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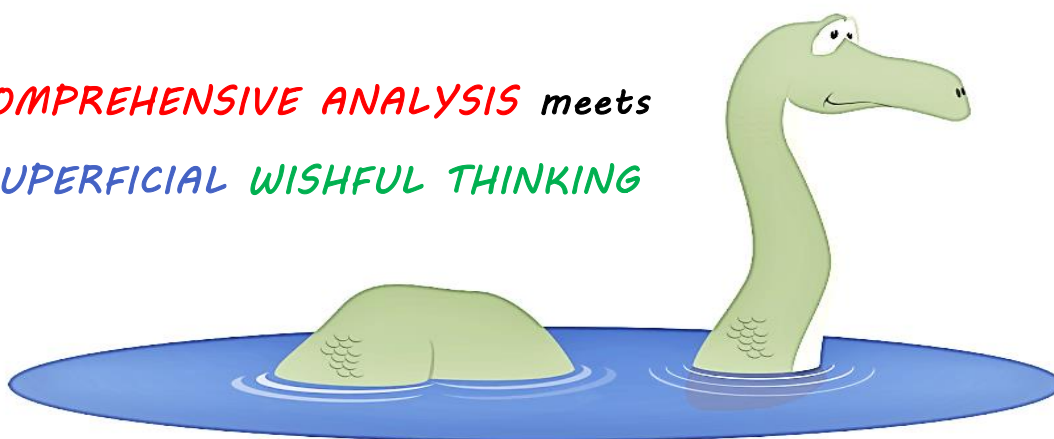


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## Graphical Abstract

Characterizing the perfect hydrocolloid stabilizer...

*COMPREHENSIVE ANALYSIS* meets  
*SUPERFICIAL WISHFUL THINKING*



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

## **The perfect hydrocolloid stabilizer: imagination *versus* reality<sup>o</sup>**

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<sup>o</sup> 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

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## 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).

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

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

44 Before proceeding further, let us clarify what we mean by the term ‘stabilizer’. Simply  
45 stated, a ‘stabilizer’ is a substance — usually polymeric in nature — which confers *long-term*  
46 physical stability on an emulsion or colloidal dispersion (Dickinson, 2003, 2009a). The  
47 stabilizing potential of any macromolecular species is dependent on its detailed molecular  
48 structure and on its thermodynamic behaviour in solution and at fluid interfaces (Semenova,  
49 2007; Semenova & Dickinson, 2010). Mechanistically, an individual biopolymer stabilizer  
50 can behave in two distinct ways. It may adsorb to the outer surface of solid particles or oil  
51 droplets forming a protective polymeric layer that prevents the dispersed entities from  
52 sticking close together. Alternatively, or simultaneously, it may modify the rheological  
53 properties of the bulk aqueous phase, thereby inhibiting the motion of individual particles and  
54 droplets under the influence of gravity, diffusional forces, and interparticle interactions.  
55 While not in any way underestimating the great importance of hydrocolloids acting as  
56 thickening agents and rheology modifiers, our main focus in this article will be on the  
57 functional stabilizing role of biopolymers *via* adsorption at oil–water interfaces.

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



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

87 Foods are complicated in terms of structure and composition. In many emulsion  
88 formulations, the pragmatic food scientist has to consider the behaviour of mixed functional  
89 ingredients having a broad range of emulsifying, stabilizing, thickening and gelling  
90 properties. Some of these stabilizing ingredients are plant-based materials of low surface  
91 activity and limited solubility. What this means is that a lot of food emulsion systems are  
92 predominantly stabilized not by macromolecular stabilizers, but by different kinds of  
93 nanoparticles or microparticles (Dickinson, 2012). Some of these particles are located  
94 directly at the surfaces of liquid droplets (Pickering stabilization) whilst others function as  
95 structuring agents in the gaps between dispersed oil droplets (Dickinson, 2015a). Currently  
96 there is considerable interest in the formation and stabilization of food emulsions with  
97 different kinds of biopolymer-based particles. These ongoing developments have been set out  
98 in recent review articles (Lam, Velikov & Velev, 2014; Xiao, Li & Huang, 2016; Dickinson,  
99 2017, 2020; Calabrese, Courtenay, Edler & Scott, 2018; Murray, 2019a; Sarkar & Dickinson,  
100 2020; Zhao, Zaaboul, Liu & Li, 2020; Shi, Feng, Wang & Adhikari, 2020; Yan et al., 2020).

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

104 Various colloid-based strategies have been devised and implemented to improve the  
105 emulsifying and stabilizing properties of existing food ingredients (Ettelaie, Zengin & Lee,  
106 2014; Ettelaie, Zengin & Lishchuk, 2017). A well-established chemical approach involves  
107 adjusting the hydrophilic/hydrophobic balance of food macromolecules. Depending on the  
108 starting material, there are two modes of chemical intervention: (i) hydrophobic modification  
109 of a hydrophilic carbohydrate polymer (starch or cellulose) to increase its amphiphilicity and  
110 surface activity, and (ii) hydrophilic modification of a globular protein to enhance its  
111 solubility and steric stabilizing ability. Chemical treatment may also modify the charge  
112 distribution along the polymer chain, thereby enhancing any electrostatic contribution to  
113 colloid stability. In addition, enzymatic treatment may be employed to enhance biopolymer  
114 solubility and surface activity. Or, starting from a binary mixture of protein + polysaccharide,  
115 a hybrid entity of enhanced interfacial functionality may be generated by electrostatic  
116 complexation or covalent conjugation (Wijaya, Patel, Setiowati & van der Meeren, 2017). It  
117 appears that the mechanistic basis underlying the functional consequences of these  
118 macromolecular transformations are now reasonably well understood, at least in intuitive or  
119 qualitative terms. But can we go one stage further and imagine what would be the precise  
120 molecular structure of a fully optimized biopolymer stabilizer? In other words, is there some  
121 ideal biopolymer structure, in terms of polymer chain length and distribution of chemical  
122 groups (hydrophilic, charged, hydrophobic), which can be expected to confer an optimum  
123 degree of stabilization? And, if we can envisage such an ideal hydrocolloid stabilizer, what  
124 are the consequences for its use in terms of oral processing and emulsion digestion?

125 The rest of the article is organized as follows. Section 2 describes the underlying  
126 theoretical framework leading to the concept of the perfect stabilizer. Section 3 sets out the  
127 behaviour of the hydrocolloid stabilizer during oral processing and sensory perception.  
128 Section 4 outlines the response to gastric and intestinal conditions of digestion. Section 5  
129 considers the influence on gut motility and interactions with gut microflora. Finally, section 6  
130 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 & Pugnali, 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  $1\ \mu\text{m}$  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

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

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

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

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

211 So far, we have not mentioned the type of interdroplet forces which the adsorbed  
212 macromolecular layers may generate. The forces need to be predominantly repulsive to  
213 counteract the van der Waals interactions between the droplets. These van der Waals  
214 interactions always exist and they cannot be turned off. Furthermore, they are always  
215 attractive for pairs of droplets composed of the same material (Russel, Saville & Schowalter,  
216 1989; Dickinson, 1992). Interoplet electrostatic repulsion may be induced by the adsorption  
217 of small charged surfactant molecules. (In food systems, for reasons of safety, the permitted  
218 ingredients are limited to anionic or zwitterionic surfactants). Adsorbed layers of amphiphilic  
219 macromolecules, if possessing the right molecular structure, are able to generate repulsive  
220 steric forces as well as repulsive electrostatic forces. These electrostatic forces can be strong,  
221 and, in formulations of low electrolyte concentration, sufficiently long-ranged to prevent  
222 droplet aggregation. At higher electrolyte concentrations, however, the surface-to-surface  
223 separation distances required for their operation is rather limited (*i.e.* only ~ 1 nm for a 0.03  
224 mol l<sup>-1</sup> NaCl solution). This renders electrostatic forces rather ineffective in providing the  
225 necessary colloidal stability for many food formulations. Furthermore, many biological  
226 macromolecules tend to have isoelectric points (*pI*) in the pH range 4–5.5. For food  
227 formulations with required pH values close to *pI*, either in the final product or at some stage  
228 during processing, this can be problematic. The loss of the charge of the protein stabilizer at  
229 pH ~ *pI* all but switches off the interdroplet electrostatic repulsion. One strategy for  
230 overcoming this problem is to work with polypeptides having unusually high or low *pI*  
231 values, *i.e.*, outside the range of interest for practical food formulations. This may be  
232 achieved by identifying an appropriately charged polypeptide fragment in a protein with a  
233 more conventional *pI* value (Ettelaie, Zengin & Lee, 2014; Ettelaie, Zengin & Lishchuk,

234 2017). The task of fragmenting the protein enzymatically to the right level of hydrolysis, and  
235 then separating out the target polypeptide from amongst the many other generated fragments,  
236 remains a challenging, but nevertheless worthwhile, future experimental task for food colloid  
237 scientists. In practice, there has to be a compromise between small fragments that adsorb  
238 rapidly during emulsification and large fragments that may provide better stabilization after  
239 emulsion formation. The negative flavour perception with some small peptides has also to be  
240 considered.

