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Graphical Abstract

Characterizing the perfect hydrocolloid stabilizer…

The LEEDS Hydrocolloid Stabilizer

Legendary **E**mulsifying **E**ncapsulating **D**ispersing **S**tabilizing

Highlights

- Assessing the concept of the ideal hydrocolloid stabilizer from various perspectives
- Thermodynamics and dynamics of adsorption, stabilization and interface deformation
- Effect of bulk rheology and tribology on oral processing and sensory perception
- Pharmacokinetic and glycaemic challenges of digestion and function as dietary fibre
- Suggested ideal ingredient: protein–polysaccharide conjugate/complex or microgel

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The perfect hydrocolloid stabilizer: imagination *versus* reality°

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° This article is respectfully dedicated to the memory of Professor Glyn Phillips (1927–2020) whose personal and professional commitment to the world of hydrocolloids research continues to be a source of inspiration to many authors and readers of this journal.

Abstract

We consider the validity of the hypothetical concept of the perfect hydrocolloid stabilizer with particular reference to its functional role in the preparation, storage, eating, and digestion of biopolymer-stabilized oil-in-water food emulsions. From an equilibrium theoretical perspective, it is demonstrated that the optimum macromolecular ingredient is a soluble hydrophilic block copolymer of low net charge containing strongly adsorbing hydrophobic groups located in a single localized region. From a dynamic colloidal perspective, the ideal macromolecular emulsifier/stabilizer is sufficiently flexible to adsorb rapidly at the interface, leading to a thick, coherent interfacial film, which is resilient to catastrophic structural failure. The ideal hydrocolloid is associated with a smooth mouthfeel as a consequence of its relatively high viscosity and its role as a saliva-interacting lubricant in thin films between oral surfaces. It acts pharmacokinetically through its resilience to proteolytic gastric digestion and by the promotion of a diffusive barrier to lipolytic enzymes within the small intestine. From a glycaemic response perspective, it retards gastric emptying by gelling under acidic conditions, and it affects lipid digestion kinetics by binding to lipases and/or chelating bile salts. As dietary fibre, it generates a high viscosity, is highly fermentable, and binds gut-beneficial compounds. Although we accept the implausibility of a single macromolecular species being able to satisfy all these separate requirements in full, we are of the opinion that the most significant of these desirable characteristics are consistent with the generic concept of the perfect stabilizing ingredient as some kind of protein–polysaccharide conjugate, complex, or microgel structure.

Keywords: Proteins; Polysaccharides; Emulsions; Emulsifiers; Oral Processing; Digestion

Contents

1. Introduction

"Perfection's unattainable, but it isn't unapproachable" (Peter Watts, *Blindsight*)

Food scientists are a pragmatic bunch. This applies particularly to those who operate within the research landscape of hydrocolloid functionality and food colloids. A common starting point might involve making a stable oil-in-water (O/W) emulsion for ultimate incorporation into some kind of food product. The modern trend away from the use of small-molecule surfactants would lead us to look increasingly towards 'natural' biopolymer-based ingredients as the source of the emulsifying ingredient. In order to make an emulsion with droplets of sub-micrometre size, we would need to employ some kind of high-intensity homogenization device. While the choices of oil/water ratio and aqueous solution conditions would tend to be mainly determined by the intended product application, the precise processing conditions and system composition could be adjusted empirically to achieve an acceptable result. Typically, we would aim for a final emulsion that is uniform in terms of its visual appearance, and one that possesses good physical stability during quiescent storage with respect to the mechanistic processes of creaming, flocculation, coalescence, and Ostwald ripening (McClements, 2005).

One is aware, of course, that the control of physical stability is only one part of the story. For an emulsion system to be properly exploitable in the food context we have to take account of the overall acceptability of ingredients in terms of their cost, safety, palatability, and potential long-term health implications. An essential requirement is to make a food product that possesses an acceptable sensory response when eaten; whether this condition is satisfied will depend, for instance, on how any added polymeric ingredient interacts with human saliva and with oral surfaces (Sarkar, Ye & Singh, 2017). It may also be desirable to have some control over the rate of emulsion breakdown and colloidal re-structuring during food digestion (Singh, Ye & Horne, 2009; Mulet-Cabero, Mackie, Brodkorb & Wilde, 2020), or to attempt to derive some benefit from the perceived nutritional attributes of certain hydrocolloids (Li & Nie, 2016; Lovegrove et al., 2017). Furthermore, we may aim to exploit food macromolecules as structural components in the fabrication of colloidal delivery systems (Gani, Masoodi, Shah & Shah, 2019) or replace traditional emulsifying ingredients of animal origin with plant-based biopolymers (Sarkar & Dickinson, 2020).

The purpose of this article to offer a challenge to the conventional narrative by addressing a few questions from a more idealist perspective.

1. Is it feasible to imagine some kind of perfect hydrocolloid stabilizer possessing all the key functional attributes required for emulsion stabilization and functionality?
2. Let us suppose that the answer to the above question is 'yes'… then what would be the notional molecular structure of this hypothetical stabilizer, assuming in principle that it could be assembled from the normal chemical building blocks of biology?
3. But if the answer is 'no', what are the theoretical or practical barriers that are preventing the realization of such a perfect solution? And what is the most favourable compromise position that can be realistically achieved?

Before proceeding further, let us clarify what we mean by the term 'stabilizer'. Simply stated, a 'stabilizer' is a substance — usually polymeric in nature — which confers *long-term* physical stability on an emulsion or colloidal dispersion (Dickinson, 2003, 2009a). The stabilizing potential of any macromolecular species is dependent on its detailed molecular structure and on its thermodynamic behaviour in solution and at fluid interfaces (Semenova, 2007; Semenova & Dickinson, 2010). Mechanistically, an individual biopolymer stabilizer can behave in two distinct ways. It may adsorb to the outer surface of solid particles or oil droplets forming a protective polymeric layer that prevents the dispersed entities from sticking close together. Alternatively, or simultaneously, it may modify the rheological properties of the bulk aqueous phase, thereby inhibiting the motion of individual particles and droplets under the influence of gravity, diffusional forces, and interparticle interactions. While not in any way underestimating the great importance of hydrocolloids acting as thickening agents and rheology modifiers, our main focus in this article will be on the functional stabilizing role of biopolymers *via* adsorption at oil–water interfaces.

An emulsifying agent is a surface-active substance that promotes emulsion formation and *short-term* stabilization by interfacial action (McClements, 2005). This functional role is most typically achieved using small-molecule surfactants (polysorbates, phospholipids, *etc*.), although we recognize that many food biopolymers can also function effectively as emulsifying agents (Dickinson, 2009a, 2016, 2017). Soluble proteins such as caseins and whey proteins are especially effective, as are some amphiphilic polysaccharides such as hydrophobically modified starches (Sweedman, Tizzotti, Schäfer & Gilbert, 2013) and certain types of pectin (Ngouémazong et al., 2015). With a capability also to confer *long-term* emulsion stability, these surface-active food biopolymers can act as both stabilizers and

emulsifying agents. In practice, the most appropriate choice of emulsifying ingredient tends to depend on the precise nature of the food product application, as determined by the oil/water ratio, the desired textural properties, and the identity of other components in the formulation. For example, when confronted with the task of making a stable liquid-like O/W emulsion for a neutral-pH dairy-type product (*e.g.* a cream liqueur), the pragmatic food scientist might sensibly choose sodium caseinate as the primary emulsifying agent. But the same investigator would probably opt for gum arabic (*Acacia senegal*) as the emulsifying agent when formulating a low-pH non-dairy O/W emulsion (*e.g.* a citrus-based soft drink). In each of these examples, the interfacial functionality of the emulsifier/stabilizer is of overriding importance to the system properties because the main technical requirement is to prepare a fine liquid-like emulsion (average droplet size < 1 μm) having a moderately low oil content. Such a formulation is required to flow like a low-viscosity Newtonian liquid, and so the droplets needs to be stable towards separating out under gravity in the absence of any polymeric thickening material dissolved in the aqueous phase. On the other hand, if the investigator intends to make a viscoelastic (gel-like) O/W emulsion with texture resembling that of a thick salad dressing or a synthetic cream, the need to rely so much on the interfacial functionality of the emulsifier/stabilizer becomes less stringent. This is simply because, in the case of a semi-solid emulsion, there are additional structuring and rheological factors that can contribute to the physical stability — notably network formation from droplet aggregation, as well as the rheological influence of added polymeric or particle-based thickening agents.

Foods are complicated in terms of structure and composition. In many emulsion formulations, the pragmatic food scientist has to consider the behaviour of mixed functional ingredients having a broad range of emulsifying, stabilizing, thickening and gelling properties. Some of these stabilizing ingredients are plant-based materials of low surface activity and limited solubility. What this means is that a lot of food emulsion systems are predominantly stabilized not by macromolecular stabilizers, but by different kinds of nanoparticles or microparticles (Dickinson, 2012). Some of these particles are located directly at the surfaces of liquid droplets (Pickering stabilization) whilst others function as structuring agents in the gaps between dispersed oil droplets (Dickinson, 2015a). Currently there is considerable interest in the formation and stabilization of food emulsions with different kinds of biopolymer-based particles. These ongoing developments have been set out in recent review articles (Lam, Velikov & Velev, 2014; Xiao, Li & Huang, 2016; Dickinson, 2017, 2020; Calabrese, Courtenay, Edler & Scott, 2018; Murray, 2019a; Sarkar & Dickinson, 2020; Zhao, Zaaboul, Liu & Li, 2020; Shi, Feng, Wang & Adhikari, 2020; Yan et al., 2020).

It should be noted, however, that the subject of particle-based stabilization lies rather outside the scope of the present article. We mainly limit ourselves here to situations involving soluble macromolecular species having the capacity to form adsorbed polymeric stabilizing layers.

Various colloid-based strategies have been devised and implemented to improve the emulsifying and stabilizing properties of existing food ingredients (Ettelaie, Zengin & Lee, 2014; Ettelaie, Zengin & Lishchuk, 2017). A well-established chemical approach involves adjusting the hydrophilic/hydrophobic balance of food macromolecules. Depending on the starting material, there are two modes of chemical intervention: (i) hydrophobic modification of a hydrophilic carbohydrate polymer (starch or cellulose) to increase its amphiphilicity and surface activity, and (ii) hydrophilic modification of a globular protein to enhance its solubility and steric stabilizing ability. Chemical treatment may also modify the charge distribution along the polymer chain, thereby enhancing any electrostatic contribution to colloid stability. In addition, enzymatic treatment may be employed to enhance biopolymer solubility and surface activity. Or, starting from a binary mixture of protein + polysaccharide, a hybrid entity of enhanced interfacial functionality may be generated by electrostatic complexation or covalent conjugation (Wijaya, Patel, Setiowati & van der Meeren, 2017). It appears that the mechanistic basis underlying the functional consequences of these macromolecular transformations are now reasonably well understood, at least in intuitive or qualitative terms. But can we go one stage further and imagine what would be the precise molecular structure of a fully optimized biopolymer stabilizer? In other words, is there some ideal biopolymer structure, in terms of polymer chain length and distribution of chemical groups (hydrophilic, charged, hydrophobic), which can be expected to confer an optimum degree of stabilization? And, if we can envisage such an ideal hydrocolloid stabilizer, what are the consequences for its use in terms of oral processing and emulsion digestion?

The rest of the article is organized as follows. Section 2 describes the underlying theoretical framework leading to the concept of the perfect stabilizer. Section 3 sets out the behaviour of the hydrocolloid stabilizer during oral processing and sensory perception. Section 4 outlines the response to gastric and intestinal conditions of digestion. Section 5 considers the influence on gut motility and interactions with gut microflora. Finally, section 6 presents our conclusions.

2. Theoretical basis of the concept of the perfect hydrocolloid stabilizer

Examination of the huge body of information in the literature on the performance of existing emulsifiers and stabilizers — biologically based or otherwise— leads us to draw certain tentative conclusions regarding the most important molecular features needed by our 'ideal' ingredient. The importance of such characteristics can be further reinforced and clarified using theoretical calculations and/or computer simulations (Ettelaie, 2003; Dalkas & Euston, 2019). In discussing these features, it is useful from the onset to make a distinction between the kinetic (or dynamic) properties of an emulsifier/stabilizer and those that pertain to its equilibrium behaviour. Broadly speaking, the equilibrium properties largely translate onto the *long-term* emulsion stabilizing properties of the ingredient, whereas the kinetic considerations tend to dictate the functional capabilities of the ingredient during emulsion formation and *short-term* stability of droplets. This mapping holds particularly true of macromolecular species, where the rates of mass transfer and adsorption tend to be slow compared to those of small-molecule surfactants. We begin by examining the equilibrium features, where we can confidently rely on well-developed machinery of statistical mechanics to provide us with some valuable generic insights into the *long-term* thermodynamic and structural behaviour of macromolecular emulsifiers adsorbed at an idealized surface (Evers, Scheutjens & Fleer, 1990; Fleer et al., 1993; Ettelaie, Dickinson & Pugnaloni, 2014). For the sake of simplicity, unless stated otherwise, we shall assume in what follows that the idealized surface is a realistic representation of the fluid oil–water interface in an emulsion of the oil-in-water (O/W) type.

2.1. Equilibrium behaviour of ideal emulsion stabilizer

The simplest macromolecular structure that can be envisaged is a linear hydrophilic homopolymer. There are many polysaccharides that come close to having such a structure. Of course, these molecules show little affinity for adsorption at oil–water interfaces and so are not of use by themselves as emulsifying agents. Nevertheless, the presence of such a non-surface-active homopolymer can still influence the nature of the colloidal interactions between dispersed oil droplets. By way of illustration, Fig. 1 shows the induced interaction between two droplets of size 1 μm as calculated from self-consistent-field (SCF) theory for the case of a 600-segment polymer present at a solution concentration of 0.1%. For full

details of the SCF approach as applied to systems containing food biopolymers, the reader is referred to previous publications (Leermakers, Atkinson, Dickinson & Horne, 1996; Ettelaie, Akinshina & Dickinson, 2008; Akinshina, Ettelaie, Dickinson & Smyth, 2008; Ettelaie, Khandelwal & Wilkinson, 2014).

