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Food colloids research: Historical perspective and outlook

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ABSTRACT

Trends and past achievements in the field of food colloids are reviewed. Specific mention is made of advances in knowledge and understanding in the areas of (i) structure and rheology of protein gels, (ii) properties of adsorbed protein layers, (iii) functionality derived from protein–polysaccharide interactions, and (iv) oral processing of food colloids. Amongst ongoing experimental developments, the technique of particle tracking for monitoring local dynamics and microrheology of food colloids is highlighted. The future outlook offers exciting challenges with expected continued growth in research into digestion processes, encapsulation, controlled delivery, and nanoscience.

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Contents

1. Introduction	0
2. Historical perspective	0
3. Advances and achievements	0
4. Microrheology and particle tracking	0
5. Challenges and outlook	0
Acknowledgements	0
References	0

1. Introduction

The biennial series of European food colloids conferences began in Leeds in the Spring of 1986. Over the intervening period of almost a quarter of a century, we have seen substantial advances in understanding and knowledge within the field of food colloids research. In addition, we have become aware of considerable changes in the nature and practice of food-related scientific research in general. Against this historical background, it seems natural to pause to recollect some of the highlights of the journey so far, and to assess the challenges that may lie on the road ahead.

One characteristic feature of much experimental research coming under the heading of food colloids is the emphasis on model systems rather than whole foods. The motivation behind this approach is obvious when it comes to trying to obtain fundamental understanding at the

physico-chemical level. But the reliance on model systems has always provided something of a problem for industrial researchers tasked with providing information relevant for the development of real food products. Indeed, in the published version of the introductory lecture back in 1986, the Unilever scientist Don Darling informed the conference audience of his view that “too much time is spent burying our heads in the proverbial ‘model system’ rather than facing up to the complex world of real food systems” [1]. In commenting on this opinion at a later conference in Dijon, this author made the observation [2] that the standing of the model system showed little sign of losing its popularity amongst academic researchers – a situation that continues to this day. Nonetheless, the issue raised by Darling is still a valid matter for discussion. And, indeed, the scope and complexity of model systems remain subject to continued scrutiny and development, especially nowadays as the efforts to understand how food colloids interact with the human body are becoming increasingly serious.

This article presents an impression of some of the trends, achievements and challenges within the research field represented by these food colloid conferences. Of course, no such brief analysis of past, present and

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future can aspire to be comprehensive in its scope or fully balanced in its judgement. The perspective adopted here is necessarily personal and rather subjective, reflecting mainly as it does the research interests and prejudices of the writer. It is meant as background and introduction to the Special Issues of *Advances in Colloid and Interface Science* and *Food Hydrocolloids* dedicated to papers presented at the 13th European food colloids conference (Granada, March 2010). The list of accompanying references consists mainly of critical reviews and discussion papers; readers can easily use these overview publications to find the relevant references to the original primary sources.

2. Historical perspective

Table 1 gives an overall impression of the main topics of investigation by food colloid scientists over the past quarter of a century. It lists the keywords that have occurred most frequently in the titles of food colloids conference lectures during the period 1986–2006. The data are compiled from the set of article titles contained in the 11 edited volumes of conference proceedings published by the Royal Society of Chemistry from 1987 to 2007 (no book was produced from the 2008 conference). The keyword frequency distribution shows that a central theme of researchers has been the behaviour of proteins in emulsions and at interfaces, with milk protein fractions representing the favoured choice of ingredient in the investigated model systems. The two most popular protein components have been casein(ate) and β -lactoglobulin. In addition to emulsions, protein-based gels and foams have also been common systems of investigation. According to the article titles, the physical properties that have received the most attention are (micro)structure, adsorption, stability and rheology. These findings are not surprising or particularly original: based on a rather smaller data set, similar trends were identified previously by Walstra [3].

In reality, of course, food colloid science is not a closed discipline with well-defined boundaries. Ongoing research activity is being continuously influenced by interactions with other areas of food science and technology, by trends and developments in related areas of physics and chemistry, and by the constraints and inducements applied to project leaders to maintain their research funding.