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

258 Having established that the ideal emulsion stabilizing agent is best achieved with  
259 macromolecules that are predominantly reliant on the provision of steric forces, how can we  
260 ensure that such forces are long-ranged and strong? Clearly, longer chains having more  
261 extended hydrophilic parts can be helpful in achieving this (Ettelaie, Holmes, Chen &  
262 Farshchi, 2016; Dickinson, 2018). Additionally, it is beneficial to have a high degree of  
263 surface coverage because this makes for interfacial films that are thick and dense. With all  
264 else remaining the same, the highest coverage tends to be achieved with molecules which do  
265 not possess any electrical charge. The same electrostatic forces that operate between adjacent  
266 films also exist between different molecules in the same layer (Ettelaie, Akinshina & Maurer,  
267 2012). The effect of these electrostatic repulsive forces is to hinder the adsorption process

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

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

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

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

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

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



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

350

## 351 *2.2. Dynamic requirements*

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

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

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

### 370 *2.2.1. Gibbs–Marangoni response and interfacial dilatational rheology*

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

$$378 \quad \varepsilon = d\gamma/dA/A = d\gamma/d\ln A \quad , \quad (1)$$

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

$$385 \quad \kappa = d\gamma/(d\ln A/dt) \quad , \quad (2)$$

386 where  $d\ln A/dt$  is the *rate* of interfacial strain. Measuring dilatational rheology by means of  
387 oscillatory deformations of the interface means that the response is characterized in terms of  
388 the dynamic interfacial dilatational storage and loss moduli ( $G_i'$  and  $G_i''$ ), which are  
389 dependent on both frequency and amplitude. The higher the value of  $\varepsilon$  (or  $G_i'$ ), the greater is  
390 the resistance to expansion; and the higher the value of  $\kappa$  (or  $G_i''$ ) the slower is the expansion  
391 in response to the applied stress. The response of the film on expansion is not necessarily  
392 equal and opposite to that on compression, and the more so the larger the magnitude of the  
393 strain (Murray, 2002; Pugnali, Ettelaie & Dickinson, 2005a,b). After all, an already close-  
394 packed film cannot become any more close-packed without ‘crumpling’, whereas the same  
395 monolayer film may be expanded indefinitely. Therefore, the frequency response of  
396 interfacial films is often asymmetric with respect to expansion and compression (Murray,  
397 2002; Pugnali, Ettelaie & Dickinson, 2005a,b). Furthermore, if the interfacial species are  
398 solid particles exhibiting Pickering stabilization, then a different set of rules applies: by

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

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

410 Other factors moderating the response include any tendency for the stabilizer molecules to  
411 form attractive interactions once they are adsorbed. These interactions might be non-covalent  
412 (H-bonding, hydrophobic, ionic) or covalent (disulfide cross-links), acting between adsorbed  
413 biopolymers as they unfold at the interface, or through bonds induced by chemical or  
414 enzymatic means (Faergemand, Murray, Dickinson & Qvist, 1999), or simply through  
415 aggregation of particles once they are adsorbed (see Fig. 4(c)). The adsorbed entities now  
416 become effectively larger and slower to respond to interfacial stresses and strains than the  
417 originally adsorbing ones. Any in-film cross-linking may cause inhomogeneities in the film  
418 structure over larger length scales (Xu, Dickinson & Murray, 2007; Murray, Xu & Dickinson,  
419 2009). Such defects lead to a distribution of local moduli within the adsorbed film and  
420 therefore specific locations of weakness at large strains.

### 421 *2.2.2. Dynamics of adsorption and desorption*

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

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

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

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

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

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

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

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

499 fracture occurs as well as to the interfacial dilatational and shear moduli (Murray et al., 2002,  
500 2003).

### 501 2.2.3. *Dynamic interfacial shear response*

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

519 Almost any disturbance of the interface in real situations will involve a combination of  
520 dilatational and shear deformations. Therefore, we can say that values of  $G_i$  and  $\eta_i$  should be  
521 high enough to provide some resistance to the deformation of the interface, but not so high  
522 that the deformation will lead to sudden fractures and drastic inhomogeneities in the stabilizer  
523 layer. The conditions underlying this behaviour can be understood through computer  
524 simulations of model adsorbed layers subjected to dilatational or shear deformation, where  
525 the stabilizer species are simply modelled as spherical particles interacting through weak  
526 (transient) or strong (permanent) interparticle cross-links (Pugnaloni, Ettelaie & Dickinson,  
527 2004, 2005a,b). Such simulations have confirmed the asymmetry in the response to  
528 compression and expansion, as well as the crumpling of strongly cross-linked films when the  
529 interparticle attractive interactions are sufficiently strong.

### 530 2.2.4. *Dynamics of competitive adsorption*

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

539 Macromolecular cross-linking improves the resistance to displacement of high-molecular-  
540 weight stabilizers by low-molecular-weight surfactants (LMWS) (Roth, Murray & Dickinson,  
541 2000; Mackie et al., 2003; Kerstens, Murray & Dickinson, 2006). This latter category  
542 includes the naturally occurring surface-active lipids (fatty acids, monoglycerides, bile salts,  
543 *etc.*) as well as various ‘synthetic’ molecules that are permitted for limited use in foods (*e.g.*,  
544 Tweens, PGPR). Typically the LMWS achieves a lower equilibrium  $\gamma$  than the adsorbed  
545 biopolymer due to the ability of the small molecules to pack more closely together at the  
546 interface. This means that a high enough LMWS concentration will always induce  
547 biopolymer displacement. Adsorbed LMWS layers typically have similar values of  
548 dilatational moduli to biopolymer layers, but their shear moduli are orders of magnitude  
549 lower (*i.e.*, with  $\eta_i < 0.01 \text{ mN s m}^{-1}$ , as shown in Fig. 6). Both experiments and computer  
550 simulations have confirmed the general ability of small surfactants to penetrate into and  
551 disrupt biopolymer layers, especially protein layers. At the displacement stage, when the  
552 adsorbed layer consists of coexisting ‘islands’ of biopolymer and LMWS, critical points of  
553 weakness and instability develop in the adsorbed layer. The rate at which this happens  
554 depends on the degree of coherence of the protein film. The protein is typically squeezed into  
555 smaller and smaller regions — a process described as orogenic displacement (Wilde et al.,  
556 2004) — until whole patches of protein are suddenly removed from the interface. This  
557 obviously has implications for the digestion of edible oil droplets initially covered in  
558 biopolymeric material (see section 4). With respect to particulate (Pickering) stabilizers, there  
559 are still many unanswered questions as to how LMWS adsorption modifies the interfacial  
560 contact angle of the particles during a competitive displacement process (Mendoza et al.,  
561 2014). Hydrocolloid stabilizers existing in the form of microgel particles (Dickinson, 2016,  
562 2017; Murray, 2019a,b) might have the advantage of absorbing more of the LMWS internally  
563 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.*  $\text{Ca}^{2+}$ ).

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 fracture. 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.



597

598

### 599 **3. Effect of hydrocolloid structure on oral processing**

600

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

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

628

629

630

631 *3.1. Transformation from bulk interactions to surface-induced interactions*

632 The rheological foundations of modern oral processing research were described half a  
633 century ago by Friedman, Whitney & Szczesniak (1963) and Shama & Sherman (1973).  
634 Following the latter authors, the viscosity at some specific shear-rate has been adopted as the  
635 gold standard in most oral processing studies as a fixed criterion to correlate and predict the  
636 perceived sensory thickness of liquid-like emulsions. Nevertheless, the inferred shear-rate  
637 values at which such a correlation is deemed to exist between the apparent viscosity ( $\eta$ ) and  
638 sensory thickness ( $M_{\text{thick}}$ ) have been reported to range from below  $10 \text{ s}^{-1}$  to nearly  $1000 \text{ s}^{-1}$ .  
639 For instance, for O/W emulsions of low volume fraction stabilized by sodium caseinate  
640 containing xanthan or pectin as thickening agent, it was found that  $M_{\text{thick}}$  could be correlated  
641 with  $\eta$  measured at  $50 \text{ s}^{-1}$  (Akhtar, Murray & Dickinson, 2006). While this arbitrary value of  
642  $50 \text{ s}^{-1}$  is often taken to be some sort of standard average oral shear-rate, the assumption is of  
643 dubious generality owing to the known variations of hydrodynamic conditions in the mouth  
644 depending on the microstructure of the consumed food. For instance, evidence to suggest that  
645 a singular shear-rate of  $50 \text{ s}^{-1}$  is insufficient to characterize oral or pharyngeal conditions is  
646 presented in the recent study of Ong, Steele & Duizer (2018). These authors demonstrated  
647 that thickened liquids of three different hydrocolloids (xanthan gum, guar gum,  
648 carboxymethylcellulose), which had been viscosity-matched at  $50 \text{ s}^{-1}$ , could be readily  
649 distinguished by trained panellists in terms of both the sensorially perceived viscosity and the  
650 ease of swallowing. Several decades earlier, Cutler, Morris & Taylor (1983) had suggested  
651 that  $10 \text{ s}^{-1}$  was actually a better measure of the effective oral shear-rate than  $50 \text{ s}^{-1}$ , as  
652 indicated by regression coefficients in the correlation of  $\log M_{\text{thick}}$  with  $\log \eta$ . But these  
653 authors added the proviso that the lower shear-rate was valid only for highly shear-thinning  
654 liquids. More recently, for whey protein-stabilized emulsions with added gum arabic as  
655 thickening agent, van Aken, Vingerhoeds & de Wijk (2011) reported a pronounced  
656 dependence on viscosity of the perceived mouthfeel attributes of thickness and creaminess.  
657 That this same dependency was not observed, however, for emulsion samples without added  
658 gum arabic indicates the importance of the nature and concentration of the hydrocolloid  
659 ingredient(s) on sensorially perceived attributes.