The interaction energy seen in Fig. 1 at close separations is negative (*i.e.* attractive). This causes the clustering of emulsion droplets. The phenomenon is known as depletion flocculation. The attraction arises from the depletion of macromolecules in the small gap between two approaching particles, driven by the restricted number of available configurations and the loss of entropy of the chains when residing in the gap (Lekkerkerker et al., 1992). This results in an osmotic pressure difference between the solution in the gap, which is devoid of macromolecules, and the solution outside which contains them. The reader may wonder why we are mentioning this phenomenon in relation to the supposed characteristics of an ideal amphiphilic emulsifier? The answer is that the same behaviour is found with any free macromolecular species that remain in excess in the bulk solution. That is to say, unless our ideal stabilizing polymer has an infinite capacity for covering the oil–water interface, there must come a time when the addition of more of the ingredient leads to the presence of some non-adsorbed molecules in the aqueous medium. So, even though the concentration of any added ingredient is not an intrinsic molecular feature, the formulator of the emulsion needs always to bear in mind that the presence of excess emulsifier — 'ideal' or otherwise — is generally not conducive to producing a stable, well-dispersed system.

Let us next now consider turning our homopolymer into an amphiphilic molecule by substituting some of the hydrophilic residues with hydrophobic ones, or by attaching a few hydrophobic residues to the main chain. Where would be the best location along the backbone for us to place them, and how many residues should we modify? Let us address the latter question first as it is simpler to answer. The emulsifier/stabilizer needs to be delivered through the continuous phase: this requirement places an upper limit on the acceptable ratio of hydrophobic to hydrophilic residues. If the ratio is too high, the ingredient will not be properly soluble in the continuous phase, leading to aggregation or precipitation. Therefore, a sufficient level of solubility is a key functional attribute of any effective emulsifying agent (Dickinson, 1992, 2009a,b). A rough estimate of the upper operational limit for the hydrophobic–hydrophilic ratio can be obtained using a simple theory of the Flory–Huggins type. Such an approach requires estimating the interaction energy of each kind of monomer residue with the solvent, as measured by the Flory–Huggins χ parameter. There is also a lower limit on how many hydrophobes the macromolecule needs to have in order to stick to

the interface. Too few and the individual chain will not adsorb at all, since the loss in the configurational entropy upon adsorption cannot be compensated by a sufficient decrease in enthalpy (Ettelaie, Holmes, Chen & Farshchi, 2016). Furthermore, even when the proportion of hydrophobic residues is high enough for adsorbed chains to cover the surfaces of the droplets, the polymers may still desorb when the gap between the two neighbouring droplets becomes sufficiently small. Fortunately, the slow kinetics of desorption normally makes this latter process not much of an issue, but should it happen we are back in a situation similar to that encountered with depletion flocculation as described above. Therefore, our ideal stabilizer should possess sufficient hydrophobic anchoring groups to entice it to stick to the surface of droplets and to inhibit desorption during droplet collisions — but preferably no more than that.

So far, we have not mentioned the type of interdroplet forces which the adsorbed macromolecular layers may generate. The forces need to be predominantly repulsive to counteract the van der Waals interactions between the droplets. These van der Waals interactions always exist and they cannot be turned off. Furthermore, they are always attractive for pairs of droplets composed of the same material (Russel, Saville & Schowalter, 1989; Dickinson, 1992). Interdroplet electrostatic repulsion may be induced by the adsorption of small charged surfactant molecules. (In food systems, for reasons of safety, the permitted ingredients are limited to anionic or zwitterionic surfactants). Adsorbed layers of amphiphilic macromolecules, if possessing the right molecular structure, are able to generate repulsive steric forces as well as repulsive electrostatic forces. These electrostatic forces can be strong, and, in formulations of low electrolyte concentration, sufficiently long-ranged to prevent droplet aggregation. At higher electrolyte concentrations, however, the surface-to-surface separation distances required for their operation is rather limited (*i.e.* only ~ 1 nm for a 0.03 mol l^{-1} NaCl solution). This renders electrostatic forces rather ineffective in providing the necessary colloidal stability for many food formulations. Furthermore, many biological macromolecules tend to have isoelectric points (p*I*) in the pH range 4–5.5. For food formulations with required pH values close to p*I*, either in the final product or at some stage during processing, this can be problematic. The loss of the charge of the protein stabilizer at pH ~ p*I* all but switches off the interdroplet electrostatic repulsion. One strategy for overcoming this problem is to work with polypeptides having unusually high or low p*I* values, *i.e.*, outside the range of interest for practical food formulations. This may be achieved by identifying an appropriately charged polypeptide fragment in a protein with a more conventional p*I* value (Ettelaie, Zengin & Lee, 2014; Ettelaie, Zengin & Lishchuk,

2017). The task of fragmenting the protein enzymatically to the right level of hydrolysis, and then separating out the target polypeptide from amongst the many other generated fragments, remains a challenging, but nevertheless worthwhile, future experimental task for food colloid scientists. In practice, there has to be a compromise between small fragments that adsorb rapidly during emulsification and large fragments that may provide better stabilization after emulsion formation. The negative flavour perception with some small peptides has also to be considered.

Another contribution to the required stabilizing repulsive force, mediated by the adsorbed macromolecular layers, is the steric interaction. When adsorbed layers overlap, there is an increase in the local concentration of polymer in the gap between the droplets. In what may be viewed as the reverse of the situation occurring with depletion flocculation, it is now the solution beyond the gap that possesses the lower polymer concentration. Consequently, this time round, the osmotic pressure difference is associated with a strong interdroplet repulsion. In addition to this, there is another smaller contribution to the net repulsion due to the loss of configurational entropy of chains trapped in the narrow gap between the droplets. The major practical advantage of emulsion stabilizers which rely on the steric stabilization mechanism is their much lower sensitivity to changes in environmental and processing conditions. Nonetheless, under any set of envisaged processing/storage conditions, it is important that the hydrophilic segments of our ideal hydrocolloid stabilizer should remain properly hydrophilic in the literal sense (*i.e.* with the bulk aqueous medium continuing to act as a 'good' solvent). If this condition is not satisfied, there is a danger that dominant attractive interactions between chains (as opposed to between chains and solvent) may swamp the osmotic effect. This would reverse the sign of the mediated colloidal force between the droplets, changing it from net repulsive to net attractive (Ettelaie & Akinshina, 2014).

Having established that the ideal emulsion stabilizing agent is best achieved with macromolecules that are predominantly reliant on the provision of steric forces, how can we ensure that such forces are long-ranged and strong? Clearly, longer chains having more extended hydrophilic parts can be helpful in achieving this (Ettelaie, Holmes, Chen & Farshchi, 2016; Dickinson, 2018). Additionally, it is beneficial to have a high degree of surface coverage because this makes for interfacial films that are thick and dense. With all else remaining the same, the highest coverage tends to be achieved with molecules which do not possess any electrical charge. The same electrostatic forces that operate between adjacent films also exist between different molecules in the same layer (Ettelaie, Akinshina & Maurer, 2012). The effect of these electrostatic repulsive forces is to hinder the adsorption process

and to reduce the level of surface coverage. Figure 2 shows the theoretically predicted amount of adsorbed macromolecular stabilizer plotted against the average charge per chain for a series of linear chains composed of 200 residues (20 hydrophobic, 180 hydrophilic). Charge density apart, all other parameters, including the bulk concentration, were kept the same in these SCF calculations. It is clear from the data in Fig. 2 that, in order to maximize the steric component of the interdroplet interaction (*i.e.* to maximize the surface coverage), it pays to reduce the charge on the adsorbed macromolecule. Given the more robust nature of colloidal stabilization *via* steric forces as compared to *via* electrostatic repulsion, these theoretical considerations suggest that our ideal stabilizer molecule should possess little or no net electrical charge, with a molecular structure composed of a large number of highly polar residues but relatively few charged residues.

Let us now turn to a more specific question: what is the optimal distribution of hydrophobic anchoring groups along the backbone of the stabilizer macromolecule? Recent theoretical studies on the surface behaviour of multi-blocked amphiphilic polymers have provided some useful guidance: it is consistently predicted that a single localized hydrophobic region, with all the anchoring groups concentrated in one place on the molecule, provides the superior stabilizing structure (Wijmans, Leermakers & Fleer, 1994; Ettelaie, Murray & James, 2003; Lishchuk, Ettelaie & Annable, 2017). There are several reasons why this should be the case. In the first place, macromolecules with anchoring groups distributed throughout the whole chain tend to lie flat on the surface. In contrast, the condition of having just a single localized hydrophobic region firmly attached to the surface allows the remaining hydrophilic parts of the amphiphilic macromolecule the opportunity to dangle further way from the surface. In other words, we expect a more extended (thicker) interfacial layer to result from the adsorption of the latter kind of molecule. This concept is simply illustrated by the numerical data in Fig. 3(a) calculated from SCF theory. The average distance from the (hydrophobic) surface of each monomer making up the 200-segment polymeric stabilizer is plotted against the monomer sequence number, as measured from one end of the chain to the other. The resulting flat configuration of the polymer having its hydrophobic segments distributed at equal intervals along the chain is clearly evident (solid line), in contrast to the highly extended configuration of the amphiphilic block copolymer with all its hydrophobic segments localized in one region (dashed line).

A second reason for not favouring polymeric stabilizers with several non-localized anchoring segments is their lower comparative affinity for adsorption. Once again this can be understood in terms of the more restrictive configurations available to chains that lie flat on

the surface, leading to a relatively higher entropy loss upon adsorption (Ettelaie, Murray & James, 2003). Figure 3(b) shows the predicted variation in the volume fraction of stabilizer in the adsorbed layer plotted against the distance away from the (hydrophobic) surface. The two lines refer to the two same model polymers as in Fig. 3(a), which, apart from the distributions of their hydrophobic segments, are identical in all other respects (*i.e.* chain length, fractions of hydrophobic and hydrophilic segments, bulk concentration). We observe that the macromolecule with the single anchoring block (dashed line) gives a substantially greater adsorbed amount, as well as a more extended adsorbed layer, than the one with hydrophobic segments distributed at equal intervals along the chain (solid line).

There is an additional third reason for avoiding multiblock structures: such arrangements are capable of inducing bridging flocculation. When two droplet surfaces get very close together, polymers with multiple anchoring blocks can have some of their hydrophobic groups attached to the surface of one droplet, whilst others are attached to the surface of the neighbouring droplet. The availability of these macromolecular 'bridging' configurations, which are impossible when the same droplets are far apart, constitutes a significant increase in the configurational entropy of the chains and hence a reduction in the overall free energy of the system. This decrease in free energy as the droplets come closer together manifests itself as an extra attractive component in the interdroplet interaction potential. For well-covered surfaces, with dense adsorbed layers, this effect tends to be swamped by the much stronger steric force, arising immediately with the slightest overlap of the two layers. But when the coverage is low, or where the solvent is only marginally a 'good' solvent (*e.g.* at a pH close to p*I* for many proteins), the effect can lead to bridging flocculation. This is one reason why most proteins, with primary structures that typically involve a fairly well-spaced distribution of hydrophobic amino-acid residues along the backbone, cannot be considered as ideal stabilizers from the purely theoretical point of view (Ettelaie, Murray & James, 2003; Ettelaie, Khandelwal & Wilkinson, 2014).

The preceding equilibrium discussion has largely focused on the concept of an idealized emulsifier/stabilizer suitable for the purpose of making a well-dispersed colloidally stable liquid emulsion. However, one has to recognize that there are practical considerations that limit the realization of O/W emulsions containing such theoretically ideal molecules. These practical complications are commonly related to kinetic factors. For example, the problem of getting the emulsifier ingredient quickly and efficiently to the newly created interface poses a whole new set of questions, irrespective of how well the ingredient may eventually behave once it becomes actually located at the oil–water interface. We have seen already that large

amphiphilic macromolecules are required in order to generate the required long-range steric forces (Ettelaie, Holmes, Chen & Farshchi, 2016). Yet molecules of larger size will tend to have smaller diffusion coefficients and lower rates of mass transfer in the vicinity of the interfaces of freshly produced emulsion droplets (Dickinson, 1992). Similarly, we have noted that the placement of all the hydrophobic monomers within a small localized region on the molecule is distinctly advantageous for designing a superior stabilizer. Yet this very same molecular feature makes the ingredient more prone to self-association and aggregation in bulk aqueous media. This kind of association, driven by hydrophobic forces, is favoured by the presence of well-defined highly hydrophobic regions. While such self-association may not greatly affect the equilibrium behaviour of the macromolecules at the interface, it is likely to limit the extent of exposure of the hydrophobic groups, which may be buried within the interior parts of the associatively formed entities in the bulk aqueous solution. And this in turn may severely retard the kinetics of the adsorption process. The possible implications of such kinetic factors for the concept of our ideal ingredient are considered in the next section.

2.2. Dynamic requirements

In addition to providing an effective electrosteric barrier under quiescent conditions, our ideal emulsifier/stabilizer must be able to respond appropriately to the stresses and strains imposed upon it by processing operations such as stirring, mixing, pumping, and hydrostatic pressure changes. These dynamic processes distort the interface and induce changes in interfacial coverage and the surface load of the adsorbed stabilizer. One can usefully distinguish two dynamic regimes: (i) the high interfacial strains and rates of strain during the usual methods of formation of emulsions and foams, and (ii) the lower rates, the longer times, and probably the smaller amounts of deformation that take place after initial formation of the dispersed system. The latter might simply be due to Brownian motion or convection, or to changes arising from mixing with other ingredients, pumping, or filling. In all such cases, in order to maintain colloidal stability, a sufficient level of surface coverage and ‘thickness’ of the adsorbed layer must be ensured in order to provide sufficiently strong repulsive colloidal interactions.

These dynamic aspects necessitate an analysis of the time-dependent mechanical properties of the adsorbed film itself, *i.e.*, its interfacial rheology (Murray, 2002, 2011). Closely connected is the issue of the dynamics of adsorption and surface coverage in relation

to droplet disruption. We begin by considering the physico-chemical implications of these interfacial area changes.