To assess the broader picture, we can look at statistical data derived from the general scientific literature relating to the major biopolymer ingredients commonly found in model colloidal systems and real food products. Fig. 1 shows the level of activity/interest as indicated by the numbers of mentions of (a) four proteins and (b) four polysaccharides in titles/abstracts of published articles over the last twenty years. Each data point is derived from the ISI *Web of Science* database specifying the year

(e.g. 1999) and the topic (e.g. casein*) as the two search items. Typically, for each ingredient, what is found is a positive systematic growth in the number of recorded hits with time, together with some non-systematic fluctuations from year to year. Additionally there is significant variation within the sets of relative average growth rates. For instance, Fig. 1(a) shows that, whereas the publications on casein(ate) outnumbered those on soy protein by about 30% in the early 1990s, the annual number of studies mentioning the vegetable protein has now reached and slightly exceeded that for the milk protein. The most striking data set in Fig. 1(a) is that for gelatin. In spite of, or possibly indeed because of, the well-known commercial problems of using gelatin as a food ingredient in certain markets, the outputs reporting research on (or relevant to) gelatin are continuing to grow at a faster rate than those dealing with all the other major food proteins. Turning to the polysaccharides, Fig. 1(b) shows that the most impressive performer in terms of the rate of growth of citations is chitosan. In the early 1990s research reports on chitosan were less numerous than those on pectin or carrageenan, but by 2008 the level of activity relating to chitosan had increased by more than a factor of 10, and it now is approaching that for the ubiquitous starch. Moreover, it seems that the absolute rate of growth of chitosan-related research papers may be still increasing.

Overall annual publications on emulsions and foams have increased in number by a factor of three over this twenty year period, and Fig. 2 shows that the relative growth has been rather higher for the case of foams. In this graph the ordinate axis is plotted on a logarithmic scale in order to encompass the outstanding and seemingly relentless growth of research activity on systems involving nanoparticles. Also shown on this same plot is the emergence during the past decade of research papers on 'nanoemulsions'. While this latter term still occurs in only a very small fraction of total outputs, as compared with those for (macro)emulsions, the high growth rate of the nanoemulsion curve (on the logarithmic scale) resembles that for the nanoparticle curve.

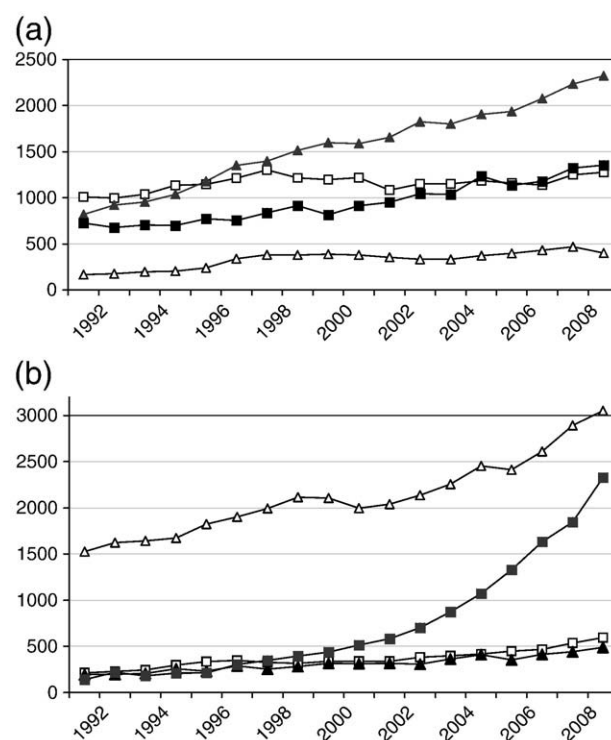


Fig. 1. Annual numbers of journal articles/titles containing some food biopolymer ingredient keywords recorded in *ISI Web of Science* database for the period 1991–2008. Searches were based on combined categories of 'topic' and 'year published': (a) proteins: \square , casein*; Δ , lactoglobulin; \blacksquare , soy* protein; \blacktriangle , gelatin*. (b) Polysaccharides: \square , pectin; \blacktriangle , carrageenan; Δ , starch; \blacksquare , chitosan.

Table 1

Number of times each of the most frequently encountered keywords appears in lecture article titles in the set of 11 edited proceedings of European food colloid conferences (1986–2006) as published by the Royal Society of Chemistry.

Keyword	Number
Protein(s)	108
Emulsion(s)	79
Interface(s)/interfacial	59
(Micro)structure(s)/structural	53
Gel(s)	43
Adsorbed/adsorption	35
Interaction(s)	33
Stability	31
Casein(ate)	28
Foam(s)	28
Rheology	22
Surfactant(s)	21
Particle(s)	20
Polysaccharide(s)	17
β -Lactoglobulin	17
Aggregation	16
Others	≤ 15

