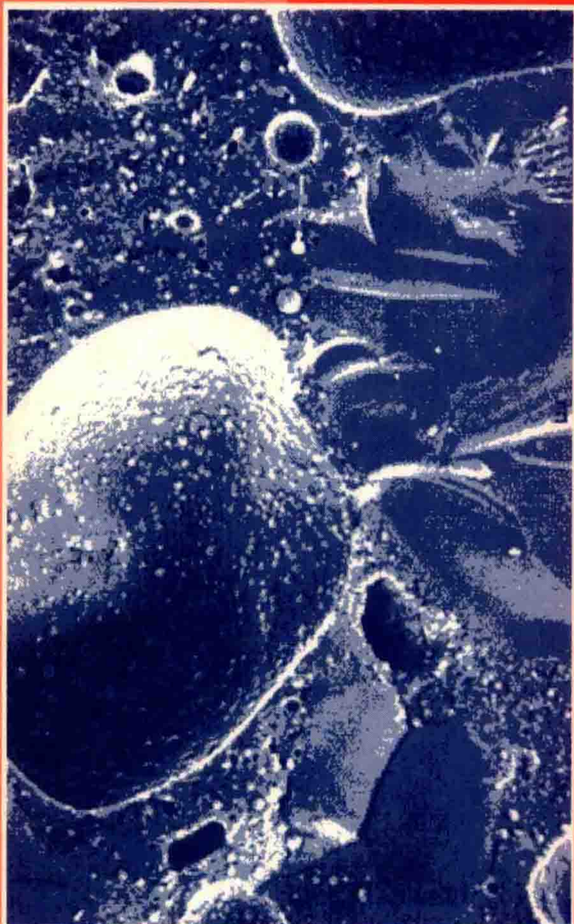
ADVANCES IN FOOD COLLOIDS



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Advances in Food Colloids

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Preface

The field of food colloids is concerned with the physical chemistry of food systems viewed as assemblies of particles and macromolecules in various states of supramolecular and microscopic organization. The objective is to relate the equilibrium and dynamic properties of the system to the interactions amongst the constituent molecular and particulate entities. The emphasis is on structure and kinetics at the colloidal scale, and with the distribution of molecular food components (proteins, lipids, polysaccharides, *etc.*) between dispersed and continuous bulk phases (water, fat, air, *etc.*) and various kinds of interfaces (oil–water, air–water, *etc.*). Food products such as butter, cheese, ice-cream, margarine, mayonnaise and yoghurt are all examples of food colloids.

This book describes some recent experimental and theoretical developments in the field of food colloids. By way of background, we start with a brief survey of the current consumer trends which may point the way towards future research opportunities in the field. Chapter 1 also attempts to illustrate the way in which advances in instrumental methods and experimental investigations of well-defined mixed protein–surfactant systems are offering new insights into the structure of protein adsorbed layers and the competitive adsorption of proteins in oil-in-water emulsion systems.

The two main macromolecular functional ingredients in food colloids are proteins and polysaccharides. Chapter 2 sets out the main factors affecting the structure and interactions of food proteins in various states of unfolding and modification. Chapter 3 focuses on the specific role of protein–polysaccharide interactions in determining the stability and rheological behaviour of mixed biopolymer systems. The increasing role for computer simulation in modelling food colloidal systems is described in Chapter 4 together with an analysis of the fundamental assumptions underlying the main simulation techniques commonly employed.

Chapters 5 and 6 describe two powerful experimental techniques—NMR and ultrasonics—which the authors consider worthy of special attention by those working in the field over the next few years. Fat crystallization and emulsifier interactions have a crucial influence on the stability and texture of many food products. Chapter 7 focuses on some fundamental issues in relation to mechanisms of fat crystallization in model oil-in-water emulsions. Chapter 8 describes the role of micellar aggregates in influencing the properties of surfactant-containing solutions and emulsions with particular emphasis on solubilization aspects. Chapter 9 describes recent progress in the formulation of fine protein-stabilized multiple emulsions having potential use for flavour encapsulation or in developing new fat-reduced products. Finally, Chapter 10 lists a few additional areas where there have been substantial advances, and then the book concludes with some final remarks about the 'image' of food colloids.