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

663 phase or in conjugation with protein when such a conjugate is used as an emulsifier/stabilizer.  
664 It should be pointed out, however, that many of the polysaccharides of shorter chain lengths  
665 that are commonly used to prepare protein–polysaccharide conjugates for emulsification  
666 purposes do not provide the level of viscosity enhancement required to achieve desirable  
667 levels of perceivable sensory thickness (Li, Woo, Patel & Selomulya, 2017; Huang et al.,  
668 2020). Consequently, when adopting some kind of protein-polysaccharide conjugate as the  
669 emulsifier/stabilizer, a carbohydrate polymer of long chain length or having extensive chain  
670 branching should be utilized in order to provide viscosity-related benefits during oral  
671 processing. An acceptable alternative strategy, avoiding polysaccharide ingredients  
672 altogether, is to use proteinaceous microgel particles as Pickering stabilizers of O/W  
673 emulsions (Dickinson, 2015b; Sarkar et al., 2016; Murray, 2019b; Zhang, Holmes, Ettelaie &  
674 Sarkar, 2020). It has been established that protein microgels can raise the bulk viscosity of  
675 aqueous media by orders of magnitude at orally relevant shear rates, as compared with the  
676 presence of non-microgelled proteins at equivalent protein concentrations (Sarkar et al.,  
677 2017a). Even though their functional role has not yet been properly established in terms of  
678 the effect on *true* sensory perception, one can reasonably hypothesize that protein microgel  
679 ingredients are likely to have an important influence on perceived sensory thickness of food  
680 emulsions by virtue of their high viscosity at orally relevant shear-rates.

681 The potential for improving the correlation between perceived sensory attributes and  
682 rheological properties through the incorporation of tribological factors has long been  
683 recognized (Bourne, 1975; Kokini, 1987; van Aken, Vingerhoeds & de Wijk (2011). The  
684 seminal work of Kokini and co-workers produced a set of phenomenological equations which  
685 involved both rheological and frictional parameters in the representation of attributes such as  
686 smoothness, slipperiness and creaminess (Kokini, Kadane & Cussler, 1977; Kokini &  
687 Cussler, 1983). It is now clearly established that one particular quantity, the friction  
688 coefficient  $\mu$  between tongue and palate, is a critical parameter in the understanding and  
689 prediction of the aforementioned sensory attributes (Pradal & Stokes, 2016; Sarkar & Krop,  
690 2019). Moreover, it is recognized that oral processing and sensory perception are time-  
691 dependent processes: sensory attributes that are related to the bulk properties of the food  
692 bolus relate more closely to the initial stages of mastication, whereas attributes related to the  
693 surface of the bolus are more relevant in the later stages (de Wijk, Janssen & Prinz, 2011).  
694 Figure 7 illustrates this transition in dynamic oral processing behaviour in the gap between  
695 tongue papillae (filiform) and the oral palate. Bulk rheological factors in the continuum  
696 dominate the early stages. As time passes during oral processing, the fluid film in the oral

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

701 Interest in tribology came to the forefront of oral processing research when the textures of  
702 foods with similar rheology but differing in fat content were demonstrated to be readily  
703 distinguishable by panellists as well as by tribological measurements (Selway & Stokes,  
704 2013; Laguna et al., 2017). Tribological research has been useful in enhancing our  
705 understanding of how fat content and fat type affects O/W emulsion stability during oral  
706 processing. For dairy colloids such as cream cheese and yoghurt, it was demonstrated by  
707 Laguna et al. (2017) that tribology could readily distinguish viscosity-matched samples of  
708 full-fat systems and their fat-free counterparts, with the former having  $\mu$  values of one order-  
709 of-magnitude lower than the latter. The corresponding difference in textural perception may  
710 be attributed to the stress-induced coalescence of fat droplets in the interfacial film of the  
711 full-fat system.

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

721 Not only the surface activity, but also the molecular size and degree of aggregation of the  
722 polymer can influence its oral surface interactions. For instance, the tribological properties of  
723 protein dispersions have been compared using globular aggregates of whey protein isolate  
724 and fibrillar aggregates of ovalbumin from egg white (Chojnicka, de Jong, de Kruif &  
725 Visschers, 2008). As well as being dependent on the concentration and mean size of the  
726 protein aggregates, the values of  $\mu$  measured in soft contact at low pressure were found to be  
727 affected by the presence of attractive aggregate–surface interactions leading to necking and  
728 adhesion. Observed differences in frictional behaviour for the ovalbumin and whey protein  
729 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  $\mu$  (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  $\mu$  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 ( $10\text{--}100\text{ s}^{-1}$ ) 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,  $>1000 \text{ s}^{-1}$ ) to facilitate extensive  
765 lowering of  $\mu$  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 ( $\sim 6.8$ ). 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  $\beta$ -  
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

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

800 The character of the in-mouth emulsion instability has a significant impact on sensory  
801 perception. Reversible depletion flocculation by whey protein-stabilized emulsions has been  
802 found to be associated with very little retention on the tongue and no significant negative  
803 influence in the perception of creaminess, fattiness or thickness (Vingerhoeds et al., 2009). In  
804 contrast, bridging flocculation of lysozyme-stabilized emulsions has been associated with a  
805 large increase in in-mouth viscosity and enhancements in the oral sensations of dryness,  
806 roughness and astringency. The increase in viscosity alone cannot explain this sensory  
807 experience. What is significant mechanistically is that the positively-charged emulsion  
808 droplets form complexes with the anionic mucin molecules, thereby depleting the mucin  
809 layers from the tongue surface, leading to an oral perception of dryness (Vingerhoeds et al.,  
810 2009). It was also demonstrated, however, that the effect of the irreversible flocculation  
811 caused by positively-charged proteins could be diminished by addition of guar gum,  
812 presumably due to its lubricating properties. Compared with protein-stabilized emulsions, it  
813 was found that the OSA-modified starch-stabilized emulsions which exhibited in-mouth  
814 coalescence received higher fat-related scores on mouthfeel and afterfeel attributes and lower  
815 scores on friction-related attributes (Dresselhuis et al., 2008).

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

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

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

845

846

#### 847 **4. Effect of hydrocolloid structure on gastric and intestinal digestion**

848

849 Another aspect of thinking about the ideal hydrocolloid stabilizer is in relation to  
850 predicting the expected fate of emulsified lipids during their transit through the  
851 gastrointestinal tract and then select the right hydrocolloid to perform the site-specific  
852 function. The background to our current thinking is the growth in understanding over the last  
853 2–3 decades about the gastric and intestinal digestion of emulsion systems and their key role  
854 in delivering bioactives as well as regulating glycaemia and lipaemia (Mackie &  
855 Macierzanka, 2010; Wilde & Chu, 2011; Singh & Sarkar, 2011; Golding et al., 2011;  
856 McClements, 2018; Sarkar, Zhang, Holmes & Ettelaie, 2019). The influence of changes in  
857 the gastrointestinal environment (pH, ions enzymes, bio-surfactants, metabolites) on stability  
858 and colloidal structuring has been described for systems stabilized by proteins (Sarkar, Goh,  
859 Singh & Singh, 2009; Macierzanka et al., 2011; Gumus, Decker & McClements, 2017; Wang  
860 et al., 2019), particles (Sarkar et al., 2016; Le, Loveday, Singh & Sarkar, 2020), mixtures of  
861 protein + polysaccharide (Qin et al., 2016; Xu, Sun & McClements, 2020) and mixtures of  
862 protein + particles (Sarkar et al., 2017b; Araiza-Calahorra & Sarkar, 2019). The biophysical



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

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

#### 884 885 *4.1. Addressing the pharmacokinetic challenge of sustained absorption*

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

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

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

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

930 effective in competitively displacing biopolymers from the oil–water interface (Maldonado-  
931 Valderrama et al., 2008; Sarkar, Ye & Singh, 2016), meaning that the structure and  
932 composition of the original biopolymer-coated interface is of little significance. For instance,  
933 establishing one- to five-layered interfaces from whey protein, pectin and chitosan, or  
934 electrostatically depositing pectin on gelatin-coated droplets, has been found to lead to  
935 similar initial rates and extents of FFA release during simulated intestinal conditions (Zeeb,  
936 Weiss & McClements, 2015; Corstens et al., 2017). Although the use of particle–polymer  
937 combinations, either as conjugated or complexed systems, can prevent displacement by bile  
938 salts, such complex interfaces are ineffective in controlling intestinal lipid digestion because  
939 the lipase molecules, being small compared to the holes in the particle-laden interface, are  
940 able to freely access the oil–water interface without an energy barrier and hence release the  
941 FFAs (Araiza-Calahorra et al., 2020). To our knowledge, the only reported success in this  
942 regard in truly delaying FFA release is that recently achieved in our laboratory (Sarkar et al.,  
943 2016) where whey protein microgel particles were crosslinked *via* heat treatment after being  
944 adsorbed at the oil–water interface. Following this thermal treatment, there was inferred to be  
945 a substantial reduction in the area of the interfacial holes; this led to a slowing down in the  
946 access of the lipase to the lipid core, resulting in a lowering of the lipid digestion rate by a  
947 factor of 20 in comparison to a normal protein monolayer.