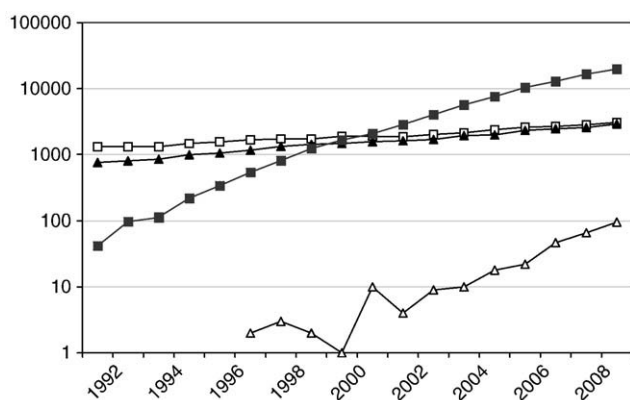


Fig. 2. Annual numbers of journal articles/titles (logarithmic scale) containing colloid-related keywords based on ISI Web of Science database for period 1991–2008: □, emulsion*; ▲, foam*; ■, nanoparticle*; △, nanoemulsion*.

The trends of Fig. 2 remind us that international research activity in surface and colloid science is generally very buoyant. This behaviour is, of course, driven in large part by the nanoscience revolution [4–6]. In our field of food colloids, the use of ‘nano’ terminology was unknown until only a few years ago, whereas now we commonly see papers in the food science literature containing references to such terms as nanotechnology, nanovehicles, nanocapsules, nanoencapsulation, and even ‘nanocolloids’! Other terms in common current use by food colloid scientists – and all noticeably absent from Darling’s 1986 conference lecture – are fractal, self-assembly¹, neutraceutical(s), and functional food. One recalls that there were also many words and expressions that were known about in those early days, but they were not really considered to form a central part of the food colloids field – terms like encapsulation, delivery, controlled release, dietary fibre, saliva, lipolysis, digestion and satiety. Of course, this reminds us that a major driver of recent food colloids research activity is the aim of the food industry to offer positive health benefits to consumers through the control of food product structure and processing.

3. Advances and achievements

A key factor contributing to progress in our field has been the increased availability of advanced instrumentation and the emergence of new experimental techniques [8,9]. These include scattering methods such as X-ray diffraction, neutron scattering/reflection, and diffusing wave spectroscopy; microscopy methods such as atomic force microscopy, confocal laser scanning microscopy, Brewster angle microscopy, and cryoscopic scanning electron microscopy; spectroscopic methods such as mass spectrometry and nuclear magnetic resonance; and other valuable techniques such as ultrasonic scanning/attenuation and differential scanning calorimetry. There have been corresponding advances in image analysis for the quantification of microstructural information [10]. There have also been improvements in the design and operation of commercial instrumentation for the measurement of various kinds of bulk rheology (shear and extensional) and surface/interfacial rheology (shear and dilatational). And over this same period small-scale computers have become increasingly involved in the routine control of experiments, in the statistical analysis of data, and in numerical simulations of model systems of increasing complexity [11].

¹ With some theoretical and linguistic justification, it has been suggested that the widely used term ‘self-assembly’ is somewhat of a misnomer. As suggested recently by Uskokovic [7], a more accurate expression would probably be ‘co-assembly’ or ‘mutual assembly’.

So what do we know now that we did not know in 1986? It is difficult to answer this question properly without becoming overwhelmed by detail. Let us be content therefore to focus on four central areas where some substantial improvements in basic knowledge and understanding have certainly been realized.