This book is meant to some extent to be a companion volume to the book *Colloids in Food* (Applied Science, London) written some 15 years ago by one of the authors (in collaboration with G. Stainsby). We do not attempt here to cover again the basic principles of colloid science or the older food science literature surveyed previously. Mostly included here is material which was not properly covered in *Colloids in Food* or new information from recent research carried out during the past 10–15 years. The emphasis is very much on fundamental studies of model systems—as opposed to more empirical studies on real foods. Readers will probably not be too surprised, therefore, to discover that a considerable proportion of the subject matter described here is taken from our own research interests. Despite this inevitable bias, we have tried, nevertheless, to take account of new developments on the broader horizon. Our aim has been to achieve a reasonable balance of coverage between theory and experiment, between principles and applications, and between the molecular and the physical approaches to the subject. Where we have fallen short of this objective, we can only apologize for any omissions or misinterpretations that may have occurred.

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1 Trends and Developments

1.1 Introduction

> "To some the word 'colloidal' conjures up visions of things indefinite in shape, indefinite in chemical composition and physical properties, fickle in chemical deportment, things infilterable and generally unmanageable". (Hedges, 1931)

Any scientist wishing to define a system that is too messy for rigorous experimentation or theoretical analysis might refer to it colloquially as a 'dog's breakfast'. With the same pejorative connotations, this phrase might also be applied to the many colloidal systems intended for human (as well as canine) consumption, since a 'colloid' is generally recognized as being at the messy end of physical chemistry, and a typical 'food colloid' is certainly amongst the most compositionally complex and ill-defined of all manufactured colloids. The traditional way of addressing this problem of food colloid complexity has been to study instead some much simpler model systems, and then to attempt to argue that the behaviour of a well-chosen model system is similar to that of the real food colloid. Although this approach does have its sceptics (Darling and Birkett, 1987), the considerable success of scientists and technologists over recent years in understanding some of the basic physico-chemical principles underlying the formulation of a wide range of food products such as salad dressings, ice-cream, low-fat spreads and cream liqueurs is a reasonable testament to the considerable value of studying these model colloidal systems (Dickinson, 1994a, 1995a).

At its best, the application of the colloid science approach enables us to filter out many of the less important molecular features that are not directly relevant to observable changes in macroscopic properties during food processing and storage. We are not concerned explicitly with the detailed chemistry of small molecules in food (*e.g.*, water, lipids, salts, sugars, *etc.*), except insofar as this chemistry affects the interactions between the dispersed entities (particles and macromolecules) and hence their state of aggregation (Dickinson, 1990a). What we are concerned with is the description of the system as a collection of dispersed particles and macromolecules in various states of organization on the colloidal and microscopic scales. We are especially interested in the way by which structure, texture and shelf-life are affected by the distribution between interfaces and bulk phases of various stabilizing species—surfactants, proteins, polysaccharides, fat crystals, protein particles, and so on.

Arguably, the most important class of food colloids is the dairy-type emulsion system, and so the study of the properties of milk proteins adsorbed at oil–water interfaces is a central research theme in this field. In relation to product stability and shelf-life, colloid scientists are not concerned with microbiological aspects *per se*, though they may be interested in how colloidal structure affects the distribution of micro-organisms or the kinetics of microbial growth (Brocklehurst *et al*., 1994).

Advances in food colloids are necessarily controlled by a number of different types of influences—some competing, some complementary. Progress in the investigation of model systems in the laboratory is highly dependent on the availability of new experimental techniques and advanced instrumentation. Covered in this book are two examples of powerful techniques with considerable potential—nuclear magnetic resonance (NMR) (Chapter 5) and ultrasonics (Chapter 6). Several other valuable techniques, covered in a separate new volume (Dickinson, 1995b), include such diverse experimental methods as laser light scattering, electron microscopy, small-angle neutron scattering, confocal laser scanning microscopy, mechanical spectroscopy (dynamic oscillatory rheology) and Fourier transform infrared spectroscopy. Undoubtedly, a major factor that has been responsible in recent years for enhancing the performance of laboratory instrumentation is the advance in microelectronics. This has led to improved quality of displayed output, computer control of experiments and on-line data analysis. In addition, the greater access to small, powerful desk-top computers and work-stations has led to more opportunity for testing experimental data against theory, and for the development of computer simulation models of colloidal aggregation and adsorption phenomena (see Chapter 4).

