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Editorial overview

Food colloids today… understanding structural change during processing, storage, eating and digestion

Food systems are highly complex forms of soft condensed matter. Their complexity arises from the biological diversity of natural raw materials, the many different ingredients that are typically combined together during their formulation, and, most especially, the various subtle changes in molecular interactions and colloidal structure that are induced by food processing and storage. Food colloid scientists attempt to address this complexity by systematically investigating those well-defined model systems that are considered to contain the minimum number of essential molecular components required to produce the characteristic textural features of real food products. Food colloid science has been traditionally concerned with laboratory-based studies of the stabilization of edible structured systems (emulsions, foams, gels) formed as a consequence of the development of interactions between biopolymers and dispersed particles in bulk phases or at fluid interfaces, and influenced by ingredient mixing and thermal/mechanical processing. More recently, however, it would appear[1] that the field has seen a substantial growth of research interest aimed at understanding how colloidal structures evolve after food is eaten, as a result of oral processing and also during breakdown and absorption within the human gastrointestinal tract. Hence, as well as drawing heavily on the traditional disciplines of the physical sciences, the food colloid researcher is increasingly required to embrace concepts and methodologies drawn from a wider palette of academic disciplines — from physiology to psychology, and from biochemistry to bioinformatics. The diverse scope of topics covered within this collection of review articles reflects this trend.

Protein aggregation plays a crucial role in controlling the microstructure and rheology of food colloids. The article by Nicolai and Durand [1] describes recent developments in the field of the self-assembly and gelation behavior of globular proteins, with particular emphasis on the functionality of the well-studied milk protein β-lactoglobulin. During thermal processing of an aqueous protein solution, aggregates with four distinct alternative morphologies may be formed — spherical particles, flexible strands, semi-flexible fibrils, and fractal clusters. Concerning their optimization in food applications, it would appear that long strands and fractal aggregates are particularly useful for viscosity modification and for making cold-set gels, whereas dense spherical particles are more effective for protein enrichment (*i.e.* fat replacement) and nutrient encapsulation/delivery. Aggregate morphology and size distribution are sensitively influenced by various factors such as protein concentration, heating temperature, and aqueous solution conditions (pH, ionic strength, calcium ions). Above some critical protein content, the process of secondary aggregation leads to either (semi-)transparent fine-stranded gels or to opaque particulate gels, depending on the ionic strength. Despite progress in understanding the microstructural mechanisms, it is disappointing to note that precise information is still lacking on the mechanical strength of network cross-links at the nanoscale level. Consequently it is not yet possible to relate the different aggregate/gel structures to the rheological properties of these protein gels.

One of the main functional roles of proteins in food colloids is their ability to adsorb at oil–water interfaces during the formation of protein-stabilized oil-in-water emulsions. The article by Wooster and coauthors [2] outlines recent progress in determining the conformational structures of adsorbed food proteins using the techniques of synchrotron radiation circular dichroism and Fourier transform infrared spectroscopy. These advanced instrumental methods are providing fresh insight into the structures of adsorbed food proteins to supplement the information previously obtained from more traditional methods such as calorimetry and enzymatic digestion studies. It is already well recognized that, following adsorption at the oil–water interface, globular proteins typically lose much of their native tertiary structure, and instead develop considerable amounts of non-native secondary structure. While the degree of conformational rearrangement varies considerably from one protein to another, and is dependent also on oil phase polarity, it is now established that two main secondary structural features predominate: the α-helix and the intermolecular β-sheet. Moreover, the preferred adsorbed conformation is the compact α-helix form. The detailed structural insight from these advanced spectroscopic techniques is enabling researchers to reassess earlier interpretations of adsorbed protein conformations based on the more intuitive concepts of surface denaturation and the molten globule state. However, the relevance of this refined molecular information for the identification and design of novel protein-based emulsifiers/stabilizers is not yet demonstrated. That is to say, while recent studies have identified some limited correlations between specific protein conformations and certain aspects of emulsion stability, the long-standing aim of explaining food colloid properties in terms of adsorbed protein conformational structure remains tantalizingly elusive.

