⁷³ analytic analyses to more recent computer simulations⁷⁴. The effects of post-yield flow are generally not discussed because they are beyond the scope of these simulations. They are conceptually possible, yet would be computationally expensive.

The effect of pressure is an important although little discussed factor. It differentiates foams from emulsions, as it acts directly on the volume fraction because of the compressibility of the gas. Clearly it is possible to induce a ‘glass transition’ (or ‘jamming transition’) just by reducing the pressure, which may occur simply by pumping a foam down a pipe. As this is a common processing operation, it is perilous in the extreme to ignore such effects.

SELF-ASSEMBLED LIQUID-CRYSTALLINE FOODS

When scaling down the design of foods to the nanometre scale, suitable physics to describe these systems has to be tackled from a different perspective. Unlike foods with larger characteristic length scales, here intra- and intermolecular forces rule the self-aggregation of molecules. This is the case for liquid crystalline foods which are nanostructured materials based on the self-assembly of short surfactants, such as monoglycerides or phospholipids and water⁷⁵. They can be found, for example, at the oil–water interface of emulsions such as salad dressing⁷⁵. These systems can be used either directly in the bulk state or re-dispersed in water to form colloidal dispersions with an internally ordered structure⁷⁶. They constitute efficient building blocks for more complex functional foods, and can be used as carriers of specific ingredients dispersed in either the hydrophobic or hydrophilic phase^{77–79}. Finally, they are also used as ‘nanoreactors’ to run and control food-specific chemical reactions, such as the Maillard reaction (where amino acids and sugars react yielding flavours and aromas), within confined geometries and under controlled conditions⁸⁰. Liquid-crystalline foods have rich phase diagrams that admit a broad range of structures including isotropic fluid

(L_{II}), lamellar phases with amorphous (L_a) or crystalline lipid domains (L_c), inverted columnar hexagonal cylinders (H_{II}), bicontinuous double gyroidal ($Ia3d$), double diamond ($Pn3m$) and primitive ($Im3m$) cubic phases^{76,81,82} (see Fig. 6).

These mesophases have viscoelastic properties that depend strongly on their specific structure and include purely plastic materials (lamellar), viscoelastic fluids (hexagonal) or strong rigid structures (cubic), with storage moduli ranging between 10 and 10^6 Pa (refs 82,83). In other words, when classified according to their elasticity, they cover a range of behaviour equivalent to that spanning from viscous fluids to rubbery solids. The rigidity of cubic phases (10^6 Pa), in particular, is remarkably high bearing in mind the surfactants' low relative molecular mass and the fact that the water and lipid phases are not physically connected, as in the case, for example, of micro-segregated block copolymer structures. The prevailing view is that the high storage modulus of cubic phases is mostly attributable to the interfacial tension of the interpenetrated lipid–water interfaces. Nevertheless, unlike for other liquid-crystalline phases, the physical mechanisms responsible for the complex viscoelastic behaviour of bicontinuous cubic phases are still controversial. At small deformations, in the linear viscoelastic regime, several relaxation mechanisms contribute to the overall viscoelastic response of the cubic phases, which can be attributed to the lipid–water interfaces and the confinement of the phases within nano-domains^{82,84–86}. At large deformations, in the nonlinear viscoelastic regime, relaxation takes place differently and is apparently dominated by a cooperative diffusion of surfactant molecules along crystalline planes^{87–89}.