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

958

#### 959 4.2. *Gastrointestinal motility*

960 The increase in obesity has driven a tendency for some food colloids research to focus on  
961 the control of glycaemia and lipaemia. One such approach aims to slow down lipid digestion.  
962 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  $\geq 50\%$  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

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

998 Evolution has driven the development of the human GI tract to efficiently extract nutrients  
999 from the food we eat. Consequently, there are a number of mechanisms that the body uses to  
1000 control the rate at which food passes down the gut. As described in section 4, hydrocolloids  
1001 can be designed to optimise the required digestion kinetics. For example, a protein may need  
1002 to be delivered quickly after exercise in order to build muscle, whereas sugars and lipids may  
1003 benefit the consumer with a more gradual release. This requirement to control digestion  
1004 kinetics has led to concepts such as the glycaemic index for carbohydrates, and the same  
1005 concept can also be applied to lipids. Many foods are now widely marketed as being of low  
1006 glycaemic index: this health-beneficial designation can be achieved through the addition or  
1007 manipulation of hydrocolloids in the form of soluble dietary fibre (Salmeron et al., 1997).  
1008 Similar principles can, of course, be employed to lower the rate of absorption of any  
1009 bioactive or nutrient.

1010 The concept of fast and slow digesting proteins is well known in the dairy arena (Boirie et  
1011 al., 1997). Indeed, there is now a significant industry built around the idea that whey protein  
1012 has the right amino-acid profile, has a fast transit through the gastric phase of digestion, and  
1013 is quickly hydrolysed and absorbed in the small intestine (Foegeding & Davis, 2011). This is  
1014 in marked contrast to the caseins which coagulate under acidic conditions and pass through  
1015 the gastric phase more slowly. The search is now on to tailor a wider range of proteins,  
1016 particularly those of plant origin, which might also demonstrate a similarly high level of  
1017 digestibility and a tuneable range of digestion kinetics (Loveday, 2020). The properties  
1018 exhibited by proteins in the GI tract are determined by their amino-acid sequence and any  
1019 post-translational modifications, including those induced by processing. If we are to find  
1020 plant proteins with similar properties, there is a need to match the primary sequence and the  
1021 applied processing requirements so as to generate the desired digestion characteristics in a  
1022 predictable way. In the case of dairy proteins, the unique molecular structures and self-  
1023 assembly behaviour of the disordered caseins leads to their specific coagulation behaviour,  
1024 and the specific globular structures of the whey proteins renders them highly soluble and  
1025 susceptible to hydrolysis (Foegeding & Davis, 2011). This susceptibility is driven by the  
1026 ability of the proteolytic enzyme to access the site of cleavage on the substrate, as determined  
1027 by a combination of interaction forces and steric considerations governed by the primary and  
1028 secondary structure of the substrate. With the right protocols in place, this would seem to  
1029 suggest that plant protein primary sequence could be linked to the desired characteristics.

1030 Similar arguments are made for the properties of starch in relation to gastric motility.  
1031 Starch can be categorized as fast digesting, slowly digesting, or resistant. Clearly these  
1032 designations indicate how quickly the absorbable sugars are released from the starch  
1033 (measured by glycaemic index), but they also indicate the extent to which the material affects  
1034 the rheological properties of the surrounding milieu. Fully gelatinized starch has a high  
1035 water-holding capacity, and so it can have a marked effect on the rheology of gastric chyme.  
1036 However, its more open structure makes it more susceptible to hydrolysis by amylase, which  
1037 in real food systems occurs throughout the GI tract. There has been a significant amount of  
1038 research addressing the link between starch structure and digestibility (Lovegrove et al.,  
1039 2017). In addition to the effect on glycaemia, recent research has also looked into the use of  
1040 Pickering emulsion systems to control the kinetics of lipid digestion by means of the  
1041 enhanced stability to coalescence and the restricting of access to the substrate (Sarkar, Zhang,  
1042 Holmes & Ettelaie, 2019).

1043 While protein and starch can contribute to the viscoelastic properties of a food, they are  
1044 both likely to be hydrolysed in the stomach, potentially reducing the chyme viscoelasticity.  
1045 However, proteins may also aggregate as the pH in the gastric phase approaches the  
1046 isoelectric point, and particularly so if accompanied by proteolysis. This is, after all, the basis  
1047 of cheese making. The aggregation of the caseins in milk makes them much more slowly  
1048 hydrolysed. Moreover it has been shown that the digestion kinetics of milk can be controlled  
1049 through the use of traditional processing methods such as homogenization and thermal  
1050 treatment (Mulet-Cabero et al., 2019). Following these ideas, it is clear that if the ideal  
1051 digestible hydrocolloid in this context is to be plant-based, it will need to be highly soluble in  
1052 the aqueous environment and able to change its susceptibility to proteolysis as a function of  
1053 processing conditions.

1054 Hydrocolloids can be considered to comprise two groups in relation to digestion: those  
1055 that are readily digestible such as proteins and starch, and those that are not digestible such as  
1056 non-starch polysaccharides (NSPs). The latter are known collectively as dietary fibre. While  
1057 the non-starch polysaccharides affect all processes in the gut from the mouth to the colon  
1058 (Lovegrove et al., 2017), they are of particular importance in the colon where they are  
1059 fermented by intestinal bacteria into short chain fatty acids (SCFA) that are essential for gut  
1060 health. Of course, dietary fibre is not the only type of hydrocolloid reaching the large  
1061 intestine. Anything that has not been digested and absorbed during its passage through the  
1062 small intestine will pass into the colon. Nutrients such as indigestible protein or resistant

1063 starch that pass into the colon may influence the gut microbiome in a positive way by  
1064 increasing diversity.

1065 Non-starch polysaccharides are resistant to hydrolysis by endogenous enzymes. They also  
1066 have an important role to play in digestion (Brownlee, 2011). While there has been some  
1067 recent research undertaken on the use of NSPs to alter digestion kinetics, this has so far only  
1068 been undertaken *in vitro* or in animals such as rodents (Chen et al., (2020a,b). In both cases,  
1069 the results have shown that the addition of NSP hydrocolloid reduces the rate of digestion  
1070 (and absorption). Furthermore, the *in vivo* results also showed physiological responses that  
1071 may be relevant to the fight against obesity. The precise nature of the NSP is clearly  
1072 important: for  $\beta$ -glucan it was reported (Regand, Tosh, Wolever & Wood, 2009) that 73% of  
1073 the bioactivity in reducing the peak blood glucose response could be explained in terms of the  
1074 peak molecular weight and the concentration. Although molecular weight is thought to be of  
1075 critical importance in relation to a hydrocolloid's role in increasing the viscosity of intestinal  
1076 chyme, the *in vitro* experiments with  $\beta$ -glucan have shown that lipid hydrolysis is not directly  
1077 correlated with solution viscosity, with other factors affecting emulsion stability also playing  
1078 an important role, due to the reduction in available surface area of substrate (Grundy,  
1079 McClements, Balance & Wilde, 2018). Similar effects have been seen with the release and  
1080 absorption of carotenoids due to their poor aqueous solubility. A review of the influence of  
1081 pectin on carotenoid bioavailability (Cervantes-Paz et al., 2017) concludes that both the  
1082 molecular weight and the degree of methylation are important in modulating the formation of  
1083 the mixed micellar phase solubilizing carotenoids. While there are many other studies  
1084 looking at similar systems, the overall conclusion is that the digestion and absorption of  
1085 bioactives can be modulated, but the mechanisms involved are varied and not usually based  
1086 on viscosity.

1087

#### 1088 4.3. Mucosal interactions

1089 Polysaccharides that gel or substantially increase the bulk viscosity have shown promise  
1090 in delaying gastric emptying and in binding with enzymes and bile salts to slow down  
1091 lipolysis kinetics. For instance, using quantitative confocal microscopy methods such as  
1092 fluorescence recovery after photobleaching (FRAP) and multiple particle tracking, it has been  
1093 demonstrated that dietary fibre such as alginate, in entanglement with intestinal mucins, can  
1094 significantly delay the transport of lipid digestion products (Mackie, Bajka & Rigby, 2016).  
1095 Using cellulose nanocrystals together with Tween as the interfacial material (Liu, Kerr &

1096 Kong, 2019) or hydrophobically modified cellulose (Le, Loveday, Singh & Sarkar, 2020), it  
1097 was shown that the cellulose nanoparticles in the continuous phase form a hydrogel network  
1098 in the gastric phase which eventually results in a lower rate and extent of digestion. The  
1099 particles also get entangled in the intestinal mucus layer; this means that they fail to reach the  
1100 underlying epithelium, thereby diminishing the extent of lipid absorption from the emulsions  
1101 (Mackie et al., 2019).