The functional properties of food proteins are commonly influenced by interactions with various kinds of food polysaccharides. In the article by Williams and coauthors [3], the stabilization of emulsions by protein–polysaccharide complexes is discussed under three different headings: natural protein-containing hydrocolloids (such as gum arabic), Maillard-type covalent conjugates made by dry-heat treatment, and biopolymer mixtures forming electrostatic complexes and coacervates. When the protein and polysaccharide species become linked together covalently within the same hybrid macromolecular entity, the amphiphilic

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[1] This intuitive impression is supported by an analysis of bibliometric data. Of the 400 or so published papers that were generated by a *Web of Science* search on the topic of *food colloid(s)* for the period 2000–2009, just 2% of the listed articles were explicitly associated with the topic of *digestion* (and 3% with the topic of *texture*). However, on repeating this same search for the 3-year period 2010–2012, the proportion of *digestion* articles was found to have increased to over 7% (but with *texture* papers still remaining at 3%).

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protein component confers a capability to adsorb strongly at the oil–water interface, and the polysaccharide component provides enhanced capacity for steric stabilization *via* the adsorbed layer's hydrophilic outer region. In the case of a binary protein + polysaccharide combination exhibiting electrostatic complexation, the effectiveness of the stabilization mechanism is dependent on a large number of contributory factors, such as the charge distribution on the two biopolymers, the order of introduction of the biopolymers to the interface, and the pH and ionic strength of the aqueous medium. In addition to its effect on emulsion stability, the systematic fabrication of adsorbed multilayers through electrostatic complexation of proteins and polysaccharides has numerous potential applications in food technology, including the encapsulation of flavors/nutrients, the protection of lipids against oxidation, and the targeted delivery of bioactive ingredients during digestion.

Fat crystals are important structural entities in the stabilization of edible water-in-oil emulsions. Renewed research interest in this topic has been stimulated by an enormous growth in activity within the wider colloid science community in the subject of Pickering stabilization of emulsions by dispersed particles of nanoscale or microscopic dimensions. The article by Rousseau [4] provides fresh insight into the structural arrangements involved in the stabilization of food emulsions by fat-based colloidal entities. In particular, three types of fat-based Pickering stabilization mechanism are identified: (i) surfactant-mediated interfacial crystallization, (ii) interfacially adsorbed nanoparticles or microparticles, and (iii) shear-crystallized droplet encapsulation matrices. In the established literature, the descriptions of the stabilization of fatty spreads by mechanism (i) have conventionally invoked the concept of interfacial solidification involving surfactant/triglyceride layers. In contrast, mechanism (ii) represents the classical Pickering stabilization mechanism by discrete fat crystals. The least familiar mechanism (iii) involves stabilization by thick crystalline fat matrices, as induced under conditions of rotational shear flow in a confined microscale geometry. Concerning the generation of crystalline stabilizing structures under shear, the author cautiously asserts that more detailed research is still required to properly establish the generic validity of this putative mechanism, notably in relation to the specific role of surfactant–triglyceride interfacial interactions and the associated means by which spheroidal assemblies are formed within encapsulated droplets.

The incorporation of dispersed gas bubbles into a food material produces a lighter texture and a smoother mouthfeel, as well as leading to changes in visual appearance, microstructure and calorific density. These features of aerated foods are desirable consumer characteristics, and air is a cheap ingredient for the food manufacturer. On the other hand, it is well recognized that bubble dispersions and liquid foams are notoriously difficult to stabilize during long-term storage. Accordingly there is considerable commercial interest in exploring novel methods of stabilizing gas bubbles in food systems, and in replacing fat droplets by dispersed gas bubbles. The article by Cox and coauthors [5] describes one such approach based on the special class of proteins called hydrophobins derived from filamentous fungi. The recent literature has reported unambiguous evidence of the capability of hydrophobins to provide long-term stability to bubbles and foams with respect to breakdown by the mechanisms of coalescence and disproportionation. The impressive functionality of the hydrophobin molecule is attributed to its compact amphiphilic structure, combined with its unique ability to adsorb and self-assemble at an air–water interface by means of specific non-covalent intermolecular interactions, leading to a close-packed elastic adsorbed film of exceptional coherence and rigidity. The authors use the story of hydrophobin as a case study to demonstrate the value of bioinformatics for exploring protein structure–function relationships and discovering novel functional ingredients. That is, by searching on-line databases of protein sequences for the key primary structural attributes of this particular protein class (*i.e.*, its low molecular weight and its characteristic eight-cysteine motif), it is demonstrated that previously unidentified hydrophobin-like proteins can be identified having potential applications as bubble-stabilizing agents in aerated foods.