The thermodynamics governing the structures of liquid crystalline phases is also still being debated. Although suitable experimental techniques are well established and have provided detailed topological information^{81,90,91}, no general quantitative theoretical framework is currently available that is capable of interpreting the lyotropic behaviour (that is, the structure changes arising with changes in temperature and composition). It seems evident that, despite the low relative molecular mass, lipids and water self-assemble into ordered structures owing to the enormous enthalpy of mixing existing between the two phases formed by (i) the solution of water and hydrophilic lipid heads and (ii) the hydrocarbon-based lipid tails. By measuring the activity of alkanes partitioning in water at room temperature, and using Flory–Huggins formalism, one can estimate this enthalpy to be of the order of $\chi \approx 3$. If one notes that for macromolecular amphiphiles the order–disorder transition occurs when $\chi N \approx 10.5$ (where N is the number of segments of the polymer backbone)⁹², one can very well appreciate that in the case of lipids, the threshold in molecular mass of the surfactants for self-assembly is $N \approx 3–4$ segments. Because for hydrocarbon chains the total number of segments N is obtained by dividing the total number of atoms by four⁹³, the order–disorder transition in water–lipid systems is expected for surfactants of the order of 12–16 atoms. This crude argument illustrates why in foods, where typical lipid-based surfactants always have a molecular mass beyond this threshold, self-assembly

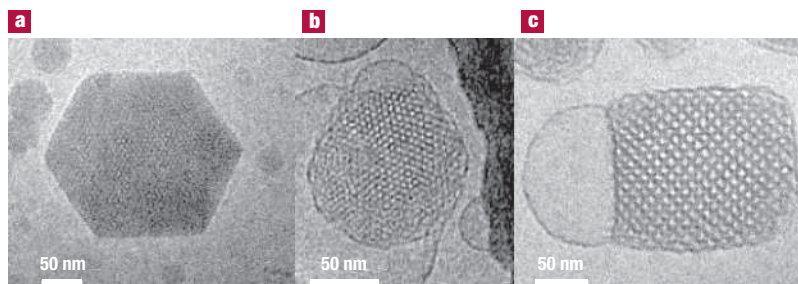


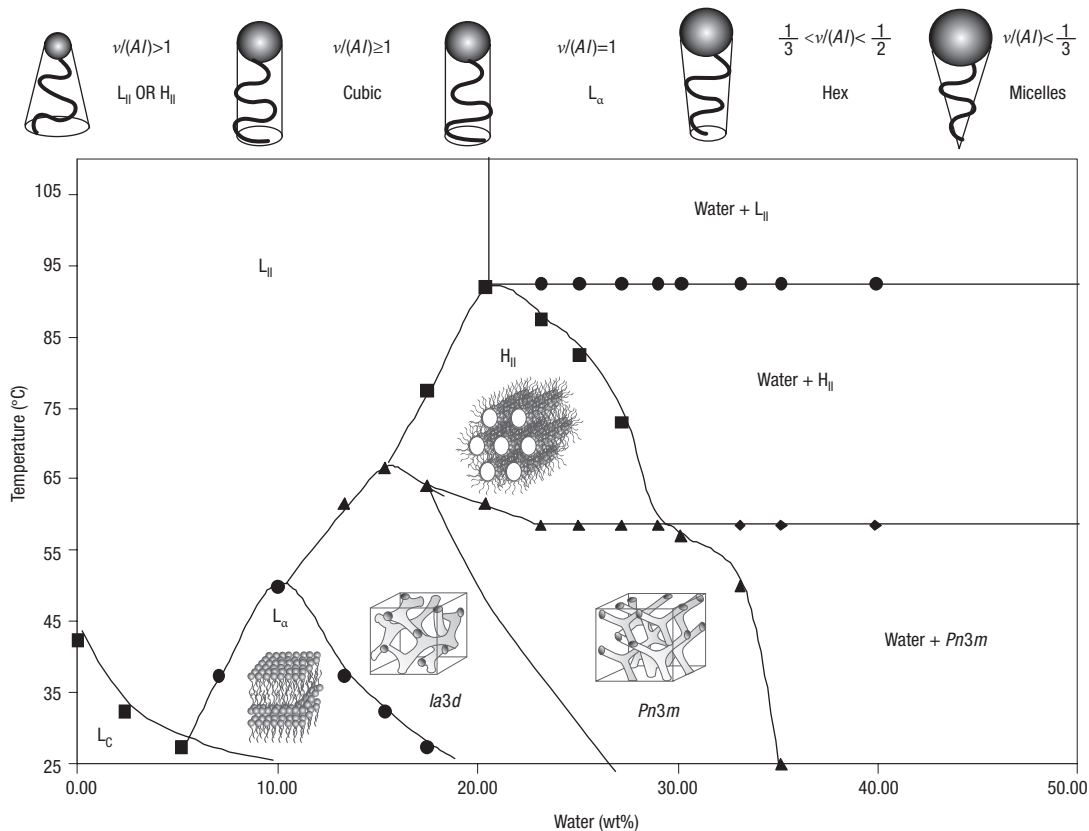
Figure 6 Cryotransmission electron micrographs of some liquid crystalline phases encountered in foods, re-dispersed in water. a, Dispersion of columnar reversed hexagonal cylinders, H_{II} , in water, also referred as hexasome. Reprinted in part with permission from ref. 108. Copyright (2005) American Chemical Society. **b**, Dispersion of $Pr3m$ bicontinuous cubic phase in water, also referred to as $Pr3m$ cubosome. Reprinted in part with permission from ref. 76. Copyright (2004) American Chemical Society. **c**, Dispersion of $Im3m$ bicontinuous cubic phase in water, also referred to as $Im3m$ cubosome. Reprinted from ref. 109 with permission from Blackwell.