2.2.1. Gibbs–Marangoni response and interfacial dilatational rheology

When the area of an interface is expanded, the coverage of the interface (Γ) by surface-active molecules will decrease and so the interfacial tension (γ) will increase, *i.e.* $\Delta\gamma > 0$. No matter how local or sudden this change is, it creates a pull of interfacial material back into the region of depressed γ in order to equalize γ (or the surface pressure, π) throughout the whole interface (see Fig. 4). This automatic process, which tends to maintain the equilibrium coverage, is known as the Gibbs effect, and its magnitude can be expressed *via* the Gibbs or dilatational elasticity (ε) defined as

$$\varepsilon = \mathrm{d}\gamma/\mathrm{d}A/A = \mathrm{d}\gamma/\mathrm{dln}A \quad , \qquad (1)$$

where dA is the change in interfacial area A, and dA/A is the area strain. Of course, like any other rheological parameter, ε depends on strain and strain-rate (Sagis, Humblet-Hua & van Kempen, 2014). That is to say, there is a limit to the speed with interfacial material can move and re-arrange to fill the region depleted of stabilizer, relative to the speed at which the interface is expanded. One therefore also needs to define the corresponding interfacial dilatational viscosity (κ):

$$\kappa = \mathrm{d}\gamma/(\mathrm{dln}A/\mathrm{d}t) \quad , \qquad (2)$$

where dln$A$/dt is the *rate* of interfacial strain. Measuring dilatational rheology by means of oscillatory deformations of the interface means that the response is characterized in terms of the dynamic interfacial dilatational storage and loss moduli (G_i' and G_i''), which are dependent on both frequency and amplitude. The higher the value of ε (or G_i'), the greater is the resistance to expansion; and the higher the value of κ (or G_i'') the slower is the expansion in response to the applied stress. The response of the film on expansion is not necessarily equal and opposite to that on compression, and the more so the larger the magnitude of the strain (Murray, 2002; Pugnaloni, Ettelaie & Dickinson, 2005a,b). After all, an already close-packed film cannot become any more close-packed without 'crumpling', whereas the same monolayer film may be expanded indefinitely. Therefore, the frequency response of interfacial films is often asymmetric with respect to expansion and compression (Murray, 2002; Pugnaloni, Ettelaie & Dickinson, 2005a,b). Furthermore, if the interfacial species are solid particles exhibiting Pickering stabilization, then a different set of rules applies: by

definition in this case, there is no suppression of the macroscopic interfacial tension, but instead capillary interactions come into play with very close approach of the particles at the interface (Binks & Horozov, 2006; Binks, 2017). At close packing the resistance to compression of a monolayer of hard particles diverges to an 'infinitely' high value.

The Marangoni effect is the flow of bulk fluid adjacent to the interface which is coupled to the motion of the stabilizer within the film, as illustrated schematically in Fig. 4(a). Larger adsorbed entities tend to drag more bulk fluid along with them, thereby contributing to the stability of the fluid–fluid interface, keeping the neighbouring interfaces further apart (see Fig. 4(b)). In this way the Gibbs–Marangoni effect maintains surface coverage and interfacial separation so long as these processes can take place faster than the timescale of the imposed interfacial deformation.

Other factors moderating the response include any tendency for the stabilizer molecules to form attractive interactions once they are adsorbed. These interactions might be non-covalent (H-bonding, hydrophobic, ionic) or covalent (disulfide cross-links), acting between adsorbed biopolymers as they unfold at the interface, or through bonds induced by chemical or enzymatic means (Faergemand, Murray, Dickinson & Qvist, 1999), or simply through aggregation of particles once they are adsorbed (see Fig. 4(c)). The adsorbed entities now become effectively larger and slower to respond to interfacial stresses and strains than the originally adsorbing ones. Any in-film cross-linking may cause inhomogeneities in the film structure over larger length scales (Xu, Dickinson & Murray, 2007; Murray, Xu & Dickinson, 2009). Such defects lead to a distribution of local moduli within the adsorbed film and therefore specific locations of weakness at large strains.

2.2.2. Dynamics of adsorption and desorption

In any real system there will be adsorption to the expanding interface as soon as the surface coverage drops below the equilibrium value, and also potentially some desorption from the interface during compression (when the equilibrium coverage might be exceeded). Thus, at high bulk concentrations of surface-active stabilizer, ε may actually be depressed in magnitude, because, as fast as the interface is expanded, new molecules will adsorb and fill in the gaps, effectively 'short-circuiting' the Gibbs–Marangoni stabilizing mechanism. Conversely, on compression, adsorbed material may desorb rapidly enough to maintain the equilibrium coverage. Therefore, the dilatational response of any stabilizer is intimately connected to its diffusional properties, and to its adsorption and desorption behaviour to and from the interface (see Fig. 4(a)).

In assessing the performance of any hydrocolloid stabilizer, what we can say is that the higher its molecular weight (M_w) or hydrodynamic diameter, the slower it will be to adsorb *via* diffusive mass transport (recognizing that the majority of mass transport during emulsification will be convective). There may also be steric and electrostatic barriers to further retard macromolecular or particle adsorption once some of the adsorbing material has started to fill up the interface (Sengupta, Razumovsky & Damodaran, 1999). Proteins are often described as 'irreversibly' adsorbed, or non-desorbing, and this may be effectively true over a timescale of at least several days. Pickering particles have such high values of the desorption energy that they are regarded as never spontaneously detaching from the interface (Binks & Horozov, 2006).

All in all, higher M_w surface-active biopolymers or biopolymer aggregates will tend to lead to higher gradients of γ at the interface on expansion, and hence to a more enhanced Gibbs–Marangoni effect. At the same time, the higher value of M_w and the larger size will tend to slow down the approach to full saturation coverage, thereby frustrating the effective stabilization of emulsions of high interfacial area (*i.e.* small droplet size).

At this point in the discussion let us return to a consideration of the two dynamical regimes: (i) high deformation during colloid formation, and (ii) low deformation after formation. Regime (i) often involves turbulent flow conditions, where packets of different fluid phases 'collide' at very high local shear-rates, causing 'particles' of disperse phase to be transiently formed and then re-coalesce over very short timescales. It is more or less impossible to access experimentally the extant rates of dilatational expansion and compression within regime (i). (It should be noted that the interface is simultaneously subjected to similarly high levels of *shear* deformation (Walstra, 2003).) While capillary pressure tensiometry can access γ changes over timescales of the order of 10^{-3}–10^{-4} s (Lotfi et al., 2014), this is still slow compared to the timescales of change during emulsification.

At scales of length and time below those of the turbulent eddy size and eddy lifetime, material is diffusing to and re-arranging itself at the interface before the interface gets subsequently destroyed. The particle size distribution emerging from the high shear mixer, homogenizer, aerator, *etc.*, depends upon the net balance of interfacial coverage and disruption in regime (i) plus the amount of further adsorption that occurs in the first few milliseconds and seconds of regime (ii). Is it actually feasible then to define the required characteristics of our ideal stabilizer in terms of its interfacial rheological response on the basis of dynamical information that is only experimentally accessible in regime (ii)?

The answer to this question is… yes, sometimes. There are certain types of colloidal instability that can be directly related to interfacial rheology measurements made over the correct time- and length-scale regimes. Most notably, the thinning of the film of liquid between two macroscopic gas bubbles can be measured directly *via* numerous techniques, and it can be related to the Gibbs–Marangoni resistance and the critical film thickness at which film rupture and coalescence take place (Platikanov & Exerowa, 2010). In addition, the preparation of minute volumes of specialist emulsions or foams using microfluidic techniques allows the linking of the colloidal stability to the hydrodynamics and deformation rates during formation (Schroder et al., 2018; Doufene, Tourne-Peteilh, Etienne & Aubert-Pouessel, 2019).

In Ostwald ripening of droplets, or disproportionation of bubbles, shrinkage is relatively slow, at least for air bubbles of tens of micrometres in diameter or for micrometre-sized oil droplets in water. This means that the corresponding deformations are readily accessible experimentally at the corresponding macroscopic interfaces. Thus, in principle, shrinkage ceases if the condition $|\varepsilon| = 0.5\gamma$ is satisfied (Dickinson, Ettelaie, Murray & Du, 2002; Ettelaie, Dickinson, Du & Murray, 2003; Meinders & van Vliet, 2004). Here it is tacitly assumed that the compressive elasticity equals the dilatational elasticity, since the film is being compressed during ripening or disproportionation. However, this also assumes a perfectly elastic film, whereas most biopolymer films are viscoelastic in compression and expansion, so that slow shrinkage can still occur, pushing material off the interface (Dickinson, Ettelaie, Murray & Du, 2002) (see Fig. 5). In contrast, films of true Pickering stabilizers are incompressible because the neighbouring solid particles come into direct contact; this is why they are the only type of stabilizer that can halt shrinkage completely. Moreover, the interface need not be close-packed for this to occur: so long as the particles can form an interfacial network that is strong enough to overcome the driving force due to the Laplace pressure difference, the interface can be stabilized at a considerably lower particle coverage than fully close-packed (Du et al., 2003; Binks, 2017).

Another case in which interfacial deformation rates may be accessed experimentally is where the system is subjected to an external pressure change. Examples include the common practice of aeration under pressure, with the excess pressure released as the foamed product exits the aerator. The interfacial film is expanded at a rate dependent on the rate and extent of the pressure drop, which is normally within the range of laboratory tensiometry techniques. Under such conditions the interface may still be subjected to a combination of both shear and dilatation, and stability to coalescence may be related to the critical strain at which film

fracture occurs as well as to the interfacial dilatational and shear moduli (Murray et al., 2002, 2003).

2.2.3. Dynamic interfacial shear response

We can define interfacial shear elasticity (G_i) and viscosity (η_i) coefficients that are easily measurable in regime (ii) by a range of available techniques. Since, by definition, shear deformation does not involve a change in interfacial area, the interpretation of these measurements is free from the complications of the dynamics of stabilizer adsorption and desorption (*cf.* dilatational measurements) as long as the film composition and structure are effectively fixed over the timescale of the measurements. Adsorbed films of stabilizers generally exhibit a much wider range of G_i and η_i values than their corresponding dilatational parameters. Measured η_i values range from 10^{-2} to 10^4 mN s m^{-1} for proteins (and even higher for adsorbed microgel particles) (see Fig. 6). Reported values of G_i' generally lie in the range 0–100 mN m^{-1}, and values of G_i'' (less frequently reported) are typically ten times higher. These trends reflect the much higher sensitivity of the shear measurements to film structure. Thus, the surface shear rheology of an adsorbed layer of a globular protein varies continuously as the protein layer builds up at the interface, and it continues to evolve long after the equilibrium surface coverage is reached, because the macromolecules continue to re-arrange internally with time. Almost any factor that affects intermolecular interactions within the layer (pH, ionic strength, temperature, *etc*.) is reflected in a change in the interfacial shear rheology (Murray, 2011).

Almost any disturbance of the interface in real situations will involve a combination of dilatational and shear deformations. Therefore, we can say that values of G_i and η_i should be high enough to provide some resistance to the deformation of the interface, but not so high that the deformation will lead to sudden fractures and drastic inhomogeneities in the stabilizer layer. The conditions underlying this behaviour can be understood through computer simulations of model adsorbed layers subjected to dilatational or shear deformation, where the stabilizer species are simply modelled as spherical particles interacting through weak (transient) or strong (permanent) interparticle cross-links (Pugnaloni, Ettelaie & Dickinson, 2004, 2005a,b). Such simulations have confirmed the asymmetry in the response to compression and expansion, as well as the crumpling of strongly cross-linked films when the interparticle attractive interactions are sufficiently strong.

2.2.4. Dynamics of competitive adsorption

Some cross-linking of the ideal adsorbed stabilizer is probably beneficial because it will lead to greater interfacial viscoelasticity. The degree to which such cross-linking can take place will depend on a host of factors: pH, ionic strength and temperature, as mentioned above, but also the rate of development of the surface coverage and the degree of molecular crowding. Interfacial reorganization tends to be inhibited under conditions of high Γ, thereby frustrating molecular rearrangements and cross-linking. This behaviour is reflected in the various equilibrium adsorbed configurations that different biopolymers can adopt as a function of bulk concentration, as discussed in section 2.1.

Macromolecular cross-linking improves the resistance to displacement of high-molecular-weight stabilizers by low-molecular-weight surfactants (LMWS) (Roth, Murray & Dickinson, 2000; Mackie et al., 2003; Kerstens, Murray & Dickinson, 2006). This latter category includes the naturally occurring surface-active lipids (fatty acids, monoglycerides, bile salts, *etc*.) as well as various 'synthetic' molecules that are permitted for limited use in foods (*e.g.*, Tweens, PGPR). Typically the LMWS achieves a lower equilibrium γ than the adsorbed biopolymer due to the ability of the small molecules to pack more closely together at the interface. This means that a high enough LMWS concentration will always induce biopolymer displacement. Adsorbed LMWS layers typically have similar values of dilatational moduli to biopolymer layers, but their shear moduli are orders of magnitude lower (*i.e.*, with $\eta_i < 0.01$ mN s m^{-1}, as shown in Fig. 6). Both experiments and computer simulations have confirmed the general ability of small surfactants to penetrate into and disrupt biopolymer layers, especially protein layers. At the displacement stage, when the adsorbed layer consists of coexisting 'islands' of biopolymer and LMWS, critical points of weakness and instability develop in the adsorbed layer. The rate at which this happens depends on the degree of coherence of the protein film. The protein is typically squeezed into smaller and smaller regions — a process described as orogenic displacement (Wilde et al., 2004) — until whole patches of protein are suddenly removed from the interface. This obviously has implications for the digestion of edible oil droplets initially covered in biopolymeric material (see section 4). With respect to particulate (Pickering) stabilizers, there are still many unanswered questions as to how LMWS adsorption modifies the interfacial contact angle of the particles during a competitive displacement process (Mendoza et al., 2014). Hydrocolloid stabilizers existing in the form of microgel particles (Dickinson, 2016, 2017; Murray, 2019a,b) might have the advantage of absorbing more of the LMWS internally before eventually being displaced by the excess surfactant.

564 *2.2.5. Multilayer and network stabilization*

565 It seems intuitively logical to assume that, once a primary adsorbed layer of stabilizer has
566 been established, it would be advantageous from a stability viewpoint if further layers
567 adsorbed on top of the first layer. This thicker multilayer structure would naturally increase
568 the minimum approach distance of the surfaces of the polymer-coated droplets. The same
569 type of adsorbing polymers may start to form multilayers depending on the extent to which
570 the initially adsorbed species change their structure on adsorption (Hirsh et al., 2013). For
571 example, the surface of an adsorbed protein monolayer may be quite different from the
572 surface of the non-adsorbed molecules on adsorption. Multilayer formation can also be
573 achieved through the introduction of a second polymeric stabilizer, especially one of opposite
574 net charge (Jourdain et al., 2009; Dickinson, 2011; Qin et al., 2016; Tomadoni, Capello,
575 Valencia & Gutierrez, 2020; Xu, Sun & McClements, 2020).

