



Review

Exploring the frontiers of colloidal behaviour where polymers and particles meet[☆]

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ABSTRACT

Two simple representations are commonly invoked to interpret the physicochemical properties of colloidal systems: the rigid particle model and the flexible polymer model. This article compares the essential features of these two ideal descriptions of the main functional entities involved in the stabilization of food suspensions, emulsions and foams. Attention is directed towards the factors that affect the structural and mechanical properties of adsorbed layers and the influence of nanoparticles and polymers on colloidal interaction forces between the surfaces of microparticles and emulsion droplets. In systems containing mixtures of particles and polymers, the various species may remain dispersed, or they may become associated into complexes, aggregates and networks. Adsorbed protein layers may be described using a polymer-like model (casein) or a particle-like model (hydrophobin), or a kind of composite representation (most globular proteins). Certain important food particles, like casein micelles and swollen starch granules, are themselves composed of interacting polymeric building blocks, and they exhibit mechanistic behaviour that deviates substantially from both simple solid spheres and simple molecular polymers. One particular type of hybrid particle–polymer entity that is attracting current interest from many researchers in soft matter physics and food colloid science is the responsive microgel.

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1. Introduction

This is an article describing one scientist's personal journey of discovery and exploration along some of the frontiers of colloid science where polymers and particles commonly meet. The main

theme of the narrative is on the way in which a combination of polymeric and particulate entities controls the interfacial and stability properties of colloidal systems. Consistent with the author's own research interests, the emphasis here is on oil-in-water emulsions formulated with biopolymer ingredients. The concepts underlying this subject matter are relevant to a large proportion of the articles currently being published in the journal *Food Hydrocolloids*, and also to the research papers presented at various international conferences devoted to the areas of food colloid functionality, nutrient delivery systems, and structure/digestion/health relationships.

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Food colloids are soft matter systems containing mixed ingredients derived from plant or animal sources. The physico-chemical processes that occur during the formulation, storage and eventual consumption of these systems depend on how the constituent ingredients interact with one another to produce a diversity of structural complexity on different length scales ranging from the molecular to the macroscopic (Dickinson, 2012; Mezzenga, Schurtenberger, Burbidge, & Michel, 2005; van der Sman, 2012). In trying to reveal the basic mechanisms that underlie complex reality, and hence to understand the key factors controlling the stability and textural properties of food colloids, it is conceptually useful to adopt a deliberately reductionist approach involving a small number of simple model systems (Dickinson, 1989, 1992). The two most familiar models are the rigid spherical particle and the flexible polymer chain. The former is convenient for describing diverse structural entities such as emulsion droplets, fat crystals, protein aggregates and starch granules, whereas the latter is an adequate representation of many polysaccharides and some proteins. However, various uncertainties and ambiguities are commonly encountered. This means that the most appropriate choice of model in many specific cases is actually not so obvious.

The colloidal behaviour of food protein ingredients may be effectively described using either or both of the above types of models, depending on the protein's specific molecular structure, the kind of functionality being considered, and the particular set of experimental conditions (Dickinson, 1994, 1999a, 2001). For instance, the rigid particle model can be used with some success to represent structural changes in solutions of globular proteins or dispersions of protein colloids (e.g. casein micelles) during the growth of fractal-type aggregates and particle gel networks, as triggered by the destabilizing influences of heating, acidification or enzyme action (Bremer, van Vliet, & Walstra, 1989; Dickinson, 1997; Nicolai, 2007). Similarly, for a globular protein that retains most of its native structure upon adsorption at a fluid interface, the rigid particle model provides a useful basis for simulating the structure and surface rheology of the adsorbed protein layer (Pugnaloni, Ettelaie, & Dickinson, 2005; Wijmans & Dickinson, 1998), and also for understanding the stability behaviour of protein-coated emulsion droplets (Dickinson, 2001). On the other hand, when considering the interfacial functionality of a highly disordered protein like casein, the behaviour is more appropriately represented in terms of the flexible polymer chain model (Dickinson, 1999b; Parkinson, Ettelaie, & Dickinson, 2005). Rather more problematic in terms of the correct choice of model system is the sort of globular protein that unfolds extensively upon adsorption, or the one that self-assembles into highly ordered structures in bulk media or at fluid interfaces (Mezzenga & Fischer, 2013).