- (i) *Structure and rheology of protein gels.* A major conceptual step forward came with the identification of the fractal-type particle gel as a discrete structural category distinct from the traditional fine-stranded polymer gel [12]. In principle, depending on the gelation conditions and basic building blocks, the same protein ingredient, whether it be casein or β -lactoglobulin, can form both kinds of gels. The theoretical description of the relationship between interactions and gel properties has been assisted by insight from computer simulations [13], and the principles of fracture mechanics have been used to explain large-scale deformation properties [14]. More recently it has been recognized that the range of aggregated protein structures is actually rather more complex [15]: there is actually a continuous change of protein gel structures and properties depending on the gelation conditions. And under certain special conditions (pH, ionic strength, etc.) most proteins can also be transformed into other kinds of structures (nanorods, nanofibres, nanotubes, etc.) having very diverse gel-forming properties. Furthermore, the subject of milk protein gelation has been influenced by developments in understanding the interactions and molecular self-assembly of the caseins [16] and the transformation of globular proteins and peptides into amyloid-like structures [17].
- (ii) *Properties of adsorbed protein layers.* Information on interfacial structure has been derived from scattering techniques and microscopic imaging methods. Neutron reflectivity at fluid interfaces has demonstrated differences in the structures of disordered and globular milk protein layers which correlate with emulsion stability properties [18]. By monitoring the complex structure of mixed protein + surfactant layers, atomic force microscopy has revealed the generic mechanism whereby proteins are competitively displaced from fluid interfaces by small-molecule surfactants [19]. This structural information on the mesoscopic scale has been supported by systematic studies of the interfacial rheological properties of films of surfactants and proteins at fluid interfaces [20,21], and by Brewster angle microscopy of phase-separated mixed layers [22]. Improved understanding of how intermolecular interactions influence interfacial structure and composition has emerged from a number of theoretical directions: the modelling of protein layers using self-consistent-field theory [23], explicit computer simulations of the mechanism of competitive adsorption [24], and the fitting of experimental data on mixed surfactant + protein layers to thermodynamic models [25]. The implications of these interfacial properties for the making and stabilizing of food emulsions and foams have become increasingly well established [26–32].
- (iii) *Functionality from protein–polysaccharide interactions.* Building on the seminal work of Tolstoguzov and his Moscow group [33–35], the significance of protein–polysaccharide interactions in influencing the properties of food colloids has received steadily increasing attention from food researchers [36–40]. It is now well recognized that repulsive protein–polysaccharide interactions are associated with thermodynamic incompatibility and depletion phenomena, whereas associative interactions are associated with complexation, precipitation and coacervation. The potential of protein–polysaccharide conjugates and complexes as emulsifying agents and colloid stabilizers is well established [41,42]. Furthermore, there has been developed an increasing insight into how protein–polysaccharide

interactions can be exploited in the technique of 'layer-by-layer' emulsion stabilization [43] and through the fabrication of nanoscale encapsulation and delivery vehicles [44].

- (iv) *Oral processing of food colloids.* The physiological and rheological aspects of oral processing are undoubtedly complex. Nonetheless, the last decade has seen some useful progress in understanding what happens to model food colloids during mastication [45,46]. A range of experimental techniques has been developed to examine the oral behaviour of foods [47]. For systems containing emulsion droplets and hydrocolloids, these studies have led to insight into the mechanistic role of lubrication and biopolymer–mucin interactions on the sensory perception of textural properties [48]. Systematic studies have established [49] that the interaction of protein-stabilized emulsions with saliva can lead to flocculation by the mechanisms of bridging or depletion, and that droplet coalescence can be induced in the mouth in the presence of saliva through a combination of frictional and hydrodynamic forces at the surfaces of tongue and palate. Progress has also been made at the fundamental level in relating oral texture perception to the rheological properties and structural breakdown behaviour during mastication of specific types of food materials such as biopolymer gels [50] and crispy solids [51].

4. Microrheology and particle tracking

An evolving experimental technique that would seem to offer considerable potential in the field of food colloids is the use of particle tracking to monitor the evolving dynamics and microrheology of dispersions, gels and emulsions [52]. In contrast to conventional bulk rheology, which is the study of material flow properties on the macroscopic scale, microrheology is the study of the viscous and viscoelastic properties of small-scale regions within a material *via* the tracking of the motion of microscopic-sized tracer particles. As food colloids are commonly heterogeneous, the technique is especially relevant to understanding the relationship between stability and dynamics at the microscopic level, *e.g.*, in a hydrocolloid-containing emulsion exhibiting micro-scale phase separation [53] or a concentrated protein solution near its sol–gel transition [54].

The fundamental assumption of passive tracer microrheology is that the Brownian motion of the diffusing particles is controlled by the mechanical properties of the surrounding medium. For particles undergoing free diffusion, the ensemble-averaged mean-square displacement (MSD) is a linear function of the time τ , *i.e.*, $\langle \Delta r^2(\tau) \rangle = 6D\tau$. For spherical particles in Newtonian media, the diffusion coefficient D is given by the Stokes–Einstein relation. For particles in viscoelastic media, the MSD may be analysed using the generalized Stokes–Einstein equation to give frequency-dependent viscous and elastic moduli. With viscoelastic media, it is convenient to plot the MSD as a function of time on a double logarithmic plot. The fitted slope α , corresponding to the exponent in the relationship $\langle \Delta r^2(\tau) \rangle \sim \tau^\alpha$ will then lie somewhere between the purely viscous limit ($\alpha = 1$) and the elastic limit ($\alpha = 0$). A value of $\alpha < 1$ indicates that the motion is sub-diffusive (or hindered).