576 In the case of particulate stabilizers, there is no obvious reason why a secondary layer of
577 the same particle should adsorb onto the first, especially if the initial particle dispersion is
578 colloidally stable. In practice, however, for most Pickering systems, the particles are
579 aggregated to some extent *before* they adsorb, and if the state of aggregation persists on
580 adsorption a 'ready-made' multilayer is produced. If the stabilizer has limited colloidal
581 stability in the bulk phase, leading to a bulk phase network, this may supplement the true
582 interfacial stabilization by trapping dispersed droplets (or bubbles) in the network. While
583 such bulk aggregation effects are obviously important in dynamic regime (ii), they can also
584 be deliberately induced by adjusting the solution conditions in the period immediately
585 following regime (i) *via* a change in pH or temperature, or by the incorporation of cross-
586 linking ions (*e.g.* Ca^{2+}).

587 What then is the ideal stabilizer from the dynamic point of view? In brief, we can say that
588 the macromolecule should be large, but also agile and flexible, adsorbing quickly and
589 preferably linking up with its neighbours to form some sort of interfacial network. Moreover,
590 the network should allow some expansion, but not too much, and not too fast, and with the
591 avoidance of catastrophic film facture. If the stabilizing ingredient can go on to form
592 multilayer films at longer adsorption times, or even in the initial stages of adsorption —
593 without compromising uniform cross-linking and coverage — then so much the better.
594 Finally, in order to stop Ostwald ripening, it would be beneficial for the interfacial film to
595 contain large, flexible, mechanically resistant entities that can resist interfacial displacement
596 on compression.

3. Effect of hydrocolloid structure on oral processing

Another desirable requirement of the perfect hydrocolloid stabilizer is that the consumed food emulsion should possess optimal taste and textural appeal as defined by key sensory attributes such as creaminess, smoothness, fattiness, and mouth coating. The psychological sensation of eating not only influences decisions of food acceptance/rejection by consumers; it also has a physiological consequence on the amount of nutrient intake and satiety (Stribiţcaia et al., 2020). There exists an extensive literature on the quantification of mouthfeel perception involving conventional descriptive sensory techniques such as sensory profiling as well as more recently adopted dynamic methods such as time intensity and temporal dominance of sensations (Di Monaco, Su, Masi & Cavella, 2014). In addition, progress has been made in understanding changes in the structural and mechanical properties of food materials during oral processing, including the behaviour of semi-solid mixtures of food and saliva during mastication and the triggering of swallowing (Pascua, Koç & Foegeding, 2013; Chen, 2015).

Against this background of bewildering complexity, it is appealing to adopt a more reductionist approach to the problem by trying to understand the mechanical and physical chemistry principles underpinning oral processing within a more simplified simulated oral environment. In particular, we can think of food oral processing as a sequential series of well-coordinated unit operations (Stokes, Boehm & Baier, 2013). These are arranged as follows: first the large deformation-driven stages of (i) first bite and (ii) comminution, followed by the mechanical/hydrodynamic stage of (iii) granulation (*i.e.* mixing with saliva), and then the rheology-driven and tribology-driven stages of (iv) bolus formation, (v) swallowing and (vi) residue formation. We shall adopt this reductionist approach in considering the concept of the perfect hydrocolloid from the oral processing viewpoint. As illustrated in Fig. 7, we consider two particular aspects of hydrocolloid functionality that are especially pertinent to mouthfeel perception: (1) the transformation from mainly bulk (rheological) interactions to mainly surface (tribological) interactions during oral processing, and (2) the colloidal aspects of saliva–hydrocolloid interactions.

3.1. Transformation from bulk interactions to surface-induced interactions

The rheological foundations of modern oral processing research were described half a century ago by Friedman, Whitney & Szczesniak (1963) and Shama & Sherman (1973). Following the latter authors, the viscosity at some specific shear-rate has been adopted as the gold standard in most oral processing studies as a fixed criterion to correlate and predict the perceived sensory thickness of liquid-like emulsions. Nevertheless, the inferred shear-rate values at which such a correlation is deemed to exist between the apparent viscosity (η) and sensory thickness (M_{thick}) have been reported to range from below 10 s^{-1} to nearly 1000 s^{-1}. For instance, for O/W emulsions of low volume fraction stabilized by sodium caseinate containing xanthan or pectin as thickening agent, it was found that M_{thick} could be correlated with η measured at 50 s^{-1} (Akhtar, Murray & Dickinson, 2006). While this arbitrary value of 50 s^{-1} is often taken to be some sort of standard average oral shear-rate, the assumption is of dubious generality owing to the known variations of hydrodynamic conditions in the mouth depending on the microstructure of the consumed food. For instance, evidence to suggest that a singular shear-rate of 50 s^{-1} is insufficient to characterize oral or pharyngeal conditions is presented in the recent study of Ong, Steele & Duizer (2018). These authors demonstrated that thickened liquids of three different hydrocolloids (xanthan gum, guar gum, carboxymethylcellulose), which had been viscosity-matched at 50 s^{-1}, could be readily distinguished by trained panellists in terms of both the sensorially perceived viscosity and the ease of swallowing. Several decades earlier, Cutler, Morris & Taylor (1983) had suggested that 10 s^{-1} was actually a better measure of the effective oral shear-rate than 50 s^{-1}, as indicated by regression coefficients in the correlation of $\log M_{\text{thick}}$ with $\log \eta$. But these authors added the proviso that the lower shear-rate was valid only for highly shear-thinning liquids. More recently, for whey protein-stabilized emulsions with added gum arabic as thickening agent, van Aken, Vingerhoeds & de Wijk (2011) reported a pronounced dependence on viscosity of the perceived mouthfeel attributes of thickness and creaminess. That this same dependency was not observed, however, for emulsion samples without added gum arabic indicates the importance of the nature and concentration of the hydrocolloid ingredient(s) on sensorially perceived attributes.

Taking account of existing knowledge, one can reasonably hypothesize that, in order to make emulsions with high degree of sensory thickness, one should use polysaccharides to increase the emulsion viscosity, either as a non-adsorbed thickening agent in the continuous

phase or in conjugation with protein when such a conjugate is used as an emulsifier/stabilizer. It should be pointed out, however, that many of the polysaccharides of shorter chain lengths that are commonly used to prepare protein–polysaccharide conjugates for emulsification purposes do not provide the level of viscosity enhancement required to achieve desirable levels of perceivable sensory thickness (Li, Woo, Patel & Selomulya, 2017; Huang et al., 2020). Consequently, when adopting some kind of protein-polysaccharide conjugate as the emulsifier/stabilizer, a carbohydrate polymer of long chain length or having extensive chain branching should be utilized in order to provide viscosity-related benefits during oral processing. An acceptable alternative strategy, avoiding polysaccharide ingredients altogether, is to use proteinaceous microgel particles as Pickering stabilizers of O/W emulsions (Dickinson, 2015b; Sarkar et al., 2016; Murray, 2019b; Zhang, Holmes, Ettelaie & Sarkar, 2020). It has been established that protein microgels can raise the bulk viscosity of aqueous media by orders of magnitude at orally relevant shear rates, as compared with the presence of non-microgelled proteins at equivalent protein concentrations (Sarkar et al., 2017a). Even though their functional role has not yet been properly established in terms of the effect on *true* sensory perception, one can reasonably hypothesize that protein microgel ingredients are likely to have an important influence on perceived sensory thickness of food emulsions by virtue of their high viscosity at orally relevant shear-rates.

The potential for improving the correlation between perceived sensory attributes and rheological properties through the incorporation of tribological factors has long been recognized (Bourne, 1975; Kokini, 1987; van Aken, Vingerhoeds & de Wijk (2011). The seminal work of Kokini and co-workers produced a set of phenomenological equations which involved both rheological and frictional parameters in the representation of attributes such as smoothness, slipperiness and creaminess (Kokini, Kadane & Cussler, 1977; Kokini & Cussler, 1983). It is now clearly established that one particular quantity, the friction coefficient μ between tongue and palate, is a critical parameter in the understanding and prediction of the aforementioned sensory attributes (Pradal & Stokes, 2016; Sarkar & Krop, 2019). Moreover, it is recognized that oral processing and sensory perception are time-dependent processes: sensory attributes that are related to the bulk properties of the food bolus relate more closely to the initial stages of mastication, whereas attributes related to the surface of the bolus are more relevant in the later stages (de Wijk, Janssen & Prinz, 2011). Figure 7 illustrates this transition in dynamic oral processing behaviour in the gap between tongue papillae (filiform) and the oral palate. Bulk rheological factors in the continuum dominate the early stages. As time passes during oral processing, the fluid film in the oral

cavity starts to decrease in thickness as bolus is swallowed. This leaves the tongue papillae in asperity contact with the palate surface, with the consequence that food–saliva or residue–saliva films of colloidal scale thickness dominate the surface interactions and consequently the perceived afterfeel (Sarkar et al., 2019).

Interest in tribology came to the forefront of oral processing research when the textures of foods with similar rheology but differing in fat content were demonstrated to be readily distinguishable by panellists as well as by tribological measurements (Selway & Stokes, 2013; Laguna et al., 2017). Tribological research has been useful in enhancing our understanding of how fat content and fat type affects O/W emulsion stability during oral processing. For dairy colloids such as cream cheese and yoghurt, it was demonstrated by Laguna et al. (2017) that tribology could readily distinguish viscosity-matched samples of full-fat systems and their fat-free counterparts, with the former having μ values of one order-of-magnitude lower than the latter. The corresponding difference in textural perception may be attributed to the stress-induced coalescence of fat droplets in the interfacial film of the full-fat system.

Tribological factors are therefore important when thinking about designing the perfect hydrocolloid stabilizer. Negative sensorial perception such as dryness and astringency are commonly experienced in the presence of certain hydrocolloids, such as plant proteins. These sensations can be attributed to oral lubrication failure and elevated values of μ (Zembyla et al., 2021). In contrast, emulsions containing hydrophobically modified polymers and phospholipids in the vicinity of a polydimethylsiloxane surface — the material often used for representing oral surfaces — have been reported to exhibit a reduced value of μ at the boundary regime; the phospholipids were found to adsorb onto the solid hydrophobic interface, thereby creating a boundary lubricant layer (Farias, Hsiao & Khan, 2020).

Not only the surface activity, but also the molecular size and degree of aggregation of the polymer can influence its oral surface interactions. For instance, the tribological properties of protein dispersions have been compared using globular aggregates of whey protein isolate and fibrillar aggregates of ovalbumin from egg white (Chojnicka, de Jong, de Kruif & Visschers, 2008). As well as being dependent on the concentration and mean size of the protein aggregates, the values of μ measured in soft contact at low pressure were found to be affected by the presence of attractive aggregate–surface interactions leading to necking and adhesion. Observed differences in frictional behaviour for the ovalbumin and whey protein aggregates were explained in terms of the fibrillar character of the ovalbumin aggregates.

730 This allows them to interact more effectively with a rough tribological surface through shear-
731 induced ordering within the contact zone. In a separate tribological study of a mixed milk
732 protein system, not only the overall protein concentration but also the ratio of casein to whey
733 protein was shown to influence the measured value of μ (Sonne, Busch-Stockfisch, Weiss &
734 Hinrichs, 2014). In our own laboratory (Sarkar et al., 2017a), it has been shown that whey
735 protein microgels can act a boundary lubricant at particle concentrations up to 75 vol%,
736 behaviour that could be relevant to the imparting of desirable creamy characteristics to a
737 Pickering emulsion of reduced fat content. Another relevant factor in microgel systems is the
738 high shear viscosity affecting lubrication in the mixed and hydrodynamic regimes. It was
739 demonstrated (Andablo-Reyes et al., 2019) that microgels can enhance the rheological and
740 tribological performance when dispersed in a continuum of relatively low viscosity, *i.e.*,
741 acting as thickeners, and also lowering the friction coefficient. But in a high viscosity
742 continuum, these same microgels were found to have the opposite effect, *i.e.*, reducing the
743 viscosity and increasing the friction coefficient.

744 Hydrocolloids in solution vary significantly in their tribological behaviour. Using a range
745 of different food polysaccharides (xanthan gum, locust bean gum, gellan gum, pectin,
746 carrageenan), Stokes et al. (2011) found that the measured value of μ the mixed regime was
747 dependent on both the surface material properties and the lubricant's viscosity at high shear
748 rates. In experiments with rough polydimethylsiloxane surfaces, it was found that locust bean
749 gum and gellan were the poorest lubricants in low-speed regimes, while carrageenan and
750 pectin were the most lubricating. The results were similar with smooth surfaces, except that
751 gellan was a poorer lubricant only for the rougher contact. The better lubricating behaviour of
752 gellan as compared to xanthan was confirmed by Torres et al. (2019). In compositionally
753 more complex systems, the lubrication properties of mixed dairy protein solutions have
754 recently been reported to be affected to variable extents by the incorporation of different
755 hydrocolloids (Zhu, Bhandari & Prakash, 2019).

756 What these ongoing rheological and tribological studies are suggesting is that the
757 optimum hydrocolloid ingredient from an oral processing perspective should possess both
758 proteinaceous and polysaccharide-based characteristics. Three conditions should be satisfied.
759 Firstly, the hydrocolloid ought to generate a sufficiently high viscosity at orally relevant
760 shear-rates (10–100 s^{-1}) by virtue of its high molecular weight. Secondly, the surface-active
761 character of its protein part should allow it to form a strongly anchored continuous elastic
762 film at oral surfaces leading to a low level of friction when the surfaces are in close contact.
763 Thirdly, the thickening effect of the water-bound polysaccharide should provide a sufficiently

764 large value of the high-shear-rate limiting viscosity (at, say, >1000 s^{-1}) to facilitate extensive
765 lowering of μ in fluid film regimes where the lubricant separates the oral surfaces on the
766 spatial scale from a few nanometres to micrometres. The presence of this ideal hydrocolloid
767 in the oral cavity would be expected to be associated with a high level of perceived
768 smoothness and creaminess.