Food colloids typically contain mixtures of particles and polymers, present together as multicomponent species in aqueous media, or adsorbing in competition at solid or fluid interfaces. Sometimes the coexisting polymers and particles repel one another; sometimes they stick together into aggregates and networks. The character and strength of these polymer–particle interactions determines the structure, stability and rheology of the overall system. Furthermore, we recognize that various important classes of particles found in food colloids are themselves made from aggregated, self-assembled or cross-linked polymers. This implies that their mechanistic behaviour deviates substantially from that of both the solid sphere and the flexible polymer. Common colloidal ingredients of this type include native casein micelles, partially gelatinized starch granules, and microgel particles based on cross-linked hydrocolloids or heat-treated whey proteins (Dickinson, 2015c).

In the present article the author outlines some of the factors that influence the choices of model systems in the field of food colloids.

Attention is given to specific cases in which additional complexity arises from the mixing together of polymers and particles, or because one particular colloidal ingredient possesses combined polymer–particle characteristics. However, quantitative theories of colloidal stability and instability are not described in any detail here, and the author makes no claim for comprehensive analysis or definitive answers. His aim is just to point out some complications and challenging ambiguities that remain to be resolved, and to highlight areas where he believes that current progress is being made at the frontiers where polymers and particles meet. As with all the best adventures, one expects the fulfilment and excitement to lie not so much in the achievement of reaching the final destination, but in the challenge of experiencing encounters with interesting characters and situations along the way.

“If you don't know where you are going, any road can take you there.”

(Lewis Carroll, *Alice's Adventures in Wonderland*)

2. Mechanisms of stabilization and destabilization: particles versus polymers

Particles and polymers share common general attributes which determine their ability to act as stabilizers and structuring agents. In the first place, each individual particle or polymer occupies some well-defined physical space in solution or dispersion. With gradually increasing concentration in aqueous media, the system's bulk viscosity steadily increases until a critical volume fraction of the added entities is reached (corresponding to solid particles approaching close-packing, or polymer molecules overlapping), whereupon the system is transformed into one exhibiting solid-like rheological behaviour. The resulting microstructure is then potentially effective in conferring stability in a multiphase colloidal system by means of entrapment of suspended oil droplets or gas bubbles held within the resulting viscoelastic network of particles or polymers. In terms of mass concentration, the absolute amount of added material required for this stabilization is, of course, much lower for high-molecular-weight polymers (hydrocolloids) than it is for dispersed solid particles—though the latter is considerably reduced for particles forming fractal aggregates and gels (Bijsterbosch, Bos, Dickinson, van Opheusden, & Walstra, 1995; Dickinson, 2000). A further consequence of the space-filling character of hydrophilic particles and polymers is their common ability, when located at surfaces of oil droplets or gas bubbles, to function as steric stabilizers of oil-in-water emulsions or aqueous foams. The physical thickness of the adsorbed layer at the oil–water or air–water interface provides an effective protective barrier against spontaneous droplet or bubble coalescence during emulsion/foam formation and storage (Dickinson, 1992, 2003).

Solid particles in food vary widely in size—from the nanoscale (similar size range to polymers) to the microscale and beyond. Familiar examples of microscopic crystalline particles (10–20 μm) are native starch granules and milled sugar particles. As well as supplying a pleasant sweet taste, sugar particles have a functional role in controlling the rheology, texture and stability of confectionery products when dispersed at high volume fractions in cocoa butter (chocolate) or a saturated aqueous sugar solution (fondant). The measured yield stress in a concentrated aqueous suspension of sugar particles (>45 wt% solids) is sufficient to prevent creaming of individual gas bubbles of similar size (10 μm) in a model aerated fondant system (Lau & Dickinson, 2007). The long-term ageing of this fondant suspension has been found to enhance further the foam/bubble stabilization by means of a strengthening of the

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