To illustrate the use of particle tracking to probe the kinetics of gelation, let us consider the case of a solution of sodium caseinate exhibiting slow steady pH lowering in the presence of glucono- δ -lactone (GDL). During the acidification process, the mobility of carboxylate-modified polystyrene microspheres (diameter 0.5 μm) was monitored under the confocal microscope as described elsewhere [55]. Fig. 3 shows ensemble-average MSD data against lag time τ for the probe particles in an acidifying system of 5 wt.% protein. During the first 40–41 min, as the pH falls from around neutral to $\text{pH} \approx 5.2$, the log–log plot retains a constant slope of unity ($\langle \Delta r^2(\tau) \rangle \sim \tau$) reflecting the purely viscous response of the surrounding medium. With further pH lowering, however, as the protein–protein intermolecular interactions become increasingly attractive and the protein aggregation more extensive, the

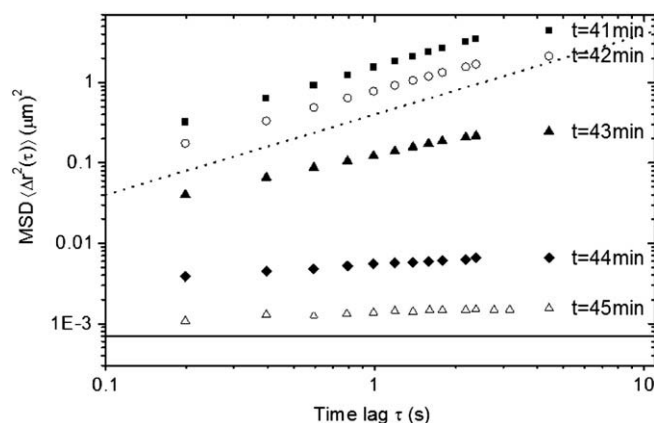


Fig. 3. Ensemble-averaged mean-squared displacement (MSD) versus lag time τ for carboxylate-modified microspheres (0.5 μm) in 5 wt.% sodium caseinate dispersion at different times (t) since the addition of GDL for acidification. The dotted line represents the limiting slope of $\alpha = 1$ while the solid line represents $\alpha = 0$. Data taken from Moschakis et al. [55].

value of the slope decreases continuously, indicating that the particles are becoming progressively more constrained and trapped by the developing casein network. After 45 min following the addition of GDL, the MSD has become essentially independent of the lag time, and the system behaviour resembles that of a purely elastic material.

The problem of precisely defining the gel point is well-known. A convenient and widely adopted criterion is that a sol(ution) becomes a gel when the value of the storage modulus G' exceeds that of the loss modulus G'' at some fixed frequency (say 1 Hz). It might be intuitively expected that the cessation of tracer particle motion in a gelling system would correlate with the onset of predominantly elastic character as determined by the bulk rheology. Such a comparison is illustrated in Fig. 4 for a set of acidified sodium caseinate systems of protein concentration in the range 2–10 wt.% [55]. Fig. 4(a) shows the time-dependent phase angle, $\delta = \tan^{-1}(G''/G')$, calculated at 1 Hz from the particle tracking data, and Fig. 4(b) shows the corresponding changes in G' (at 1 Hz) as determined by conventional bulk shear rheometry. There is reasonably good agreement between the two sets of results in terms of the times at which there is a sharp increase in G' or decrease in δ . Nevertheless, the gelation times inferred from the particle tracking are slightly lower than those indicated by bulk rheological measurements, particularly at the lower protein concentrations. This difference may be attributed to the fact that, in the vicinity of the sol–gel transition, fluctuating regions of varying local aggregate structure and viscoelasticity are generated. At low protein content the individual particle movement due to Brownian motion in isolated regions of the system may become significantly affected before an overall network elasticity is measurable by macroscopic rheometry. In other words, the microrheological technique appears to be more sensitive to the pre-gelation structural changes. The observed discrepancy could also be because the particle tracking methodology picks up the energy dissipation term (loss modulus G'') to a much lesser extent than bulk rheometry does. Rather similar differences in the sensitivity to G' and G'' around the gel point were identified previously for temperature-dependent caseinate emulsions investigated by bulk rheology and diffusing wave spectroscopy [56,57]. At the higher protein concentrations, the protein network is transformed more quickly into a structure that is more uniform in mechanical properties, which may explain why the gel point information in Fig. 4 from particle tracking and conventional rheology appear in closer agreement. To test these various hypotheses further, it would be necessary to analyse the change in phase angle with time in more detail as a function of caseinate concentration using a combination of particle tracking microrheology and frequency-dependent bulk rheology measurements.