769

770 ### *3.2. Saliva-induced interactions*

771 The pivotal role of saliva in food oral processing is often underestimated. In part, this is
772 due to the fact that human saliva has not yet been properly characterized in terms of all its
773 relevant physicochemical and mechanical properties, with the consequence that there is no
774 generally harmonized protocol to replicate saliva under laboratory conditions (Sarkar, Xu &
775 Lee, 2019). Another reason is that real human saliva varies significantly across populations
776 and even within the same individual at different times. Moreover, the colloidal stability of
777 proteins in saliva following collection is poor, with the consequence that stored saliva does
778 not replicate the properties of freshly collected saliva. That being said, the role of saliva in
779 relation to emulsion flocculation and coalescence is now acknowledged by colloid scientists,
780 as set out in several reviews (Mosca & Chen, 2017; Sarkar, Ye & Singh, 2017). We briefly
781 focus here on those aspects of the interactions of saliva with hydrocolloids that may be
782 relevant to the concept of the ideal hydrocolloid ingredient from the oral processing
783 perspective (see Fig. 7).

784 The main macromolecules in saliva — glycosylated mucins — carry a net negative charge
785 at oral pH (~ 6.8). The anionic nature of the mucin polymers is determined by the presence of
786 sialic acids ($pK_a = 2.5$) attached to both the polypeptide core and the terminal groups, together
787 with some other acidic oligosaccharides (sulfate, $pK_a = 1$) (Durrer, Irache, Duchene &
788 Ponchel, 1995). The charge density of the hydrocolloid plays a prominent role in its
789 interaction with saliva. Using real human saliva as well as model systems containing mucins
790 and small ions, it has been established experimentally that O/W emulsions stabilized by
791 negatively-charged proteins such as whey proteins and caseins tend to generate depletion
792 interactions, whilst positively charged proteins such as lysozyme, lactoferrin and β-
793 lactoglobulin (at acidic pH) lead to bridging interactions (Vingerhoeds, Blijdenstein, Zoet &
794 van Aken, 2005; Silletti, Vingerhoeds, Norde & van Aken, 2007a,b; Sarkar, Goh & Singh,
795 2009). In contrast, as illustrated in Fig. 7, the presence of OSA-modified starch as an

emulsifier/stabilizer leads to droplet coalescence under oral conditions as a consequence of the rupture of the interfacial stabilizing layer by amylase, leading to a lowering of in-mouth friction due to the film of coalesced oil between the oral surfaces (Dresselhuis et al., 2007; Chiu et al., 2017; Torres, Andablo-Reyes, Murray & Sarkar, 2018).

The character of the in-mouth emulsion instability has a significant impact on sensory perception. Reversible depletion flocculation by whey protein-stabilized emulsions has been found to be associated with very little retention on the tongue and no significant negative influence in the perception of creaminess, fattiness or thickness (Vingerhoeds et al., 2009). In contrast, bridging flocculation of lysozyme-stabilized emulsions has been associated with a large increase in in-mouth viscosity and enhancements in the oral sensations of dryness, roughness and astringency. The increase in viscosity alone cannot explain this sensory experience. What is significant mechanistically is that the positively-charged emulsion droplets form complexes with the anionic mucin molecules, thereby depleting the mucin layers from the tongue surface, leading to an oral perception of dryness (Vingerhoeds et al., 2009). It was also demonstrated, however, that the effect of the irreversible flocculation caused by positively-charged proteins could be diminished by addition of guar gum, presumably due to its lubricating properties. Compared with protein-stabilized emulsions, it was found that the OSA-modified starch-stabilized emulsions which exhibited in-mouth coalescence received higher fat-related scores on mouthfeel and afterfeel attributes and lower scores on friction-related attributes (Dresselhuis et al., 2008).

The effect on sensory perception of electrostatic interactions in saliva-induced flocculation has been investigated using tribology (Upadhyay & Chen, 2019). In a comparison of emulsions prepared with negatively charged whey protein (WP^-, pH = 6.7), neutral modified starch (MS), positively charged lysozyme (L), and positively charged whey protein (WP^+, pH = 3.5), the observed trend in μ values with the addition of simulated saliva was found to lie in the order $WP^+ > L > WP^- > MS$, which correlated inversely with the corresponding oral and tactile smoothness scores. These findings are consistent with results previously mentioned on the amylase responsiveness of starch-based emulsions and the role of electrostatic interactions in protein-stabilized emulsions (Silletti, Vingerhoeds, Norde & van Aken, 2007a,b; Vingerhoeds, Blijdenstein, Zoet & van Aken, 2005; Sarkar, Goh & Singh, 2009). A convenient way to systematically control fat release caused by in-mouth droplet coalescence is to use a mixed emulsifier system, as recently demonstrated by Karthik, Ettelaie & Chen (2019) for O/W emulsions containing OSA-starch + whey protein. Such studies are providing a strong motivation to determine the optimum way of combining

protein with starch or a non-starch polysaccharide in a suitable ratio, either as a covalent conjugate or in a mixed layer, in order to control emulsion flocculation and coalescence during oral processing.

To summarize the current position, it seems crucial to take full account of properties of saliva upfront in order to optimize the behaviour of emulsions in the oral phase and to converge on the most desirable sensory properties that can be delivered by the hydrocolloid stabilizer. If our goal is simply to realize the generally positive sensory attributes of smoothness and creaminess, the use of amylase-responsive starch as a stabilizing ingredient would appear to be an effective strategy. On the other hand, the use of chemical modification to enhance starch surface activity and emulsification ability may not be considered appropriate as the food industry orientates towards the use of sustainable natural ingredients. In such circumstances, from the viewpoint of optimum hydrocolloid stabilizer design, it is clear that negatively-charged biopolymers are greatly to be preferred over positively-charged ones, in order to avoid any negative sensory responses related to complexation and precipitation of the lubricating salivary mucins.

4. Effect of hydrocolloid structure on gastric and intestinal digestion

Another aspect of thinking about the ideal hydrocolloid stabilizer is in relation to predicting the expected fate of emulsified lipids during their transit through the gastrointestinal tract and then select the right hydrocolloid to perform the site-specific function. The background to our current thinking is the growth in understanding over the last 2–3 decades about the gastric and intestinal digestion of emulsion systems and their key role in delivering bioactives as well as regulating glycaemia and lipaemia (Mackie & Macierzanka, 2010; Wilde & Chu, 2011; Singh & Sarkar, 2011; Golding et al., 2011; McClements, 2018; Sarkar, Zhang, Holmes & Ettelaie, 2019). The influence of changes in the gastrointestinal environment (pH, ions enzymes, bio-surfactants, metabolites) on stability and colloidal structuring has been described for systems stabilized by proteins (Sarkar, Goh, Singh & Singh, 2009; Macierzanka et al., 2011; Gumus, Decker & McClements, 2017; Wang et al., 2019), particles (Sarkar et al., 2016; Le, Loveday, Singh & Sarkar, 2020), mixtures of protein + polysaccharide (Qin et al., 2016; Xu, Sun & McClements, 2020) and mixtures of protein + particles (Sarkar et al., 2017b; Araiza-Calahorra & Sarkar, 2019). The biophysical

and biochemical environments encountered by these model emulsion systems lead to a series of instabilities ranging from flocculation to coalescence and eventual phase separation. These phenomena are influenced by various factors, including the residence time and the physiological site (stomach or specific section of the intestine), as well as by the type of hydrocolloid stabilizer used, the sizes of the droplets, and the initial aggregation state. Emulsified lipids finally self-assemble into various forms of colloidal structures that are essential for lipid absorption — micelles, vesicles, and liquid crystals.

Consistency in laboratory methodology for determining the products and kinetics of emulsion digestion has been enhanced by the development and adoption of the INFOGEST static and semi-dynamic *in vitro* digestion protocols (Minekus et al., 2014; Mulet-Cabero et al., 2020a). Understanding has progressed in incremental steps by the study of relatively simple model food systems such as the aforementioned O/W emulsions having simple or complex interfaces, as well as model emulsions embedded in more complex matrices (*e.g.* lipid droplets trapped in hydrogel network) (Guo et al., 2014) and some real foods (Mulet-Cabero, Rigby, Brodkorb & Mackie, 2017). Against this background, it is our belief that, in order to design a perfect hydrocolloid stabilizer with optimized capability in the most realistic and complex gastrointestinal milieu, we need first to identify the precise function that it might be supposed to perform. Two particular objectives can be identified: the pharmacokinetic function (increasing and sustaining the absorption rate) and the glycaemic function (decreasing the absorption rate). To best address one or other of these functions, the choice or design of the hydrocolloid stabilizer might well have to be rather different.

4.1. Addressing the pharmacokinetic challenge of sustained absorption

Emulsions are often used for the delivery of biologically active hydrophobic compounds such as fat-soluble vitamins, curcumin, *β*-carotene, *etc.* (Zhang & McClements, 2016; Nowak, Livney, Niu & Singh, 2019; Sarkar & Mackie, 2020). The core concept is to protect these compounds within certain sites in order to inhibit the breakdown and digestion of oil droplets (*e.g.*, in the gastric phase), and then to release them within the intestines at a certain specified rate (fast/sustained/controlled) so as to maximize absorption and ensure bioavailability (Sarkar & Mackie, 2020). In many, if not all cases, the stomach is the first site of mechanistic complexity, with its increasingly acidic pH and the presence of various ions and enzymes (pepsin and gastric lipase). In this environment, a dramatic change in emulsion microstructure can occur leading to a degradation of the encapsulated bioactive. Hence, the

choice of a simple protein-based monolayer as the stabilizing material might not be appropriate, as the interfacial protein will be digested by pepsin leading to uncontrolled flocculation and coalescence in the gastric phase (Sarkar, Goh, Singh & Singh, 2009; Golding et al., 2011). Under these conditions, the use of modified starch-stabilized systems may be considered more suitable because starch is only partially hydrolysed in the stomach (due to limited amylase activity) and the branched amylopectin chains can provide effective steric stabilization against coalescence (Lin et al., 2018). The application of starch granules as particle stabilizers has also gathered momentum in research studies aimed at preventing the gastric coalescence of emulsion droplets (Marefati et al., 2017). But, of course, the rapid digestion of starch-based systems in the oral regime should not be overlooked, despite the short oral residence time.

Interfacial materials composed of biopolymers that are unresponsive to human enzymes can be particularly appealing for providing stability under gastric conditions. Two examples of particle-based stabilizers are regenerated chitin particles and hydrophobically modified cellulose nanocrystals (Xiao et al., 2018; Le, Loveday, Singh & Sarkar, 2020). Another popular strategy to try to achieve gastric stability of droplets is to fabricate more complex interfaces consisting of multilayers of protein + polysaccharide (Corstens et al., 2017), two kinds of biopolymer particles (Sarkar et al., 2018), or a combination of proteinaceous microgel + polysaccharide in conjugated or complexed forms (Araiza-Calahorra, Glover, Akhtar & Sarkar, 2019; Araiza-Calahorra & Sarkar, 2019). The assumption is that the enhanced steric stabilization provided by the multilayer protects against interfacial degradation by pepsin and so improves stability during gastric incubation. For example, due to the formation of a thicker interfacial layer, an O/W emulsion stabilized by a composite whey protein + pectin interface has been found to increase the gastric stability of the droplets as compared to the pure whey protein-stabilized counterparts, regardless of whether the pectin is free or directly conjugated to the protein (Xu et al., 2014). Interfaces resilient to gastric degradation have been fabricated by the enzymatic cross-linking of gelatin to pectin using laccase (Zeeb, Lopez-Pena, Weiss & McClements, 2015).

In addition to protecting droplets at one particular physiological site, another key objective of pharmacokinetic control is to regulate the kinetics of release of free fatty acids (FFAs). In other words, one aspires to organize the hydrocolloid at the interface in such a way that the lipase–colipase complex can get access to the interface at a controlled rate. This is a particularly challenging objective, with real success limited despite two decades of research. The reason for this is that the body's own digestive surfactants (the bile salts) are especially

effective in competitively displacing biopolymers from the oil–water interface (Maldonado-Valderrama et al., 2008; Sarkar, Ye & Singh, 2016), meaning that the structure and composition of the original biopolymer-coated interface is of little significance. For instance, establishing one- to five-layered interfaces from whey protein, pectin and chitosan, or electrostatically depositing pectin on gelatin-coated droplets, has been found to lead to similar initial rates and extents of FFA release during simulated intestinal conditions (Zeeb, Weiss & McClements, 2015; Corstens et al., 2017). Although the use of particle–polymer combinations, either as conjugated or complexed systems, can prevent displacement by bile salts, such complex interfaces are ineffective in controlling intestinal lipid digestion because the lipase molecules, being small compared to the holes in the particle-laden interface, are able to freely access the oil–water interface without an energy barrier and hence release the FFAs (Araiza-Calahorra et al., 2020). To our knowledge, the only reported success in this regard in truly delaying FFA release is that recently achieved in our laboratory (Sarkar et al., 2016) where whey protein microgel particles were crosslinked *via* heat treatment after being adsorbed at the oil–water interface. Following this thermal treatment, there was inferred to be a substantial reduction in the area of the interfacial holes; this led to a slowing down in the access of the lipase to the lipid core, resulting in a lowering of the lipid digestion rate by a factor of 20 in comparison to a normal protein monolayer.

In some model studies containing complex interfaces, it has been found that not all the potentially available FFAs are actually released, *i.e.*, there is incomplete lipid digestion. This is undesirable because, if we do want to encapsulate a bioactive species and then release it, we would normally aim to release it completely rather than have some of it remain in association with the non-digested lipidic phase and hence unavailable for absorption. We can sum up what is required of an ideal hydrocolloid stabilizer from the pharmacokinetic perspective as follows: it should be resilient to pepsin digestion in the gastric phase, and it should create an effective diffusive barrier to liopolytic enzymes in the intestinal phase, such that complete lipid digestion does occur, but at a controlled rate, or following a suitable lag phase.