Combinations of proteins and small-molecule surfactants are commonly found in food emulsions and foams. Consequently the surface properties of adsorbed layers at fluid interfaces are affected by the nature of the interfacial protein–surfactant interactions and by the associated competitive adsorption phenomena. The article by Miller and coauthors [6] reviews recent theory and experiments from the Potsdam group directed towards understanding the adsorption and surface rheology of mixed protein + surfactant layers. The group's established statistical thermodynamic model is extended to include contributions from protein–surfactant interactions, as well as effects of competitive adsorption between surfactants and surfactant–protein complexes. An impressive experimental advance is the development of a reliable protocol for comparing the surface properties of mixed layers formed by two alternative experimental procedures — sequential adsorption and simultaneous adsorption. In the case of proteins mixed with ionic surfactants, measurements of dilatational rheology have shown contrasting results from the two procedures, suggesting different compositions for the two kinds of binary surface layers, despite the absence of any such evidence from complementary tensiometry measurements. Significant variations in protein–surfactant complex behavior are reported for air–water and oil–water interfaces, as a consequence of the inferred deeper penetration of hydrophobic protein regions into the liquid oil phase. But the effect of the nature of the non-aqueous phase on adsorbed layer properties is apparently rather too subtle to be described by the authors' current theoretical model.

The article by Moschakis [7] reports on some exciting developments in the application of the technique of passive particle tracking microrheology in the field of food colloids. This experimental technique makes use of the transient weak forces generated by the Brownian motion of colloidal particles. The soft solid under investigation is distorted with the minimum strain possible, facilitating the highly sensitive monitoring of viscoelastic properties on the microscopic length scale. It is clear that particle tracking cannot yet be considered a routine technique for the food colloid scientist, if only because there are several precautions and corrections that have to be carefully applied in order to make sure that any results are reliable and free from experimental artifacts. In the case of biocolloidal systems, the correct choice of tracer particles is crucially important in order to ensure that the particle's diffusion motion is not influenced by adsorption of macromolecular ingredients (especially proteins) or by association with the investigated matrix. However, once the relevant technical challenges have been met, the technique of particle tracking microrheology offers a valuable opportunity for the delivery of a level of detailed structural and textural information that would otherwise be inaccessible from conventional rheology or microscopy. Two specific examples of food-based model systems are described in detail: (i) the determination of the gel point and mean pore size during protein gelation, and (ii) the study of viscoelastic phase separation and depletion flocculation in a heterogeneous protein-stabilized emulsion containing added hydrocolloid.

Understanding the relationship between food texture and sensory perception remains a crucial longstanding objective within the discipline of food science. The article by Foegeding and coauthors [8] assesses current progress towards realizing this aim with particular emphasis on the contributions from oral processing and material science. Part of the complexity of this field arises from the large number of different terms that are commonly used in the literature to characterize the perceived textural attributes of solid and semi-solid foods. Based on results from many published studies, it would appear that textural attributes evaluated by tongue–palate compression and ‘first chew’ can be reasonably well explained in terms of the structural and mechanical properties of the food. But those attributes that are assessed after some degree of mastication cannot so readily be predicted from measurements of the food material properties alone. In part, this lack of predictability is attributable to limitations in our current knowledge of certain fundamental aspects of oral processing: the physicochemical role of saliva, the role of food–surface interactions, and the dynamical mechanism(s) of food bolus formation. According to the authors, substantive future progress will require three main areas of advancement: improvement in the consistency of sensory terminology, a more quantitative approach to the study of structural change during oral processing, and an enhanced level of cross-disciplinary investigation.

The interrelationships of microstructure, texture and oral processing are examined further by Stieger and van de Velde [9] in the context of extensive model studies by the Wageningen group with phase-separated mixed protein/polysaccharide gels and emulsion gels. The authors' overall objective is to use a basic understanding of the breakdown properties of semi-solid or soft-solid foods during oral processing to design food material systems having a lower content of salt or sugar, but without compromising the taste perception. From studies with mixed biopolymer gels of variable microstructure (homogeneous, coarse stranded, bicontinuous, *etc.*), it is established that significant reductions in the concentration of the tastant (sugar or salt) are achievable in semi-solid or soft-solid foods by increasing the extent of serum release, or by adjusting the spatial distribution of the tastant within the food macroscale structure. In the latter case, it is postulated that the perceived taste enhancement is triggered by the experience of a short period of discontinuous stimulation of taste receptors during the mastication process. Based on evidence from studies of emulsion gels of variable microstructure, there is inferred to be a tendency for the perception of creaminess and other fat-related attributes to increase along with the level of fat concentration differences in fabricated heterogeneous model systems. It is suggested that the presence of high-fat zones on product surfaces can be exploited to deliver significant enhancement of fat-related sensory attributes.