We must not forget, of course, that there are also various non-technical factors that can have a major effect on the priorities of research funding organizations, and therefore on the types of projects undertaken by individual groups of researchers. In particular, governmental and commercial funders of food research are likely to pay increasing attention to perceived changes in consumer preferences or social trends. Two specific priorities which have had already increasingly important (positive) implications for the funding of research in the food colloids field are (i) the development of improved low-fat dairy-type products, especially low-fat yellow spreads (Keogh, 1995), and (ii) the development of 'natural' ('green') emulsifiers as replacements for 'synthetic' food emulsifiers (Dickinson, 1993a). Scientific research which has been stimulated by these trends includes work on protein–polysaccharide interactions (Chapter 3) and multiple emulsions (Chapter 9). Other possible future issues of relevance to food colloid scientists can perhaps be recognized by a careful consideration of current social trends in the preparation, purchasing and consumption of foods.

1.2 Consumer Trends

It seems reasonable to assume that what every consumer looks for is food that is (i) tasty, (ii) wholesome, (iii) varied (exciting!), (iv) convenient and, of course, (v) inexpensive. To satisfy fully all these requirements in the same product is a difficult (maybe impossible) challenge for the food industry. In reality, of course, while we all have the same list of basic requirements, an individual consumer may differ considerably from others in the relative emphasis that he or she places on these different requirements. Amongst the very large number of socio-economic factors affecting individual diets and food choice are appetite, ingrained habits, time pressure, age, personal income, state of health, cultural background, advertising, media reports, government advice, family food attitudes and so forth. While for an individual consumer the relative emphasis given to the various factors may change substantially with time and place, some average trends in whole populations of consumers can be usefully identified.

The top ten trends in the United States in 1994 were identified by the journal *Food Technology* as follows (Sloan, 1994):

(1) Increasing role of food and food ingredients in self-medication and disease prevention (H).
(2) Switch to 'fresh' in most food categories (H, T).
(3) Return to 'organic' food production (H, T).
(4) Gradual shift from animal-derived to plant-based meals (H, T).
(5) Demand by 'ordinary' consumers for foods which are 'energy enhancing'—both physically and mentally (H, C).
(6) Desire for foods that are speedily and easily prepared—yet are nevertheless tasty, fresh, and nutritionally sound (C, T).
(7) Disenchantment with microwave cooking (T).
(8) Inclination to eat exactly where and when it is convenient (C).
(9) Experimentation with more highly flavoured and ethnic foods (T).
(10) Health-based demand for products containing active cultures (H).

In the above list we identify each of the trends as being strongly associated with one (or two) of three main 'drivers': diet and health (H), taste (T) and convenience (C).