4.2. Gastrointestinal motility

The increase in obesity has driven a tendency for some food colloids research to focus on the control of glycaemia and lipaemia. One such approach aims to slow down lipid digestion. Initially it was thought that the flocculation of emulsions could be an elegant strategy to delay

963 gastric emptying. In reality, though, it has been found that gastric acid-unstable emulsions
964 exhibit phase separation and faster emptying profiles than do gastric acid-stable ones
965 (Steingoetter et al., 2015). However, it is worth noting that particles in the stomach do need to
966 reach a certain size (>1–2 mm) in order for them to create some degree of resistance to being
967 emptied into the duodenum (Hellström, Grybäck & Jacobsson, 2006). Floc sizes above 2 mm
968 are not so common in the literature of liquid emulsions; reported values are mostly in the
969 range of tens of micrometres (Wang et al., 2019). Nevertheless, appropriate types of dairy
970 protein can be useful for reducing gastric emptying. For instance, samples rich in casein (*i.e.*
971 (≥50% casein in 8% total protein) have been found to produce a solid coagulum in the gastric
972 phase; this causes a delay in nutrient emptying in comparison with the more soluble whey
973 protein-rich phase (Mulet-Cabero et al., 2020b). Similarly, unheated milk has been shown to
974 form a solid clot in the stomach, which influences the rate of emptying (Ye et al., 2019).

975 Hydrocolloids affect digestion kinetics in a number of ways — reducing gastrointestinal
976 motility, altering intestinal mucus permeability and barrier properties, binding exogenous
977 molecules, and finally influencing the phylogenetic profile of the gut microflora through
978 fermentation. Factors governing gastrointestinal motility include the nutritional composition
979 of the digesting food (chyme) and its bulk rheological properties (Marciani et al., 2001). Both
980 of these factors have a significant influence because the digestion process is tightly controlled
981 through a number of different feedback mechanisms driven by nutrient and stretch sensors at
982 various locations along the GI tract. For example, in the early phase of digestion, gastric
983 emptying is largely driven by two factors, namely the concentrations of nutrients sensed at
984 the duodenal epithelium and the rheological properties of the gastric chyme (Mackie et al.,
985 2013). In the former case, the presence of more nutrients, especially lipid and protein, leads
986 to slower emptying, as does an increase in the rheological properties of the gastric chyme.
987 The rheology also affects mixing and thus the transport of enzymes and digestion products
988 throughout the GI tract. The nutrient sensors control motility and drive appetite (Hajishafiee,
989 Bitarafan & Feinle-Bisset, 2019).

990 Another approach to influencing lipid digestion rate is by the sequestering of bile salts.
991 For example, systems stabilized by commercial cellulose ethers have shown to possess a
992 strong binding capability to bile salts both in aqueous media and at the oil–water interface,
993 which could have an influence on lipid digestion (Torcello-Gómez & Foster, 2014). Multi-
994 layered emulsions with secondary layers composed of various different polysaccharides
995 (chitosan, pectin, methylcelluloses) have been used to complex with bile salts and lipolytic

enzymes in order to attempt to slow down the overall release of lipid digestion products into the circulation (Espinal-Ruiz et al, 2014).

Evolution has driven the development of the human GI tract to efficiently extract nutrients from the food we eat. Consequently, there are a number of mechanisms that the body uses to control the rate at which food passes down the gut. As described in section 4, hydrocolloids can be designed to optimise the required digestion kinetics. For example, a protein may need to be delivered quickly after exercise in order to build muscle, whereas sugars and lipids may benefit the consumer with a more gradual release. This requirement to control digestion kinetics has led to concepts such as the glycaemic index for carbohydrates, and the same concept can also be applied to lipids. Many foods are now widely marketed as being of low glycaemic index: this health-beneficial designation can be achieved through the addition or manipulation of hydrocolloids in the form of soluble dietary fibre (Salmeron et al., 1997). Similar principles can, of course, be employed to lower the rate of absorption of any bioactive or nutrient.

The concept of fast and slow digesting proteins is well known in the dairy arena (Boirie et al., 1997). Indeed, there is now a significant industry built around the idea that whey protein has the right amino-acid profile, has a fast transit through the gastric phase of digestion, and is quickly hydrolysed and absorbed in the small intestine (Foegeding & Davis, 2011). This is in marked contrast to the caseins which coagulate under acidic conditions and pass through the gastric phase more slowly. The search is now on to tailor a wider range of proteins, particularly those of plant origin, which might also demonstrate a similarly high level of digestibility and a tuneable range of digestion kinetics (Loveday, 2020). The properties exhibited by proteins in the GI tract are determined by their amino-acid sequence and any post-translational modifications, including those induced by processing. If we are to find plant proteins with similar properties, there is a need to match the primary sequence and the applied processing requirements so as to generate the desired digestion characteristics in a predictable way. In the case of dairy proteins, the unique molecular structures and self-assembly behaviour of the disordered caseins leads to their specific coagulation behaviour, and the specific globular structures of the whey proteins renders them highly soluble and susceptible to hydrolysis (Foegeding & Davis, 2011). This susceptibility is driven by the ability of the proteolytic enzyme to access the site of cleavage on the substrate, as determined by a combination of interaction forces and steric considerations governed by the primary and secondary structure of the substrate. With the right protocols in place, this would seem to suggest that plant protein primary sequence could be linked to the desired characteristics.

Similar arguments are made for the properties of starch in relation to gastric motility. Starch can be categorized as fast digesting, slowly digesting, or resistant. Clearly these designations indicate how quickly the absorbable sugars are released from the starch (measured by glycaemic index), but they also indicate the extent to which the material affects the rheological properties of the surrounding milieu. Fully gelatinized starch has a high water-holding capacity, and so it can have a marked effect on the rheology of gastric chyme. However, its more open structure makes it more susceptible to hydrolysis by amylase, which in real food systems occurs throughout the GI tract. There has been a significant amount of research addressing the link between starch structure and digestibility (Lovegrove et al., 2017). In addition to the effect on glycaemia, recent research has also looked into the use of Pickering emulsion systems to control the kinetics of lipid digestion by means of the enhanced stability to coalescence and the restricting of access to the substrate (Sarkar, Zhang, Holmes & Ettelaie, 2019).

While protein and starch can contribute to the viscoelastic properties of a food, they are both likely to be hydrolysed in the stomach, potentially reducing the chyme viscoelasticity. However, proteins may also aggregate as the pH in the gastric phase approaches the isoelectric point, and particularly so if accompanied by proteolysis. This is, after all, the basis of cheese making. The aggregation of the caseins in milk makes them much more slowly hydrolysed. Moreover it has been shown that the digestion kinetics of milk can be controlled through the use of traditional processing methods such as homogenization and thermal treatment (Mulet-Cabero et al., 2019). Following these ideas, it is clear that if the ideal digestible hydrocolloid in this context is to be plant-based, it will need to be highly soluble in the aqueous environment and able to change its susceptibility to proteolysis as a function of processing conditions.

Hydrocolloids can be considered to comprise two groups in relation to digestion: those that are readily digestible such as proteins and starch, and those that are not digestible such as non-starch polysaccharides (NSPs). The latter are known collectively as dietary fibre. While the non-starch polysaccharides affect all processes in the gut from the mouth to the colon (Lovegrove et al., 2017), they are of particular importance in the colon where they are fermented by intestinal bacteria into short chain fatty acids (SCFA) that are essential for gut health. Of course, dietary fibre is not the only type of hydrocolloid reaching the large intestine. Anything that has not been digested and absorbed during its passage through the small intestine will pass into the colon. Nutrients such as indigestible protein or resistant

starch that pass into the colon may influence the gut microbiome in a positive way by increasing diversity.

Non-starch polysaccharides are resistant to hydrolysis by endogenous enzymes. They also have an important role to play in digestion (Brownlee, 2011). While there has been some recent research undertaken on the use of NSPs to alter digestion kinetics, this has so far only been undertaken *in vitro* or in animals such as rodents (Chen et al., (2020a,b). In both cases, the results have shown that the addition of NSP hydrocolloid reduces the rate of digestion (and absorption). Furthermore, the *in vivo* results also showed physiological responses that may be relevant to the fight against obesity. The precise nature of the NSP is clearly important: for β-glucan it was reported (Regand, Tosh, Wolever & Wood, 2009) that 73% of the bioactivity in reducing the peak blood glucose response could be explained in terms of the peak molecular weight and the concentration. Although molecular weight is thought to be of critical importance in relation to a hydrocolloid's role in increasing the viscosity of intestinal chyme, the *in vitro* experiments with β-glucan have shown that lipid hydrolysis is not directly correlated with solution viscosity, with other factors affecting emulsion stability also playing an important role, due to the reduction in available surface area of substrate (Grundy, McClements, Balance & Wilde, 2018). Similar effects have been seen with the release and absorption of carotenoids due to their poor aqueous solubility. A review of the influence of pectin on carotenoid bioavailability (Cervantes-Paz et al., 2017) concludes that both the molecular weight and the degree of methylation are important in modulating the formation of the mixed micellar phase solubilizing carotenoids. While there are many other studies looking at similar systems, the overall conclusion is that the digestion and absorption of bioactives can be modulated, but the mechanisms involved are varied and not usually based on viscosity.

4.3. Mucosal interactions

Polysaccharides that gel or substantially increase the bulk viscosity have shown promise in delaying gastric emptying and in binding with enzymes and bile salts to slow down lipolysis kinetics. For instance, using quantitative confocal microscopy methods such as fluorescence recovery after photobleaching (FRAP) and multiple particle tracking, it has been demonstrated that dietary fibre such as alginate, in entanglement with intestinal mucins, can significantly delay the transport of lipid digestion products (Mackie, Bajka & Rigby, 2016). Using cellulose nanocrystals together with Tween as the interfacial material (Liu, Kerr &

Kong, 2019) or hydrophobically modified cellulose (Le, Loveday, Singh & Sarkar, 2020), it was shown that the cellulose nanoparticles in the continuous phase form a hydrogel network in the gastric phase which eventually results in a lower rate and extent of digestion. The particles also get entangled in the intestinal mucus layer; this means that they fail to reach the underlying epithelium, thereby diminishing the extent of lipid absorption from the emulsions (Mackie et al., 2019).

In all regions of the GI tract, including the mouth, a layer of mucus protects the mucosal surfaces. Mucus is a viscous layer comprising glycoprotein mucins, DNA, and other peptides and proteins (Mackie et al., 2017), and the barrier properties of this hydrocolloid layer vary both spatially and temporally. The intestinal mucus carries a net negative charge due to its relatively high degree of sulfation and the presence of sialic acids (Corfield, 2015). This means that positively charged moieties tend to bind electrostatically to the mucus and so are unable to diffuse through it. Indeed, mucoadhesive hydrocolloids such as chitosan are used for just this purpose (Mackie et al., 2017).

Hydrocolloids inevitably encounter the gut wall as they pass down the GI tract and the nature of that contact is determined by the properties of the hydrocolloid. The mucus layer that covers and protects the underlying gastrointestinal epithelium is negatively charged and it exhibits a range of rheological behaviour from a viscoelastic fluid to a soft gel (Lai, Wang, Wirtz & Hanes, 2009). The gel network has a pore size of ~100 nm, but again this may vary significantly in the heterogeneous regions of the small intestine (Lai, Wang & Hanes, 2009). All nutrients and bioactives must diffuse through this layer in order to be absorbed by the underlying enterocytes. It would appear that negative charge plays a critical role in the passage of colloidal particles and solutes. For example, lipid droplets or mixed micelles formed from the hydrolysis of lipids containing bile acids and fatty acids that carry negative charges can traverse the mucus layer, whilst emulsion droplets without bile adsorbed to their interface are unable to penetrate the mucus (Macierzanka et al., 2011). The same rules apply to the penetration of polysaccharides, with anionic polymers such as alginate able to diffuse through the intestinal mucus, whereas cationic polymers such as chitosan are mucoadhesive — they simply form a separate layer on the mucus surface (Mackie et al., 2017).

The consequence of the diffusion of anionic polymers into the mucus is to lower its permeability to other particulates by reducing the pore size. As the local concentration of polymer increases, the overlap concentration is approached; this has the potential to increase the local viscosity significantly, providing a more effective barrier to bacteria. Experiments

involving both 100 nm latex beads and lipid digestion products have shown a reduction in diffusion coefficient in the presence of polysaccharides such as alginate (Mackie et al., 2016) or oat β-glucan (Mackie, Rigby, Harvey & Bajka, 2016). Similarly, insoluble particulate polysaccharides such as cellulose have been found to be unable to penetrate intestinal mucus or to form a surface layer in a similar manner to soluble cationic polymers (Mackie et al., 2019). In the case of cellulose nanocrystals, this may be due to a combination of size and surface properties. One of the primary roles of the intestinal mucus layer is to act as a barrier to pathogenic bacteria; the limitation on the sizes of the colloidal particles that are able to penetrate the mucus at a significant rate fits in with that requirement.

5. Fermentation and transport into the colon

The microbiota in the colon survive on food that we consume but are unable to digest. This is normally considered to be dietary fibre in the form of soluble or insoluble polysaccharides, but it may also include other peptides, oligosaccharides, lipids, *etc*., which can have an impact on the gut microbiota (Macfarlane & Macfarlane, 2012). Rather than the more traditional view of good and bad bacteria, more recent evidence suggests that a broader range of bacteria is the healthier position (Le Chatelier et al., 2013). A consequence of this is that a wide spread of fermentable substrates passing down the gut is likely to be beneficial. Additionally, the continuous flow of chyme along the GI tract will tend to prevent bacterial overgrowth in the more proximal sections. Therefore, the properties of the ideal hydrocolloid in relation to colonic fermentation should, under the most favourable circumstances, be related to the promotion of a diverse range of bacteria. This implies the presence of a soluble dietary fibre that might be associated with other compounds that could be released as a result of fermentation. There is a range of cereal polysaccharides that might fit this description and they all carry with them a selection of phenolic compounds and oligosaccharides (Schar et al., 2018). The ability of non-starch polysaccharides to resist digestion also means that they are capable of acting as carriers of both exogenous and endogenous cargo into the colon. One of the most researched examples is oat β-glucan in relation to cholesterol lowering by virtue of the limiting of bile recycling in the distal ileum (Wood, 2007; Othman, Moghadasian & Jones, 2011). The evidence suggests that the ability of such a high-molecular-weight polymer to increase viscosity is at the heart of the effect, with the polymer entrapping the bile rather than binding to it through hydrophobic or other interactions. Other examples include the

interaction between dietary fibre and phenolic compounds such as isoflavones which are subsequently metabolized to more bioactive compounds (Lampe, Karr, Hutchins & Slavin, 1998). Again, it is unclear whether the beneficial health effects are a consequence of the viscosity increase induced by the fibre or through direct binding. Regardless of the mechanism, it is clear that the ideal hydrocolloid should continue to impart significant viscosity throughout the upper GI tract, it should be highly fermentable, and it should preferably have the capacity to bind beneficial compounds.