The article by Stokes and coauthors [10] is concerned with describing the methodologies and concepts that are required to understand the various stages of oral processing in dynamic terms. Broadly speaking, it is supposed that the textural features sensed in the early stages of oral processing are dominated by bulk properties (rheology) whereas those sensed later are mainly determined by frictional effects and thin film flow behavior (tribology). For the purposes of establishing reliable *in vitro* approaches for the rational design of food structures, the authors invoke six discrete stages of oral processing: first bite, comminution, granulation, bolus formation, swallowing, and residue formation. The comminution stage involves a tribological interaction between the food particles and the oral surface. Granulation involves capillary bridging of saliva between aggregated particles, followed by dispersion of particles within the saliva to form a paste-like bolus. The process of swallowing is influenced by various factors, including particle size, moisture content, and bolus rheology; and, in the final stage of oral processing, residual structures left after swallowing contribute further to the perceived mouthfeel. Recent experimental advances in the tribological study of oral processing are categorized under three headings: imitative approaches, like those using a pig's tongue; empirical approaches, which simply seek some kind of relationship between a friction coefficient and a measure of texture/mouthfeel perception; and fundamental studies of soft tribology, which attempt to take proper account of discrete physical variables like film thickness, sizes of particles/droplets, and surface properties (polymer adsorption). An ongoing challenge for researchers in this field is how to properly incorporate the influence of human saliva in these various experimental studies.

Recent advances in determining the key structural and biochemical factors involved in the digestion of protein-stabilized emulsions are outlined in the review of Singh and Ye [11]. The trajectory of structural change of the ingested colloidal system is typically considered to be represented in terms of a multi-stage process. The fat globules of the partially destabilized food emulsion are located initially in a phase-separated cream layer at the top of the stomach. During subsequent gastric processing, the regular muscle contractions of the stomach and the intense shear forces in the antrum/pylorus region facilitate a (re)emulsification of this fat in the presence of bile salts and phospholipids. Enzyme activity takes place within the aqueous phase (proteolysis) and at the surface of emulsion droplets (lipolysis). While some fat digestion by gastric lipase does take place in the stomach under acidic conditions, it mostly occurs in the small intestine through the action of pancreatic lipase (and colipase). Critical evaluation of results from recently published studies of emulsion digestion is complicated by the diversity of *in vitro* digestion methodologies used by the various research groups; these range from simple batch processing experiments to equipment that attempts to mimic the operation of the entire gastrointestinal tract. There are also significant differences in the investigators' choices of biochemical conditions (pH, ionic strength, enzyme concentration, *etc.*). In terms of the realization of emulsion design approaches to control the rate of lipid digestion, there is evidence from a number of studies that kinetic control can be achieved to a limited extent by changing the usual set of food colloid system variables, namely the surface layer composition, the oil droplet size, the calcium ion content, and the physical state of the fat phase. Nevertheless, it would also appear that considerable further work involving *in vivo* animal models is required in order to validate the existing *in vitro* studies, and also to understand fully the breakdown processes of different emulsion structures under the realistic physiological conditions of the living gastrointestinal tract.

The final article by Gidley [12] is concerned with the structural role of hydrocolloids within the gastrointestinal tract and the related health implications. In the hunter–gatherer diets that existed for most of the long period of human evolution, hydrocolloid ingredients were mainly represented by unprocessed plant foods. The development of modern processed foods with improved health benefits is an attempt to mirror the functionality of pre-agricultural foods, while maintaining the advantages of convenience and appealing taste/texture. Hence, the characteristic digestion properties of traditional plant tissue foods are imitated in processed foods by, for instance, the gelation of hydrocolloid-based ingredients in the stomach, or the slowing down of intestinal digestion processes *via* viscoelastic structuring of the carbohydrate polymers. Looking forward, it appears that the continuing use of hydrocolloid ingredients (dietary fiber) in processed food products provides a considerable opportunity for manufacturers to generate a range of substantial health benefits by means of various well-established physiological strategies: the manipulation of gastric emptying (satiety enhancement) and the ileal brake mechanism (obesity treatment), the control of the glycemic response (diabetes) and plasma cholesterol levels (cardiovascular disease), and the promotion of favorable types of carbohydrate fermentation in the large intestine (protection against colon cancer). A cautionary observation is that, although the low-molecular-weight oligosaccharides also fall within the internationally accepted definition of 'dietary fiber', these short carbohydrate oligomers have little to contribute in terms of controlling satiety or reducing enzymatic digestion rates. In other words, it is the high molecular weight of the hydrocolloid polymer which is its key physicochemical attribute in relation to conferring potential health benefits as a component of a balanced human diet.

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