1102 In all regions of the GI tract, including the mouth, a layer of mucus protects the mucosal  
1103 surfaces. Mucus is a viscous layer comprising glycoprotein mucins, DNA, and other peptides  
1104 and proteins (Mackie et al., 2017), and the barrier properties of this hydrocolloid layer vary  
1105 both spatially and temporally. The intestinal mucus carries a net negative charge due to its  
1106 relatively high degree of sulfation and the presence of sialic acids (Corfield, 2015). This  
1107 means that positively charged moieties tend to bind electrostatically to the mucus and so are  
1108 unable to diffuse through it. Indeed, mucoadhesive hydrocolloids such as chitosan are used  
1109 for just this purpose (Mackie et al., 2017).

1110 Hydrocolloids inevitably encounter the gut wall as they pass down the GI tract and the  
1111 nature of that contact is determined by the properties of the hydrocolloid. The mucus layer  
1112 that covers and protects the underlying gastrointestinal epithelium is negatively charged and  
1113 it exhibits a range of rheological behaviour from a viscoelastic fluid to a soft gel (Lai, Wang,  
1114 Wirtz & Hanes, 2009). The gel network has a pore size of ~100 nm, but again this may vary  
1115 significantly in the heterogeneous regions of the small intestine (Lai, Wang & Hanes, 2009).  
1116 All nutrients and bioactives must diffuse through this layer in order to be absorbed by the  
1117 underlying enterocytes. It would appear that negative charge plays a critical role in the  
1118 passage of colloidal particles and solutes. For example, lipid droplets or mixed micelles  
1119 formed from the hydrolysis of lipids containing bile acids and fatty acids that carry negative  
1120 charges can traverse the mucus layer, whilst emulsion droplets without bile adsorbed to their  
1121 interface are unable to penetrate the mucus (Macierzanka et al., 2011). The same rules apply  
1122 to the penetration of polysaccharides, with anionic polymers such as alginate able to diffuse  
1123 through the intestinal mucus, whereas cationic polymers such as chitosan are mucoadhesive  
1124 — they simply form a separate layer on the mucus surface (Mackie et al., 2017).

1125 The consequence of the diffusion of anionic polymers into the mucus is to lower its  
1126 permeability to other particulates by reducing the pore size. As the local concentration of  
1127 polymer increases, the overlap concentration is approached; this has the potential to increase  
1128 the local viscosity significantly, providing a more effective barrier to bacteria. Experiments



1129 involving both 100 nm latex beads and lipid digestion products have shown a reduction in  
1130 diffusion coefficient in the presence of polysaccharides such as alginate (Mackie et al., 2016)  
1131 or oat  $\beta$ -glucan (Mackie, Rigby, Harvey & Bajka, 2016). Similarly, insoluble particulate  
1132 polysaccharides such as cellulose have been found to be unable to penetrate intestinal mucus  
1133 or to form a surface layer in a similar manner to soluble cationic polymers (Mackie et al.,  
1134 2019). In the case of cellulose nanocrystals, this may be due to a combination of size and  
1135 surface properties. One of the primary roles of the intestinal mucus layer is to act as a barrier  
1136 to pathogenic bacteria; the limitation on the sizes of the colloidal particles that are able to  
1137 penetrate the mucus at a significant rate fits in with that requirement.

1138

## 1139 **5. Fermentation and transport into the colon**

1140

1141 The microbiota in the colon survive on food that we consume but are unable to digest.  
1142 This is normally considered to be dietary fibre in the form of soluble or insoluble  
1143 polysaccharides, but it may also include other peptides, oligosaccharides, lipids, *etc.*, which  
1144 can have an impact on the gut microbiota (Macfarlane & Macfarlane, 2012). Rather than the  
1145 more traditional view of good and bad bacteria, more recent evidence suggests that a broader  
1146 range of bacteria is the healthier position (Le Chatelier et al., 2013). A consequence of this is  
1147 that a wide spread of fermentable substrates passing down the gut is likely to be beneficial.  
1148 Additionally, the continuous flow of chyme along the GI tract will tend to prevent bacterial  
1149 overgrowth in the more proximal sections. Therefore, the properties of the ideal hydrocolloid  
1150 in relation to colonic fermentation should, under the most favourable circumstances, be  
1151 related to the promotion of a diverse range of bacteria. This implies the presence of a soluble  
1152 dietary fibre that might be associated with other compounds that could be released as a result  
1153 of fermentation. There is a range of cereal polysaccharides that might fit this description and  
1154 they all carry with them a selection of phenolic compounds and oligosaccharides (Schar et al.,  
1155 2018). The ability of non-starch polysaccharides to resist digestion also means that they are  
1156 capable of acting as carriers of both exogenous and endogenous cargo into the colon. One of  
1157 the most researched examples is oat  $\beta$ -glucan in relation to cholesterol lowering by virtue of  
1158 the limiting of bile recycling in the distal ileum (Wood, 2007; Othman, Moghadasian &  
1159 Jones, 2011). The evidence suggests that the ability of such a high-molecular-weight polymer  
1160 to increase viscosity is at the heart of the effect, with the polymer entrapping the bile rather  
1161 than binding to it through hydrophobic or other interactions. Other examples include the

1162 interaction between dietary fibre and phenolic compounds such as isoflavones which are  
1163 subsequently metabolized to more bioactive compounds (Lampe, Karr, Hutchins & Slavin,  
1164 1998). Again, it is unclear whether the beneficial health effects are a consequence of the  
1165 viscosity increase induced by the fibre or through direct binding. Regardless of the  
1166 mechanism, it is clear that the ideal hydrocolloid should continue to impart significant  
1167 viscosity throughout the upper GI tract, it should be highly fermentable, and it should  
1168 preferably have the capacity to bind beneficial compounds.

1169

## 1170 **6. Concluding remarks**

1171

1172 We have aspired to approach the properties of the perfect hydrocolloid stabilizer from  
1173 various conceptual and operational perspectives — the statistical thermodynamics of  
1174 adsorption and colloid stabilization; the dynamics of interfacial formation, adsorption and  
1175 deformation; the rheology, lubrication, and interactions with saliva during oral processing;  
1176 the pharmacokinetic and glycaemic challenges of digestion; and the control of gut motility  
1177 and microflora. We have seen that the ideal stabilizing macromolecule from the equilibrium  
1178 theoretical viewpoint is a soluble hydrophilic block copolymer of low net charge containing  
1179 strongly adsorbing hydrophobic groups located in a single localized region. From a dynamic  
1180 perspective, the ideal macromolecule should be sufficiently flexible to adsorb rapidly at the  
1181 fluid interface, leading to the development of an interfacial film that is thick and coherent, but  
1182 one also resilient to catastrophic structural failure under large stress and strain. To produce a  
1183 smooth in-mouth textural perception, the (negatively charged) hydrocolloid should be able to  
1184 generate a relatively high viscosity at orally relevant shear-rates and should act as a  
1185 continuous lubricating film between oral surfaces on the spatial scale from a few molecular  
1186 thicknesses up to micrometres. From a pharmacokinetic perspective, the ideal hydrocolloid  
1187 should be resilient to proteolytic digestion within the gastric environment to some extent,  
1188 whilst generating an effective diffusive barrier to lipolytic enzymes in the intestinal phase,  
1189 depending on the rate of lipid digestion that is most appropriate for the individual concerned.  
1190 From the optimal glycaemic perspective, it needs to have the capability to form a gel under  
1191 acidic conditions so as to retard gastric emptying and therefore inhibit rapid rises in blood  
1192 glucose; an ability to bind with lipases and bile salts to control lipid digestion kinetics could  
1193 also be an advantage. Finally, in its functional role as dietary fibre, whilst generating a  
1194 substantial viscosity throughout the whole GI tract, the ideal hydrocolloid should be highly

1195 fermentable in the colon and capable of acting as a binding site for gut-beneficial compounds  
1196 like phenolics and oligosaccharides.

1197 The pragmatic food scientist might bluntly observe that it should have been blindingly  
1198 obvious from the outset that no single hydrocolloid stabilizer could possibly satisfy all the  
1199 many functional requirements involved in the making, processing, storing, eating, and  
1200 digesting of a colloidal food system. And, indeed, even from the purely theoretical viewpoint  
1201 it is quite difficult to reconcile the partially conflicting positive and negative functional  
1202 attributes exhibited by some highly contrasting categories of materials possessing the  
1203 hydrocolloid designation, *e.g.*, modified starch *versus* non-starch polysaccharides, or soluble  
1204 polymeric stabilizers *versus* particle-based stabilizers. Accepting these reservations, though,  
1205 and assuming that we are strictly limiting our considerations to the specific case of a  
1206 *polymer*-based emulsifier/stabilizer at the interface of an O/W emulsion, it seems reasonable  
1207 to assert that we do now have the solid conceptual framework with which to approach the  
1208 imaginary state of hydrocolloidal perfection — although not, of course, to fully attain it.