6. Concluding remarks

We have aspired to approach the properties of the perfect hydrocolloid stabilizer from various conceptual and operational perspectives — the statistical thermodynamics of adsorption and colloid stabilization; the dynamics of interfacial formation, adsorption and deformation; the rheology, lubrication, and interactions with saliva during oral processing; the pharmacokinetic and glycaemic challenges of digestion; and the control of gut motility and microflora. We have seen that the ideal stabilizing macromolecule from the equilibrium theoretical viewpoint is a soluble hydrophilic block copolymer of low net charge containing strongly adsorbing hydrophobic groups located in a single localized region. From a dynamic perspective, the ideal macromolecule should be sufficiently flexible to adsorb rapidly at the fluid interface, leading to the development of an interfacial film that is thick and coherent, but one also resilient to catastrophic structural failure under large stress and strain. To produce a smooth in-mouth textural perception, the (negatively charged) hydrocolloid should be able to generate a relatively high viscosity at orally relevant shear-rates and should act as a continuous lubricating film between oral surfaces on the spatial scale from a few molecular thicknesses up to micrometres. From a pharmacokinetic perspective, the ideal hydrocolloid should be resilient to proteolytic digestion within the gastric environment to some extent, whilst generating an effective diffusive barrier to lipolytic enzymes in the intestinal phase, depending on the rate of lipid digestion that is most appropriate for the individual concerned. From the optimal glycaemic perspective, it needs to have the capability to form a gel under acidic conditions so as to retard gastric emptying and therefore inhibit rapid rises in blood glucose; an ability to bind with lipases and bile salts to control lipid digestion kinetics could also be an advantage. Finally, in its functional role as dietary fibre, whilst generating a substantial viscosity throughout the whole GI tract, the ideal hydrocolloid should be highly

fermentable in the colon and capable of acting as a binding site for gut-beneficial compounds like phenolics and oligosaccharides.

The pragmatic food scientist might bluntly observe that it should have been blindingly obvious from the outset that no single hydrocolloid stabilizer could possibly satisfy all the many functional requirements involved in the making, processing, storing, eating, and digesting of a colloidal food system. And, indeed, even from the purely theoretical viewpoint it is quite difficult to reconcile the partially conflicting positive and negative functional attributes exhibited by some highly contrasting categories of materials possessing the hydrocolloid designation, *e.g.*, modified starch *versus* non-starch polysaccharides, or soluble polymeric stabilizers *versus* particle-based stabilizers. Accepting these reservations, though, and assuming that we are strictly limiting our considerations to the specific case of a *polymer*-based emulsifier/stabilizer at the interface of an O/W emulsion, it seems reasonable to assert that we do now have the solid conceptual framework with which to approach the imaginary state of hydrocolloidal perfection — although not, of course, to fully attain it.

To pursue the pragmatic argument a little further, it seems intuitively obvious that the physico-chemical properties of any hydrocolloid ingredient used to make and stabilize a food emulsion are likely to be quite relevant to the oral processing and sensory perception of that same emulsion during the first few moments the emulsion is eaten. But the further that this same hydrocolloid traverses along the GI tract, the more it will tend to get separated from the originally emulsified oil, and become mixed in with all the other components of the diet — including different proteins, carbohydrates, lipids and nutrients. Set against the relatively modest amount of hydrocolloid ingredient that would be needed to stabilize the food emulsion portion of a substantial meal, it is highly likely that some other macromolecular components of our nutritionally well-balanced diet could well turn out to be rather more functionally effective in addressing the pharmacokinetic or glycaemic challenges, or in functioning as dietary fibre. This pragmatic attitude might then lead us to towards being prepared to give rather less emphasis to trying to satisfy the later stage digestion functionality requirements of our perfect hydrocolloid stabilizer. From such a simplified perceptive, the molecular and functional requirements of the perfect ingredient appear more well-defined and technically manageable:

- a high-molecular-weight flexible polymer generating effective steric stabilization
- an amphiphilic chain with extended hydrophilic region and localized hydrophobic region
- a molecule composed of mainly polar uncharged groups (or just a few negative charges)
- surface activity, rapid adsorption behaviour, and network/multilayer forming ability

- bulk thickening and lubricating capability at oral surfaces in the presence of saliva

Additionally, of course, for food-related applications, this ingredient should be non-toxic, exhibit no unpleasant taste, and satisfy all the regulatory standards.

The desirable characteristics highlighted above appear to be consistent with the idea of an ideal hydrocolloid consisting of some kind of protein–polysaccharide conjugate/complex. The excellent emulsifying and emulsion stabilizing properties of natural gums and Maillard conjugates possessing this sort of hybrid polymeric structure are already very well described in the food hydrocolloid literature. Moreover, this same class of protein–polysaccharide conjugates would seem to possess general characteristics that are rather favourable for the enhancement of lubrication behaviour during oral processing. It can further be suggested that microgel particles based on conjugated or complexed biopolymer components might be especially effective in combining the specific molecular attributes of both proteins and polysaccharides with the particular functional advantages of particle-like behaviour.

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FIGURE LEGENDS

Fig. 1. Interaction potential between two droplets of size 1 μm, induced by the presence of a dilute solution (0.1 vol%) of non-adsorbed linear homopolymers of 600 monomers. The interaction energy (units of k_BT) is plotted against the surface-to-surface separation.

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Figure 1

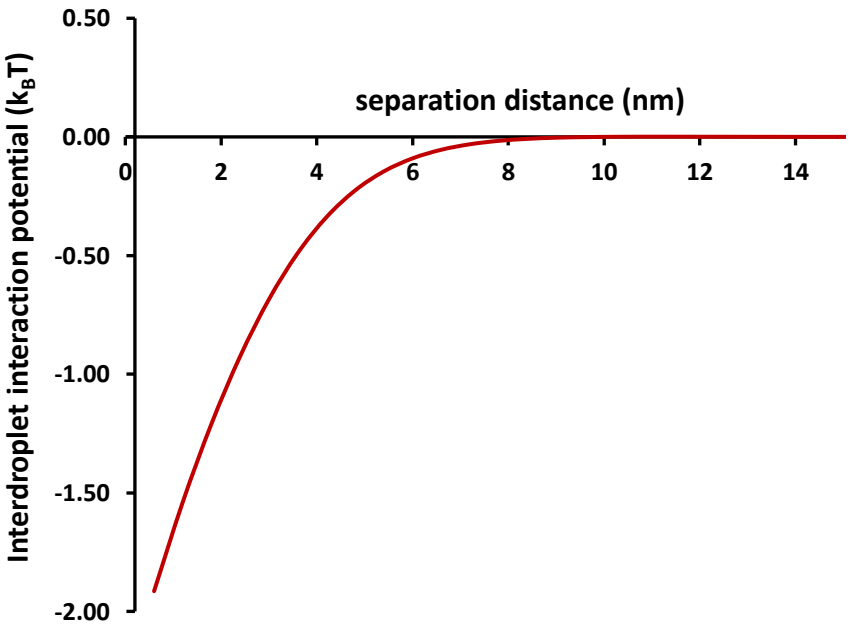

0.50
0.00
-0.50
-1.00
-1.50
-2.00
0
2
4
6
8
10
12
14
separation distance (nm)
Interdroplet interaction potential (k_BT)

Figure 2

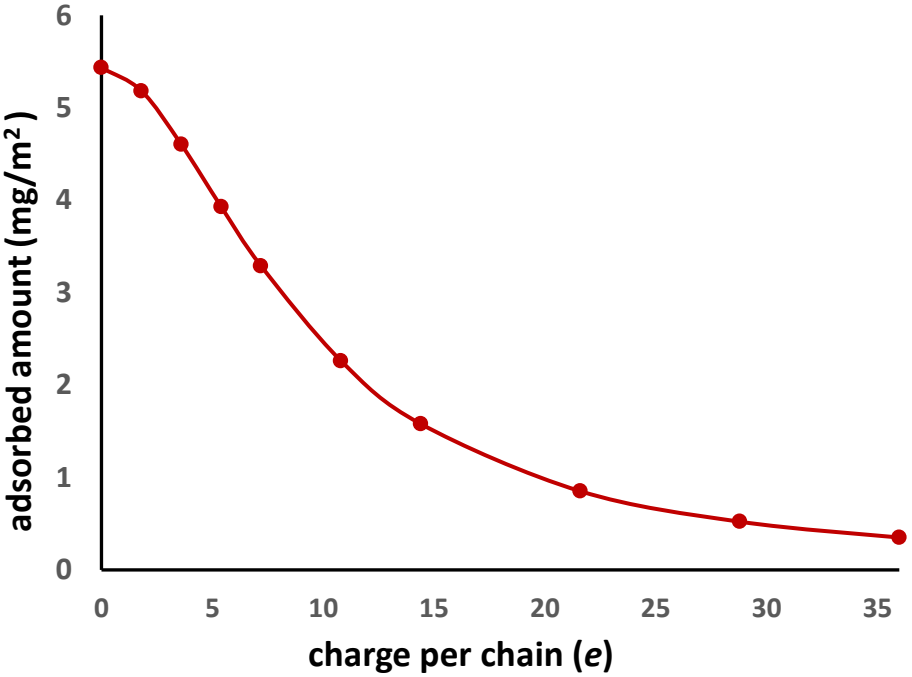

adsorbed amount (mg/m²)
0
1
2
3
4
5
6
0
5
10
15
20
25
30
35
charge per chain (e)

Figure 3

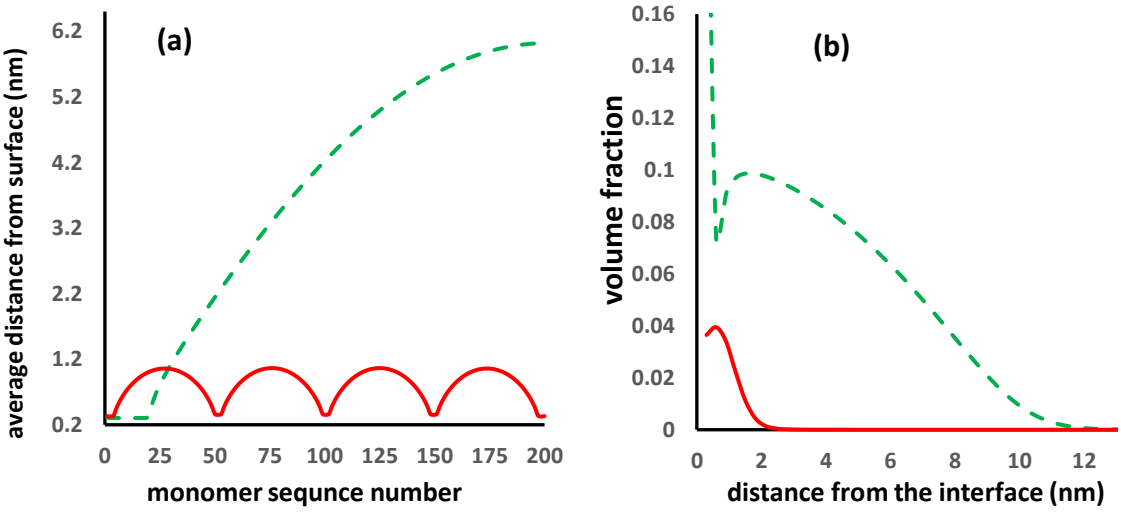

(a)
average distance from surface (nm)
6.2
5.2
4.2
3.2
2.2
1.2
0.2
0
25
50
75
100
125
150
175
200
monomer sequnce number
(b)
volume fraction
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
2
4
6
8
10
12
distance from the interface (nm)

Figure 4

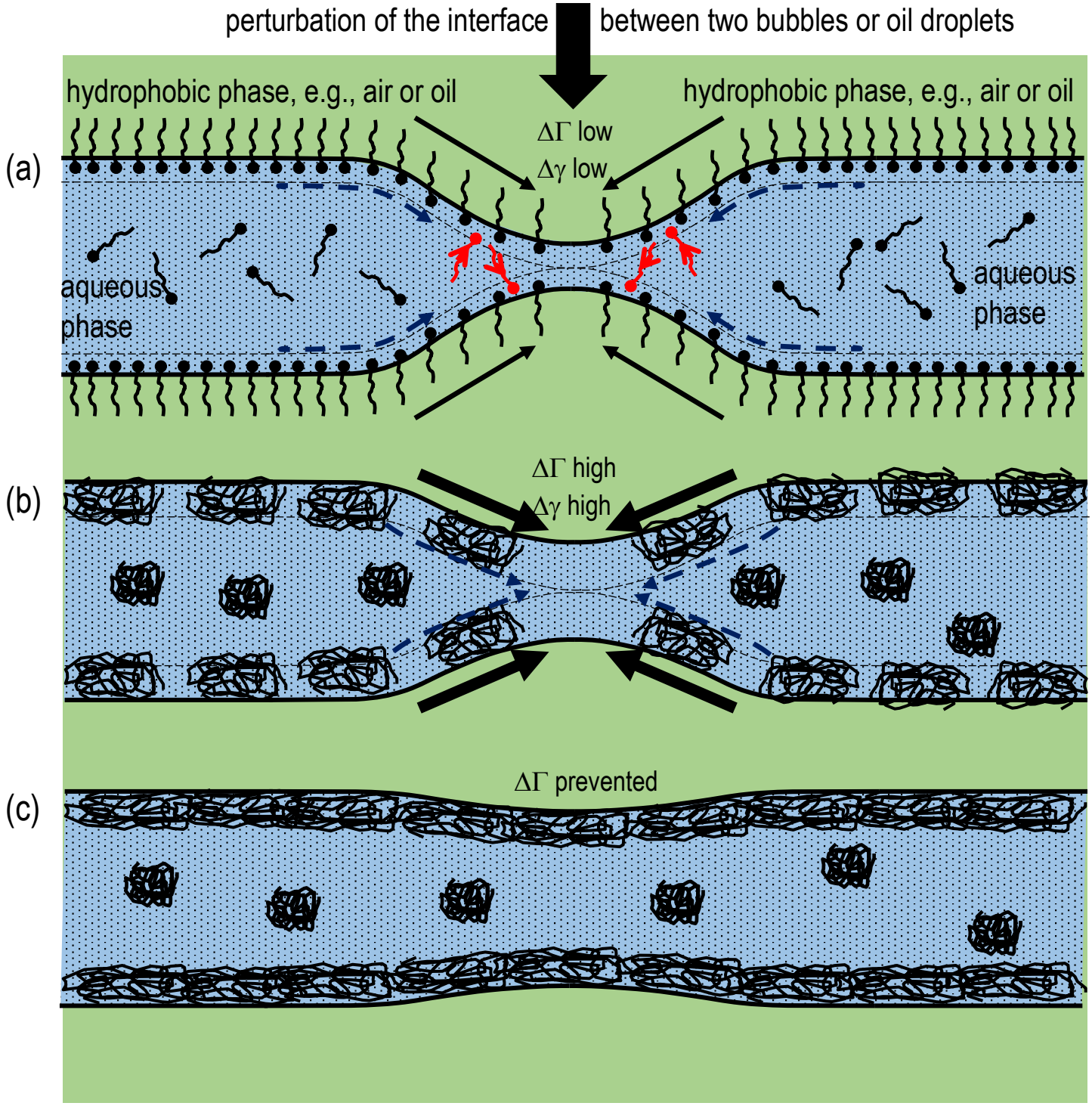

perturbation of the interface between two bubbles or oil droplets
hydrophobic phase, e.g., air or oil
hydrophobic phase, e.g., air or oil
ΔΓ low
Δγ low
(a)
aqueous phase
aqueous phase
ΔΓ high
Δγ high
(b)
ΔΓ prevented
(c)