is routinely observed. Therefore, in contrast with block copolymers and synthetic amphiphiles, self-assembly of liquid-crystalline foods is principally ruled by enthalpy, rather than by competing enthalpy and entropy of mixing. This fact, as we shall see below, has by no means simplified theoretical approaches aimed at the prediction of phase diagrams in lipid–water systems.

A simple but efficient approach extensively used for a first rough classification of the various structures of liquid-crystalline foods is based on the concept of critical packing parameter (CPP)⁹⁴. This is expressed as the ratio between the volume of the hydrophobic lipid tail, v , and the product of the cross-sectional lipid head area, A , and the lipid chain length, l . Thus, different liquid-crystalline phases may be predicted from the curvature of the water–lipid interface^{94,95} (see Fig. 7) The critical packing parameter can explain qualitatively a number of features of liquid crystalline foods, such as their thermotropic behaviour. For example, raising the temperature decreases the number of water molecules hydrating the polar heads of the lipids, owing to breaking of hydrogen bonds. Consequently A decreases and the CPP increases, inducing a cubic to H_{II} transition, which corresponds to experimental observations⁸¹. Similar arguments have been used to explain the L_a -to-cubic transition with increasing temperature. Nevertheless, the approach based on CPP remains mostly qualitative; it can neither fully describe liquid-crystal phase diagrams nor provide detailed insight into the topology of complex structures such as bicontinuous cubic phases. Figure 7 illustrates the richness of phase diagrams in liquid-crystalline foods and the usefulness of the CPP concept in their interpretation.

Advances in the description of topology of cubic phases encountered in foods have been made by applying triply periodic minimal surface concepts⁹⁶. Bicontinuous cubic phases have been described as three-dimensional periodic lipid bilayers with zero mean curvature at each point. This requirement allows the interfacial energy and the frustration of lipid chains to be minimized simultaneously⁹⁷. The interface is then described by a parametric general integral equation

Figure 7 Phase diagram of a food system based on water and an industrial grade of monolinolein. A large region of liquid-crystalline phases of different types is observed. This can be interpreted in terms of the critical packing parameter (CPP), expressing the ratio between the volume v of the hydrophobic lipid tail and the product of cross-sectional area A and lipid chain length l . Different values of CPP correspond to different expected structures. Main plot reprinted with permission from ref. 82. Copyright (2005) American Chemical Society.



(Weierstrass–Enneper), which captures the nature of *Ia3d*, *Pn3m* and *Im3m* cubic phases when the set of parameters is suitably changed. However, this approach, which is purely mathematical, is not suitable to describe phase diagrams of charged/neutral lipid–water systems.