1209 To pursue the pragmatic argument a little further, it seems intuitively obvious that the  
1210 physico-chemical properties of any hydrocolloid ingredient used to make and stabilize a food  
1211 emulsion are likely to be quite relevant to the oral processing and sensory perception of that  
1212 same emulsion during the first few moments the emulsion is eaten. But the further that this  
1213 same hydrocolloid traverses along the GI tract, the more it will tend to get separated from the  
1214 originally emulsified oil, and become mixed in with all the other components of the diet —  
1215 including different proteins, carbohydrates, lipids and nutrients. Set against the relatively  
1216 modest amount of hydrocolloid ingredient that would be needed to stabilize the food  
1217 emulsion portion of a substantial meal, it is highly likely that some other macromolecular  
1218 components of our nutritionally well-balanced diet could well turn out to be rather more  
1219 functionally effective in addressing the pharmacokinetic or glycaemic challenges, or in  
1220 functioning as dietary fibre. This pragmatic attitude might then lead us to towards being  
1221 prepared to give rather less emphasis to trying to satisfy the later stage digestion functionality  
1222 requirements of our perfect hydrocolloid stabilizer. From such a simplified perceptive, the  
1223 molecular and functional requirements of the perfect ingredient appear more well-defined and  
1224 technically manageable:

- 1225 • a high-molecular-weight flexible polymer generating effective steric stabilization
- 1226 • an amphiphilic chain with extended hydrophilic region and localized hydrophobic region
- 1227 • a molecule composed of mainly polar uncharged groups (or just a few negative charges)
- 1228 • surface activity, rapid adsorption behaviour, and network/multilayer forming ability

1229 • bulk thickening and lubricating capability at oral surfaces in the presence of saliva  
1230 Additionally, of course, for food-related applications, this ingredient should be non-toxic,  
1231 exhibit no unpleasant taste, and satisfy all the regulatory standards.

1232 The desirable characteristics highlighted above appear to be consistent with the idea of an  
1233 ideal hydrocolloid consisting of some kind of protein–polysaccharide conjugate/complex.  
1234 The excellent emulsifying and emulsion stabilizing properties of natural gums and Maillard  
1235 conjugates possessing this sort of hybrid polymeric structure are already very well described  
1236 in the food hydrocolloid literature. Moreover, this same class of protein–polysaccharide  
1237 conjugates would seem to possess general characteristics that are rather favourable for the  
1238 enhancement of lubrication behaviour during oral processing. It can further be suggested that  
1239 microgel particles based on conjugated or complexed biopolymer components might be  
1240 especially effective in combining the specific molecular attributes of both proteins and  
1241 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  $\mu\text{m}$ , induced by the presence of a dilute solution (0.1 vol%) of non-adsorbed linear homopolymers of 600 monomers. The interaction energy (units of  $k_{\text{B}}T$ ) is plotted against the surface-to-surface separation.

Fig. 2. Effect of electrical charge on the equilibrium adsorption behaviour of an amphiphilic macromolecule at a plane hydrophobic interface. The adsorbed amount is plotted against the charge per chain for a 200-monomer linear polymer of molecular weight 25 kDa.

Fig. 3. Influence on adsorbed layer structure of the distribution of hydrophobic anchoring groups along the backbone of a 200-segment amphiphilic macromolecule: (a) average distance from surface as a function of sequence number; (b) volume fraction as a function of distance from the surface. The dashed line represents a polymer having all its hydrophobic segments in a localized region. The solid line represents a polymer having its hydrophobic groups spaced out evenly along its backbone.

Fig. 4. Illustration of the Gibbs–Marangoni effect for (a) low-molecular-weight surfactants (LMWS), (b) adsorbed macromolecular stabilizers, and (c) adsorbed and cross-linked macromolecular stabilizers. Solid arrows indicate the movement of adsorbed molecules due to interfacial tension gradients ( $\Delta\gamma$ ) induced by the perturbation of the interface and changes in interfacial coverage ( $\Delta\Gamma$ ), *i.e.*, the Gibbs effect. Thin dashed lines indicate the approximate limit of the Marangoni flow of the solution due to movement of adsorbed molecules. Dashed arrows indicate the direction of Marangoni flow. In (a), the (four) LMWS icons with short (red) arrows superimposed on them represent rapidly moving molecules that can fill the gaps at the interface and reduce  $\Delta\gamma$  (and  $\varepsilon$ ,  $\kappa$ , *etc.*), so lowering the restoring force that dampens down the perturbation. In (b),  $\Delta\gamma$  is higher because macromolecules move more slowly at the interface and adsorb more slowly into gaps; and the extent of Marangoni flow is greater because the molecules are bigger. In (c), the adsorbed macromolecules are entangled and/or cross-linked; the mechanical strength of the resulting film is such that small perturbations are largely prevented. This whole diagram is not to scale: in reality, macromolecules will normally be of much greater relative size compared to LMWS.

Fig. 5. Kinetics of disproportionation of air bubbles beneath a planar air–water interface for solutions of different food proteins (0.05 wt% in pH 7 buffer): sodium caseinate, whey protein isolate (WPI), gelatin, ovalbumin,  $\beta$ -lactoglobulin, and soy glycinin. The curves of

bubble radius *versus* time,  $R(t)$ , are theoretical fits to each data set using the value given in brackets for the dilatational elasticity  $\varepsilon$  (in  $\text{mN m}^{-1}$ ). Towards the end of shrinkage with  $\beta$ -lactoglobulin (and also soy glycinin), non-spherical protein aggregates were formed (see inset image) and then slowly dissolved away. The ovalbumin curves could not be fitted by the theory: the bubbles showed extensive filamentous threads (see inset image) protruding from the interface as shrinkage progressed. (Based on data and images taken from Dickinson, Ettelaie, Murray & Du, 2002).

Fig. 6. Illustration of the wide range of measured values of interfacial shear viscosity ( $\eta_i$ ) for adsorbed films of food proteins. Viscosity on a logarithmic scale is plotted against time for adsorption at the *n*-tetradecane–water interface (bulk protein concentration =  $10^{-3}$  wt%, pH = 7, 20–25 °C). The dashed horizontal line represents typical values for LMWS and surface-active lipids, *i.e.*,  $< 0.1 \text{ mN s m}^{-1}$ .