The issue of 'diet and health' seems destined to become an increasingly important influence affecting new food product development over the next few years. Health authorities in many developed countries are now actively recommending an increased consumption of complex carbohydrates (starch) and fibre, and a reduced consumption of total and saturated fats. The evidence supporting these recommendations is generally strong (Topping, 1993). Moreover, recent surveys in Europe and the United States indicate that a large majority of consumers do now believe that there is a strong relationship between good eating habits and the prevention of serious illnesses such as heart disease and cancer. While this knowledge by itself does not necessarily lead on to the actual adoption of a healthy diet, it does mean that today's nutrition-literate consumers are giving a notionally higher weighting to health issues when choosing from the menu in the restaurant or deciding about what to put in the trolley at the supermarket. Furthermore, consumer beliefs in the United States have now gone well beyond the traditional understanding of nutrition. According to Sloan (1994), over 60% of Americans believe that there is a connection between food and mood, and three-quarters link diet with longevity and appearance. While there remains considerable concern by consumers over the intake of potentially harmful ingredients (*e.g.*, fat, cholesterol,† salt, 'additives'), a new trend is for consumers actively to select health-promoting ingredients for inclusion in their diets (*e.g.*, antioxidant vitamins, fibre, folic acid)—irrespective or not of whether the health claims for such ingredients are approved by the recognized international authorities. One positive consequence of the growing interest in vitamins and minerals is the welcome increase in fresh fruit and vegetable consumption. Other consequences are (a) the increased appeal of conventional manufactured foods when fortified with vitamins or antioxidants, and (b) the rapid growth in availability, especially in Japan and Germany, of neutraceuticals and phytochemical-fortified drinks. What this implies is a general trend for previously established boundaries between food and medicine to become less well defined.

Tasty food is still very much synonymous with fresh food or freshly prepared food. The word 'fresh' now tops the list of the most desirable label claims; 'fat-free' is a distant second (Sloan, 1994). To respond to this demand, it seems likely that manufacturers of packaged (non-fresh) food will increasingly attempt to adopt packaging or processing techniques that lead to a 'fresh' taste, and to attempt to incorporate added flavour compounds or particulate materials that give the appearance of 'freshness'. Further research into topics such as gas-flushed packaging, high-pressure processing and flavour release are likely be strongly encouraged by the continuing demand for the 'freshness' attribute in the food products of the future.

At the same time, there remains a continuing drive towards convenience in the style and location of our eating habits (*e.g.*, 'take-aways', 'eating-on-the-run', 'single-serve packaging'). However, the convenience requirement is now counterbalanced by an increasing unwillingness by many consumers to sacrifice taste and nutrition simply in order to get 'fast food'. This trend is epitomized, for instance, by some recent disenchantment with microwave technology. Whether used in the home or at the fast-food restaurant, it is

†The role of various dietary ingredients in relation to blood cholesterol levels remains a controversial issue (Kritchevsky, 1994).

becoming generally accepted that the microwave oven produces food with a less satisfying taste than conventional cooking methods. So it seems that the microwave oven is now regarded by consumers more as a method of heating food than as a method of major meal preparation.

1.3 Attitudes to Fat in the Diet

Of all the diet-related factors relevant to general health, the control of the amount and type of fat in our food probably still remains the most prominent issue of concern to medical authorities in western countries. Many respected bodies have drawn links between fat consumption and chronic conditions such as obesity and cardiovascular diseases, and this has resulted in widespread recommendations from government health departments for reduced human consumption of fats in general, and of certain saturated fatty acids in particular.† It would seem reasonable to suppose (Mela and Raats, 1995) that these recommendations will continue to have enormous implications for the attitudes and purchasing behaviour of western consumers. In turn, this means that manufacturers will continue to strive to produce high-quality, low-fat alternatives to compete in the marketplace against traditional dairy-based food colloids. The removal of fat from these traditional products without loss of perceived texture or flavour characteristics represents a formidable challenge for the food technologist (Lucca and Tepper, 1994; Kilara, 1995). Since fat is typically replaced by a mixture of water and food macromolecules, a spin-off from the development of low-fat products has been greatly increased fundamental research interest in mixed aqueous biopolymer systems and the interactions of biopolymers with other food ingredients (protein–protein, protein–lipid, protein–polysaccharide, and so on). Structures and textures in food gels, emulsions and dispersions containing mixtures of proteins and polysaccharides have generated considerable recent interest (Chapter 3). It seems to us that a proper appreciation of the textural significance of these various kinds of mixed interactions—and of general colloidal phenomena like competitive adsorption, thermodynamic incompatibility and depletion flocculation—is a necessary pre-condition for a genuine understanding of the key processing factors affecting the formulation of these low-fat dairy products (Dickinson, 1995a).