A general approach has recently been proposed^{98,99} for describing quantitatively the physics of self-assembly for lipids and water as a function of temperature and composition. The model is based on a mean-field approach, in which the individual lipid chains ‘see’ the field exerted by the other surrounding chains. This method is well known in polymer physics and has been successfully applied to polymer–polymer interfaces and block copolymer melts, yielding remarkable quantitative agreement with experimental phase diagrams. Despite the great flexibility of this powerful method, in the case of lipid–water mixtures the quantitative agreement remains poor. This is due mostly to two limitations of the method, at least in the form it was applied to lipid–water systems. The first drawback is related to the way lipid tails were treated. For simplicity and direct analogy with polymer melts, lipid tails were considered as fully flexible chains, and their contribution to the overall free energy of the system was that of a typical random walk with gaussian statistics. In reality, lipid chains behave more like semi-flexible chains than random walks. Eventually, if several unsaturations are present along the backbone of the lipid tails, these can even act as rod-like segments. Thus the first improvement needed to allow quantitative predictions would be to implement semi-flexible chain models for the lipid tails¹⁰⁰. A further complication with lipids is that the

enthalpy of mixing between polar heads and lipid tails increases with temperature, rather than decreasing as for most synthetic polymer pairs. This is due to the breaking of hydrogen bonds between the polar head and water caused by temperature, and it is the same mechanism responsible for the existence of a lower critical solubility temperature in water-soluble polymers^{3,101}. Molecular dynamics simulations are then needed to assess, as a function of temperature, the variation of the enthalpy of mixing between the lipid tail and polar heads in the presence of water. Thus, this method could be used to evaluate the polar head/lipid tail enthalpy of mixing needed to build that total free energy functional, which needs to be minimized in the mean-field-theory approach, to yield equilibrium self-assembled structures. One final difficulty to overcome in order to improve the quantitative predictive capability of self-consistent field models of lipid/water systems is to describe water properly as a structured solvent. This can be done, in principle, by introducing a suitable interaction potential between individual water molecules.

PROSPECTS FOR STIMULI-RESPONSIVE FUNCTIONAL FOODS

Although interest in functional foods is rapidly growing, foods with finely controlled structure and functionality are not routinely designed¹⁰². A functional food must be structured in such a way as to accomplish a specific function whilst being palatable enough to eat. If active ingredients are to be released, the food needs to alter its structure in response to an external environmental change such as in temperature or pH

fast enough to be an efficient delivery carrier, but slow enough to preserve the structure during the tasting and perception process. The engineering of these properties is necessary and extremely challenging. As a corollary, along with the limited possible ingredients, nutritional considerations tend to restrict possibilities further by suppressing sugars and fat as building blocks. Clearly, complex functional foods able to respond to stimuli such as pH or temperature will have to be heterogeneous and designed at multiple length scales. At the nanometre level, hierarchical supramolecular assemblies based on hydrogen bonds or ionic interactions, such as those used to design soft materials^{103,104}, could be an appealing strategy. With this approach, complex foods at or close to local thermodynamic equilibrium can be generated by self-assembly of simpler food-grade components such as protein, polysaccharides and lipids, without need of covalent bonds, which could alter the food-grade nature of the assembly.

Because structural elements relating to food texture are usually of micrometre scale and above, these are almost inevitably non-equilibrium structures and as such are the result of the interaction of processing and thermodynamics. For these kinetically controlled structures the control needs to be very fine with respect to the transport phenomena (flow, heat and mass transfer). Microfluidics and micro-manufacturing techniques would seem to have a key role to play, as they offer the possibility of separately controlling crucial parameters, which in industrial processing cannot be as finely tuned¹⁰⁵. The challenge for tomorrow's food scientists will be to integrate technology and SCM physics over a broad range of relevant length scales and states.

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