Figure 5

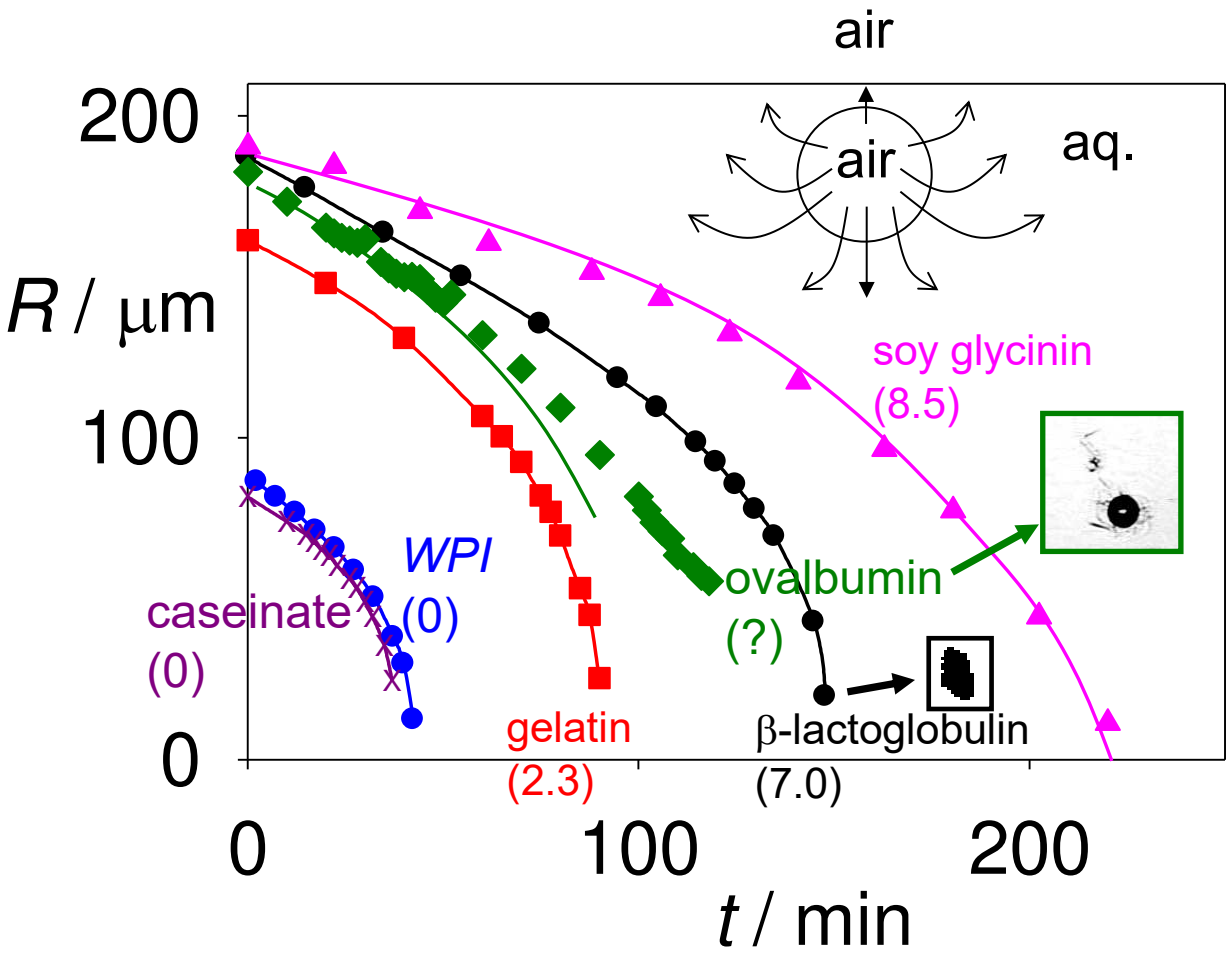

air
200
air
aq.
R / μm
100
soy glycinin
(8.5)
WPI
(0)
caseinate
(0)
ovalbumin
(?)
gelatin
(2.3)
β-lactoglobulin
(7.0)
0
0
100
200
t / min

Figure 6

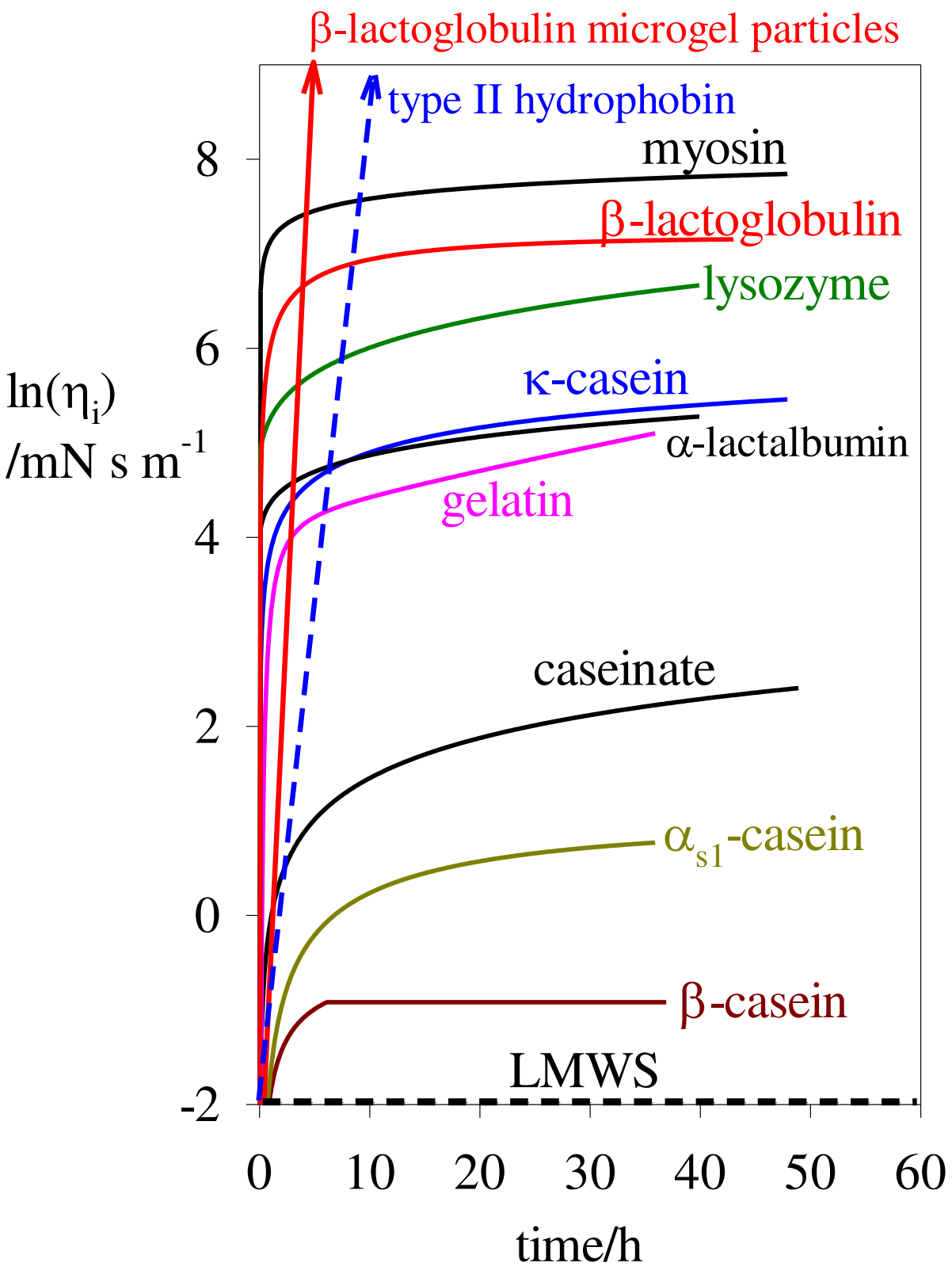
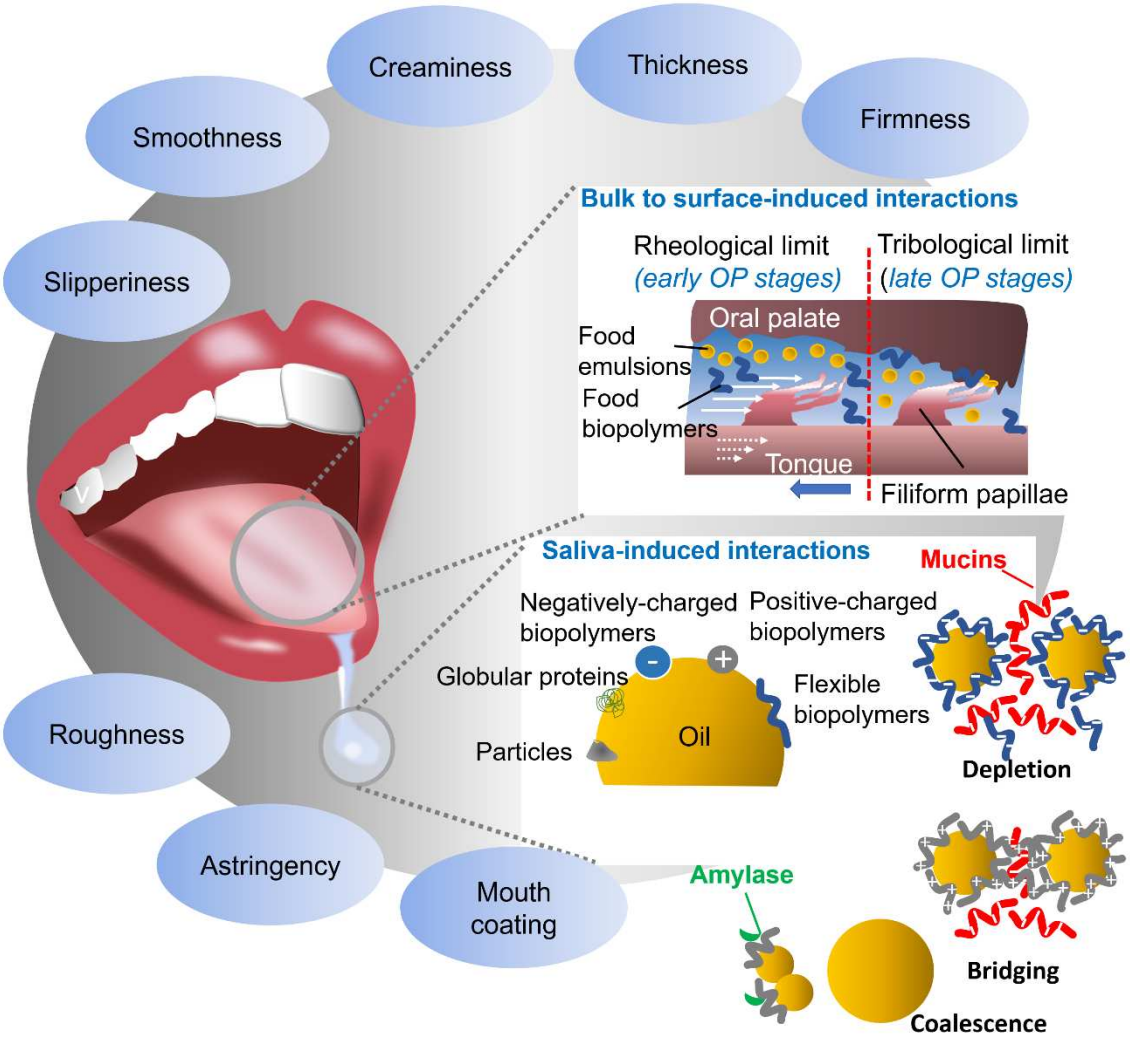

β-lactoglobulin microgel particles
type II hydrophobin
myosin
β-lactoglobulin
lysozyme
κ-casein
α-lactalbumin
gelatin
caseinate
α_{s1}-casein
β-casein
LMWS
ln(η_i) /mN s m^-1
8
6
4
2
0
-2
0
10
20
30
40
50
60
time/h

Figure 7


Creaminess
Thickness
Smoothness
Firmness
Slipperiness
Roughness
Astringency
Mouth coating
Bulk to surface-induced interactions
Rheological limit
(early OP stages)
Tribological limit
(late OP stages)
Oral palate
Food emulsions
Food biopolymers
Tongue
Filiform papillae
Saliva-induced interactions
Mucins
Negatively-charged biopolymers
Positive-charged biopolymers
Globular proteins
Flexible biopolymers
Particles
Oil
Depletion
Amylase
Bridging
Coalescence

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