While eating is for many people one of the main pleasures of life, the pleasure to be derived from eating different types of food is far from equal. The perceived conflict between hedonistic and health-pursuing influences

†A number of aspects of lipid nutrition do, nevertheless, remain rather controversial. One contentious issue is the extent to which particular saturated fatty acids or *trans* fatty acids raise the blood cholesterol level, and the relative values of monounsaturated and polyunsaturated fatty acids in counteracting this effect (Beare-Rogers, 1995).

has led to an ambivalent attitude by many people towards high-fat foods. Surveys of food preferences indicate that most consumers, especially children, have a strong liking for fat-containing foods such as chocolate, cheese and ice-cream (Tuorila-Ollikainen and Mahlamäki-Kultanen, 1985; Tuorila and Pangborn, 1988). Pleasurable characteristics associated with these products include both the flavour (including sweetness) and the textural features. Amongst the attributes universally cited as positive are textural characteristics such as 'smoothness', 'creaminess' and 'melt-in-the-mouth'. Intriguingly, it has been found that the very same people who express a strong liking for chocolate, ice-cream, *etc.*, give a predominantly negative response when asked whether they like 'high-fat foods' in general (Tuorila and Pangborn, 1988). What this tells the psychologists is that laudable general long-term intentions about healthy eating can, in practice, be overcome by more immediate impulses towards the pursuit of pleasure. This tendency is further reinforced by some advertisers of products like chocolate or ice-cream who aim to put into the minds of consumers the prospect of a more exciting and sexy lifestyle!

There is little doubt that the overall fat content and the emulsion structural properties have a crucial influence on the texture and mouthfeel of most dairy products. It is also recognized (Cooper, 1987) that these favourable characteristics are rather difficult to mimic with non-fat ingredients. Sensory assessment of fat content by consumers does seem to be largely a function of the oral textural characteristics of food—it has been demonstrated (Mela, 1988) that eliminating the ability to detect volatile fat-associated flavour compounds (*e.g.*, by placing nose clips on the assessors) has virtually no influence on judgements of the fat content or the creaminess of fluid milk products. While visual cues may be used by consumers to discriminate amongst milk samples of different fat content (Pangborn and Dunkley, 1964; Tuorila, 1986), it seems that judgements of fat content can also be made reliably in the absence of such visual cues (Mela, 1988). Assessment of apparent viscosity in the mouth at a shear-rate of *ca.* 50 s^{-1} (Sharma and Sherman, 1973) appears to be a very relevant factor in the perception of fat content. It has been shown (Mela *et al.*, 1994) that increasing the viscosity of a model oil-in-water emulsion (by changing homogenization conditions, fat types and non-fat ingredients) can produce an enhancement in the perceived fat content. At the same time, however, it is suggested (Mela and Raats, 1995) that there is a textural contribution of emulsified fat *per se* which is not readily imitated by these viscosity manipulations. One such factor is undoubtedly the influence of fat content on flavour perception and acceptability. (Lucca and Tepper, 1994)

In practice, despite apparent evidence to the contrary, distinguishing between textural considerations and flavour-related perceptions may not be an entirely straightforward matter. Fats such as butterfat contain many naturally occurring flavour compounds. Also the presence of fat in a food may modify the perception of other non-fat flavour compounds. It would appear that there is a need for combined physico-chemical and sensory research to understand better the factors affecting the perception of flavour in emulsified foods. The sort of question for which there is as yet no adequate answer is this: during eating, how quickly, and to what extent, are the flavour compounds distributed between the oil phase, the saliva and the taste receptor cell membranes within the oral cavity? Arriving at a convincing answer to such a question raises such issues as the colloidal nature of saliva (Rykke *et al.*, 1995), the theory of flavour release from emulsions (McNulty, 1987; Bakker, 1995), and the mechanism of emulsion phase inversion in the mouth (Barylko-Pikielna *et al.*, 1994). This seems like a fruitful area of food research where colloid scientists, working in close collaboration with nutritionists and biochemists, should reasonably be encouraged to direct their collective attention over the next few years.