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Figure 1

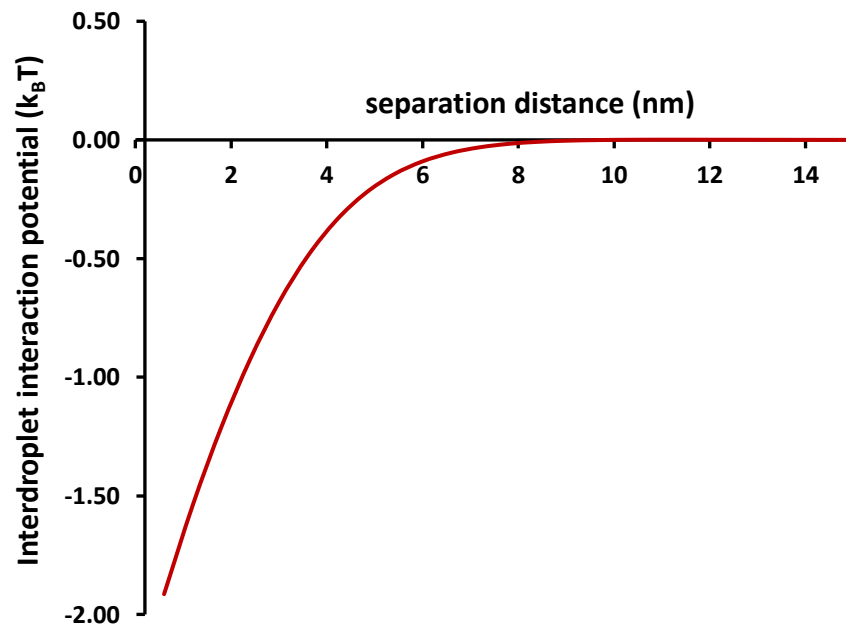


Figure 2

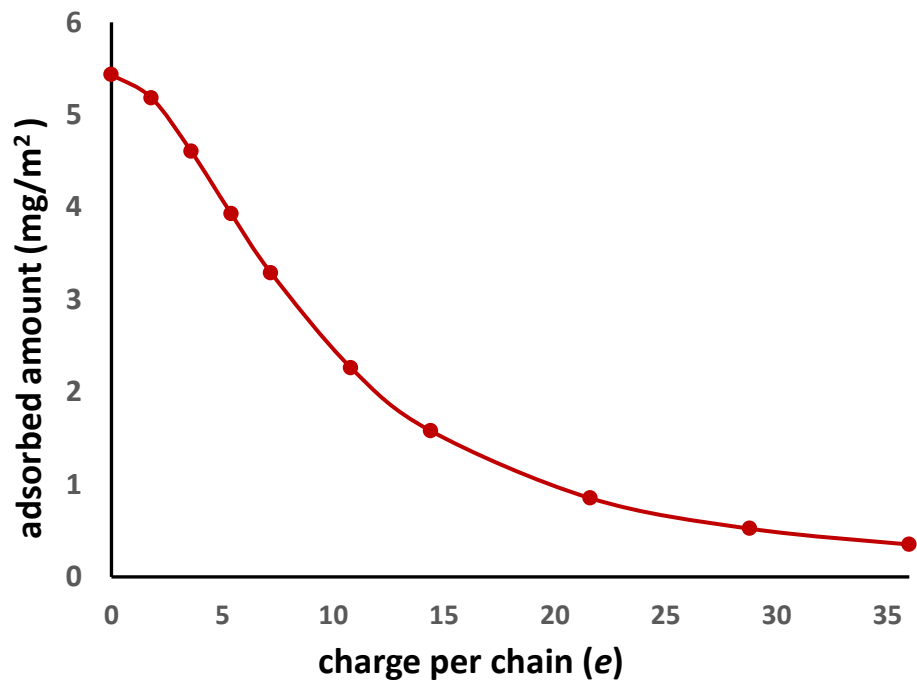


Figure 3

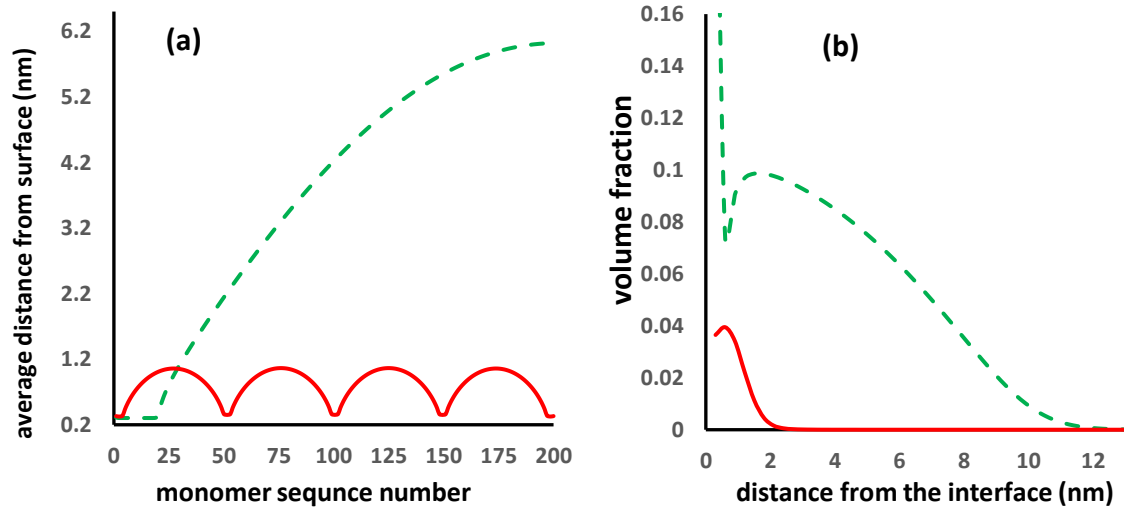




Figure 4