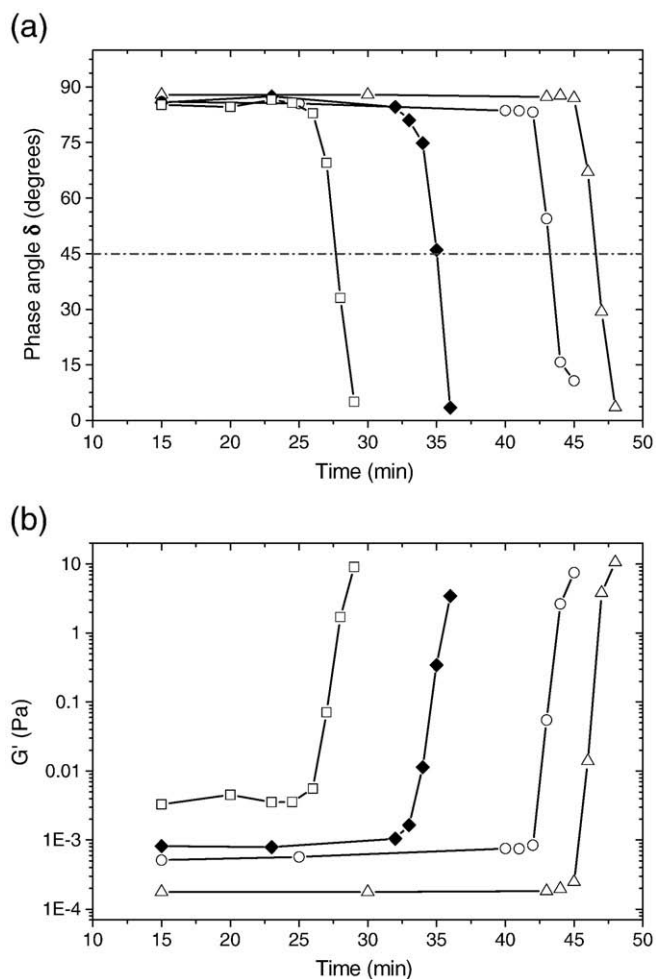


Fig. 4. Comparison of microrheology with bulk rheology for acidification of sodium caseinate solutions of different concentrations: Δ , 2 wt.%; \circ , 5 wt.%; \blacklozenge , 7 wt.%; \square , 10 wt.%. (a) Time-dependent development of phase angle δ calculated from particle tracking data at 20 °C. (b) Time-dependent development of storage modulus G' (1 Hz) from small deformation bulk shear rheology at 20 °C. Data taken from Moschakis et al. [55].

Experiments similar to those described above were carried out [55] on acid sodium caseinate systems containing fluorescent colloidal particles of various sizes (0.2–0.9 μm) and having different surface coatings (polyethylene glycol, carboxylate groups or polystyrene). In each case it was observed [55] that individual particles adhered to the aggregated protein network at pH values closely approaching the casein pI . That is, all the particles were found to be incorporated into the developing caseinate gel network, with none remaining in the pores. A similar finding was also reported [58] for acid milk gels as studied by combined particle tracking and diffusing wave spectroscopy.

Another exciting application of added tracer particles is to probe microstructure and microrheology of liquid interfaces [59]. Particle tracking has been used recently to monitor the development of the microrheology of an interfacial protein layer [60]. Fig. 5 shows some recently published MSD data for polystyrene particles (diameter 1 μm) at the air–water interface during the adsorption of β -lactoglobulin at pH = 5.2. In the early stages after (a) $t = 3$ min and (b) $t = 45$ min, all the particles have MSD values that increase linearly with lag time τ , indicating diffusion within a purely viscous interface. At intermediate film ages, corresponding to (c) $t = 52$ min or (d) $t = 60$ min, the trajectories are divided into two distinct populations exhibiting either diffusive motion ($\alpha \sim 1$) or non-viscous localized motion ($\alpha \sim 0$). This bimodal distribution is indicative of mechanical heterogeneity within the adsorbed layer. At the late adsorption stage ($t = 110$ min) the constancy of the MSD values for all the particles in Fig. 5(e) indicates