1.4 Colloid Science Issues in Food Emulsion Processing

During manufacture, most food emulsions are subject to processing operations involving variation in temperature (pasteurization, sterilization, evaporation, spray drying, freezing, crystallization, cold storage) or application of mechanical forces (*e.g.*, stirring, mixing, flow along pipes, packaging). With some foods (milk, cream liqueur, *etc.*) it is important that the emulsion remains stable over a wide range of temperatures and flow conditions, whereas for others (butter, margarine, whipped cream, ice-cream, *etc.*) the controlled emulsion destabilization is an integral part of the production. Against this technical background, it would seem to be extremely important for the food scientist to be able to obtain a detailed understanding of the effect of heat and shear forces on the molecular and colloidal aspects of food emulsions. Surprisingly, however, the effects of such processing conditions on emulsion properties has so far received relatively little attention from scientists carrying out fundamental research in this field.

Many food emulsions are stabilized by proteins which are particularly susceptible to alteration of their molecular and functional properties as the temperature changes. The molecular structure and interactions of proteins in aqueous solution depend principally on physical forces that are rather sensitive to temperature (see Chapter 2). The contributions of the hydrophobic effect and configurational entropy increase with increasing temperature, whereas the effects of hydrogen bonding, electrostatic interactions and van der Waals forces decrease with increasing temperature. Heating leads to changes in macromolecular structure and interactions of proteins. Globular proteins tend to unfold, and the increase in the strength of the hydrophobic effect leads to enhanced protein–protein interactions at elevated temperatures. These molecular changes lead to various phenomena such as the flocculation of protein-stabilized emulsions during sterilization, the formation of β-lactoglobulin–casein complexes in heated milk,† the thermal gelation of whey proteins and the dissociation of casein micelles on cooling. Temperature-induced changes in the structure and interactions of adsorbed proteins at the oil–water interface or suspended in the aqueous phase will affect the stability and rheology of a protein-stabilized emulsion. Enhanced interfacial protein–protein interactions may lead to an increase in the thickness and mechanical strength of the adsorbed layer, thereby promoting stability against coalescence. On the other hand, increased protein–protein interaction will typically produce a reduction in stability against flocculation.

Dispersed droplets coated by milk proteins in a quiescent emulsion are stable to coalescence because the adsorbed protein layer provides good steric stabilization. However, coalescence does become much more evident if droplets are subjected to shear forces, or are kept close together for extended periods, *e.g.*, in a creamed layer or concentrated emulsion (Dickinson, 1992a). Stability of emulsions to shear forces (orthokinetic stability) depends on the composition and structure of the adsorbed protein layer. The presence of low concentrations of calcium ions or small-molecule emulsifiers can have a large effect on the orthokinetic stability (Chen *et al.*, 1993). Further work is needed on the relationship between the structural and mechanical properties of adsorbed layers and on the effect of various types and strengths of flow fields on the stability of well-defined emulsion systems.

Variations in temperature may also influence the properties of the dispersed oil phase. The droplets in many food colloids—notably dairy emulsions—are partially crystalline at temperatures commonly encountered during manufacture, storage and consumption. In practice, the proportion of crystalline fat is dependent not only on temperature, but also on the size of the emulsion droplets, the type(s) of emulsifier present and the temperature history of the product. Droplet density changes as the oil crystallizes and this affects the rate of creaming. Partially crystalline droplets are susceptible to a phenomenon called 'partial coalescence' (van Boekel and Walstra, 1981; Darling, 1982; Boode and Walstra, 1993) in which a crystal on one droplet penetrates into the liquid part of another droplet; as the fat crystal is 'wetted' better by the oil than by the aqueous phase, the collision leads to the pair of particles becoming stuck together. The rate of this process is greatly enhanced by mild stirring or temperature cycling of the emulsion. The result of partial coalescence is a dramatic increase in the

†An important preliminary step in yoghurt manufacture is the heat treatment of the milk. This causes β-lactoglobulin to interact *via* disulphide linkages with κ-casein on the casein micelles. The treatment specified to give the best yoghurt texture is usually 85–95 °C for 5–10 min (Haylock *et al.*, 1995).