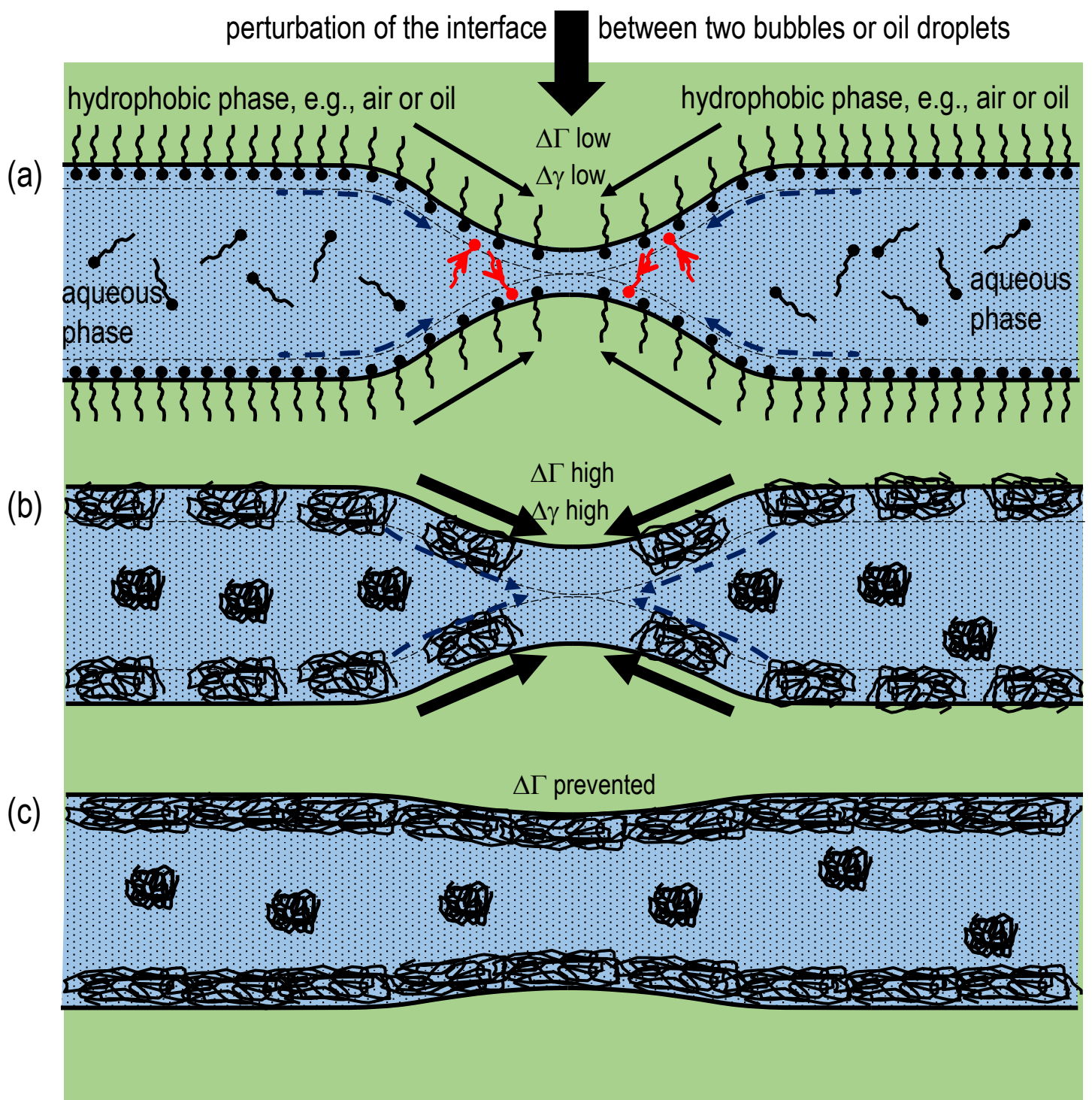


Figure 5

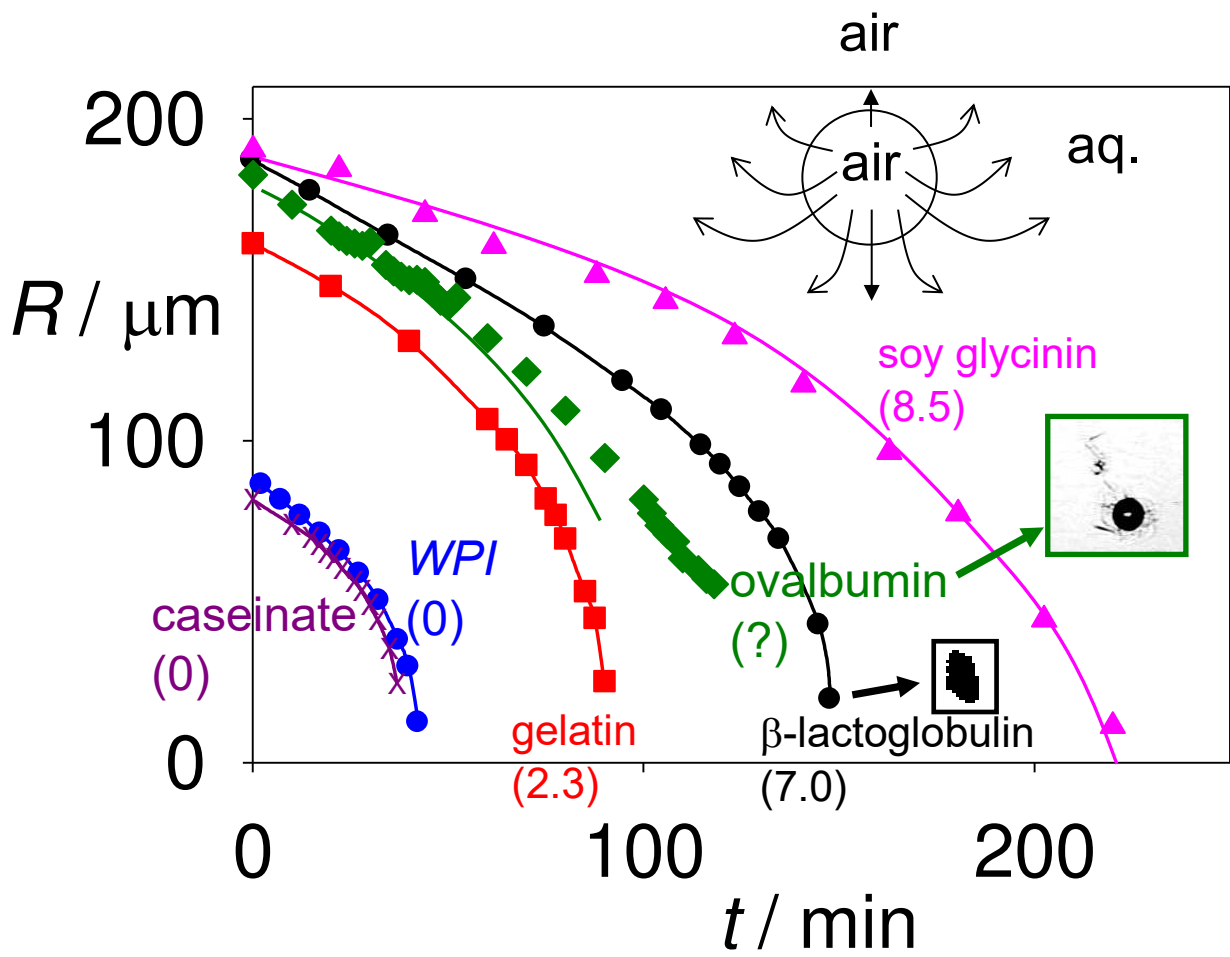


Figure 6

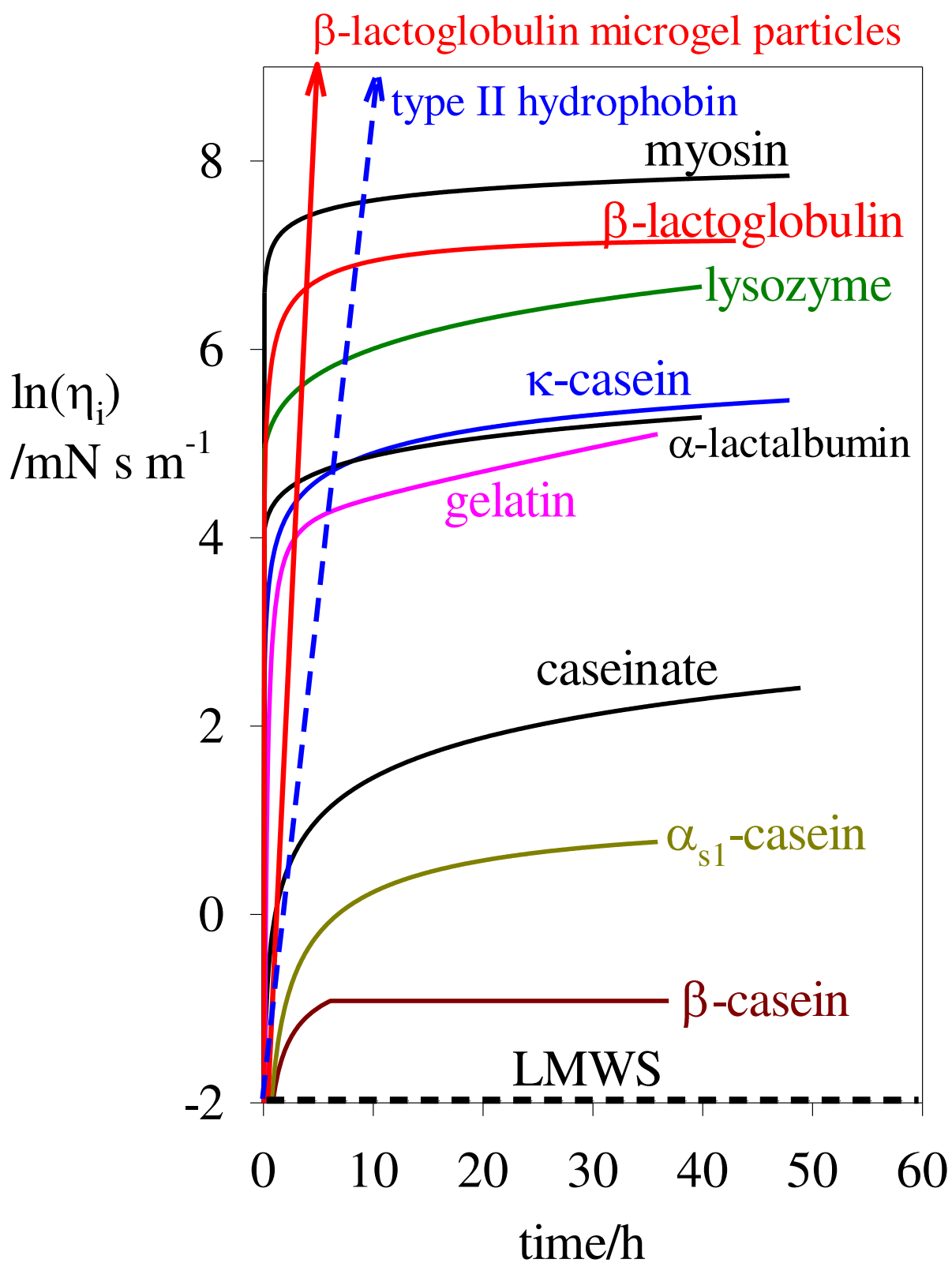
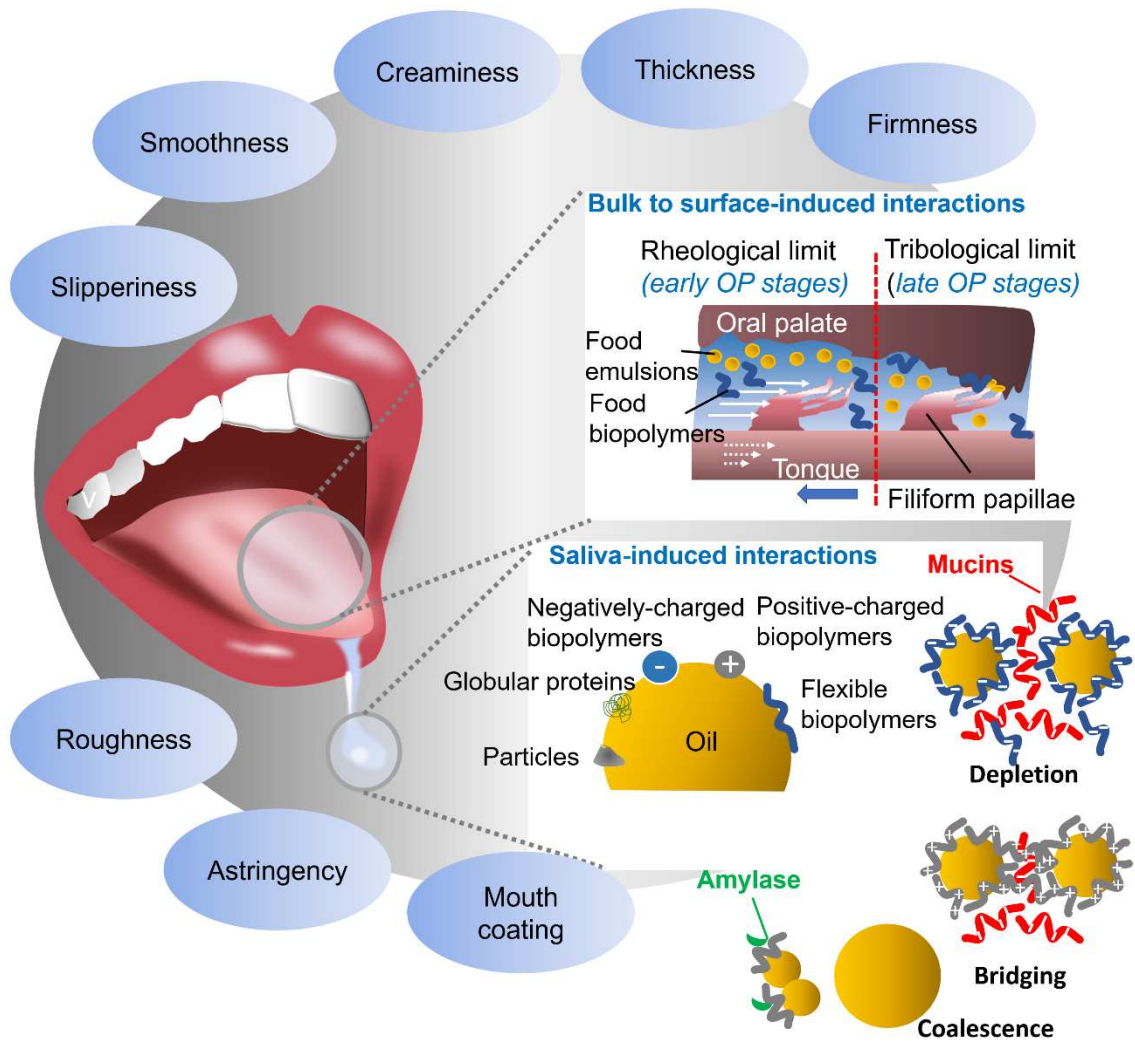


Figure 7



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