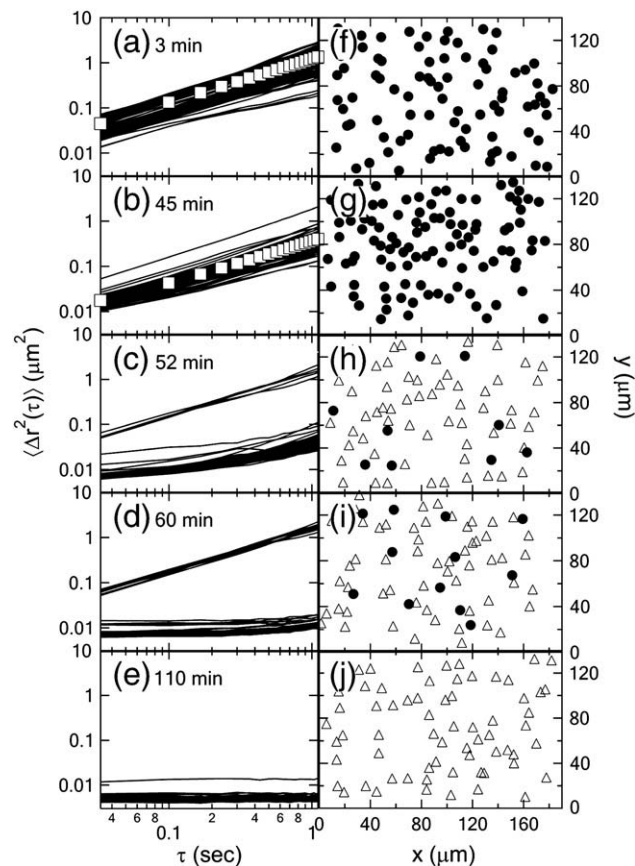


Fig. 5. Mean-squared displacement (MSD) versus lag time τ for individual microspheres (1 μm) confined to the air–water interface of a solution of 50 $\mu\text{g mL}^{-1}$ β -lactoglobulin at pH = 5.2 as a function of time since introducing the protein: (a) 3 min, (b) 45 min, (c) 52 min, (d) 60 min, and (e) 110 min. The open squares in (a) and (b) are ensemble-averaged data. The scatter diagrams (f)–(j) show the positions of the individual particles at ages (a)–(e) exhibiting diffusion (\bullet) or localized motion (Δ). Reproduced from Lee et al. [60] with permission.

that the protein film has achieved a homogeneous elastic character. The same authors reported results of experiments of the *active* microrheology of adsorbed β -lactoglobulin layers using ferromagnetic nanowires (lengths 10–30 μm). These results also showed an increasing interfacial viscosity at early times and evidence of mechanical heterogeneity at intermediate times. However, whereas passive particle tracking showed behaviour that was insensitive to pH, the active microrheology at late times was strongly pH dependent, with rigid elastic behaviour observed at pH = 5.2, but a predominantly viscous response at pH = 7. This contrasting behaviour was attributed [60] to the relatively low yield stress of the protein film under neutral pH conditions.

A further technical advance in particle tracking methodology is known as two-particle (or two-point) microrheology. This is based on cross-correlating the motion of pairs of tracer particles in order to probe viscoelastic properties of the medium on the larger length scale of the particle separation. The advantage of this analysis method is that the results are independent of the size and shape of the particles, and of any depletion effects of biopolymers in the immediate vicinity of individual particles. Hence the method tends to show a much closer correlation with bulk rheological measurements. This technique of two-particle microrheology has been applied with some success to solutions of guar gum [61] and pectin gels [62]. Two-particle microrheology has also been applied recently to the behaviour of charged polystyrene particles adsorbed at the oil–water interface [63] where the technique minimizes the effects of tracer particle surface chemistry (hydrophobic/hydrophilic balance) on the measured results, especially for oil phases that are highly viscous or viscoelastic [64].

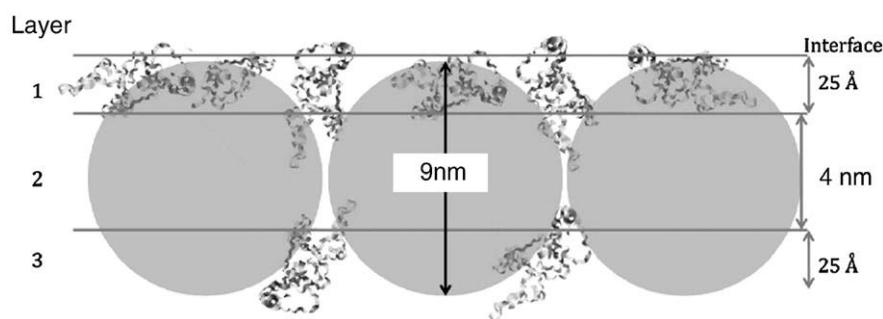


Fig. 6. Schematic representation of the interfacial structure of an adsorbed layer of β -casein-nanoparticle complex at pH = 7 based on neutron reflectivity measurements with isotopic contrast variation between protein and silica nanoparticles (diameter 9 nm). Reproduced from Ang et al. [86] with permission.

5. Challenges and outlook

The behaviour of dispersed systems within the human digestive system has now emerged as a major topic of research interest. This problem is a lot more complex than most of the problems tackled so far by food colloid researchers. Any real progress will necessarily have to involve collaboration with scientists from various other disciplines such as biochemistry, microbiology, and medicine. It is recognized that some useful preliminary progress has already been made, as described in recent review articles [65–69]. However, the research landscape still remains somewhat incoherent and immature, as reflected in the diverse nature of *ad hoc* experimental approaches currently being adopted by different research groups.

Any understanding of what happens to food colloid systems as they pass through the digestive system must surely take account of how the stability and interactions between the various molecular and colloidal components are influenced by the changing local environmental conditions. This includes variations in pH and ionic strength, and the presence of varying concentrations of lipases, proteases, bile salts, phospholipids, and so on. As much of the existing published data on the stability of food colloids relates to aqueous systems of constant pH (around neutral) and low ionic strength, there is need for systematic *in vitro* studies of model systems under more extreme conditions. Experiments on systems containing various kinds of biopolymers and fats need to be performed at 37 °C as well as at ambient and elevated temperatures. The physico-chemical properties of model systems containing bile salts and/or phospholipids require detailed comparison with those also containing synthetic food emulsifiers. There is the question of how the enzymatic activities of lipases and proteases are affected by the details of colloidal structure, and how the hydrodynamic conditions existing *in vivo* influence the mechanisms of structural breakdown and nutrient absorption.

Another outstanding influence on future food colloids research has a strong biomedical emphasis — this is the topic of controlled release and nutrient delivery. To some extent this is more technology than science, since it involves applying the existing knowledge of the structures and properties of colloidal systems for the fabrication of capsules for encapsulation and release of specific bioactives [70–73]. A wide range of self-assembled delivery systems are under investigation based on proteins [74,75], polysaccharides [76], monoglyceride liquid crystals [77,78] and microemulsions [79]. Solid knowledge is still limited, however, concerning the internal structure of mixed biopolymer nanocapsules and the structure of mixed biopolymer layers. In particular, information is lacking on how the sequence of introduction of biopolymers to the interface affects the time-dependent structure of mixed layers of protein + protein [80] or protein + polysaccharide [81]. In the future, this writer believes that food researchers should make more use of the powerful techniques of small-angle neutron scattering and neutron reflectometry [82] to establish the detailed structure of biopolymer nanoparticles and multilayers at solid and fluid interfaces [83–85]. An example of the level of useful structural information that can

be provided is illustrated schematically in Fig. 6 for the case of β -casein-nanoparticle complexes adsorbed at the air–water interface at neutral pH [86]. It was inferred from reflectometry data on the equilibrium adsorbed layer that the interfacial silica nanoparticles were ‘sandwiched’ by layers of protein, with two β -casein molecules for every particle in layer 1 and one in layer 3, where layer 1 represents locations closest to the air–water interface (see Fig. 6).

An extremely active current area of research in general colloid science is the stabilization of emulsions and foams by particles of microscopic or nanoscale dimensions [87,88]. Although the proportion of this research that is as yet directly applicable to foods is necessarily limited, it does appear that the special properties of particle-laden interfaces may have much to offer to food colloid scientists [89,90]. Fat crystals are a particularly important structural component of many aerated and emulsified products [91], and the development of microbeam X-ray diffraction facilities is offering exciting opportunities to study microstructure and crystallization mechanisms at the interface of a single oil droplet [92]. As part of the trend towards fat replacement technologies, a key challenge is to develop functionally effective nanoparticles and microparticles based on ingredients acceptable for use in food manufacturing. In this context, there is need to understand better the properties of colloidal assemblies composed of mixtures of (nano)particles and biopolymers, including the interfacial structuring of particles in phase-separated biopolymer mixtures [93]. The protein component in food colloids commonly exists in both molecular and aggregated forms, but in many situations it is unclear as to the relative extent to which each of these two forms controls the (in)stability behaviour. A notable attempt to address this issue directly has recently been reported for aqueous foam films stabilized by β -lactoglobulin [94] and protein–polysaccharide electrostatic complexes [95].

In summary, here is the list of the four main topics (the ‘known unknowns’) which the author considers worthy of increased research attention over the next few years:

- Emulsion stability under extreme conditions (pH, ionic strength, enzymes, *etc.*)
- Breakdown of particles, aggregates, gels, *etc.*, under different hydrodynamic conditions
- Structure of multicomponent layers at oil–water and air–water interfaces
- Properties of colloidal systems composed of mixtures of biopolymers and nanoparticles (including protein aggregates).

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