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Pickering Emulsions for Food and Drinks

Brent S. Murray

Food Colloids & Bioprocessing Group, School of Food Science & Nutrition
University of Leeds, Leeds LS2 9JT, UK
Tel. 44 (0)113 3432962
E-mail b.s.murray@leeds.ac.uk

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Abstract

The scientific literature from 2016 onwards on aspects of Pickering emulsions relevant to food and drink has been reviewed. Ongoing unsolved issues surrounding the general Pickering stabilization mechanism are discussed, such as contact angles of microscopic, irregularly size particles; adsorption and desorption barriers; competition and complex formation with other surface active species. The main types of emulsion that have been studied are surveyed: oil-in-water (O/W), water-in-oil (W/O), water-in-water (W/W) and multiple emulsions. There is still a lack of food-grade particle types suitable for W/O and therefore multiple emulsions. Finally, work on different types of Pickering emulsifiers is discussed, the principal types being organic crystals, prolamins, cellulose, starch and microgel particles. The latter are highlighted as particularly versatile in terms of their properties and the food components from which they can be formed.

Keywords: Pickering; emulsions; proteins; biopolymers; microgels

1. Introduction

The scientific literature relevant to Pickering emulsions in foods and beverages from 2016 onwards has been reviewed. There have been other reviews in this period that have also covered aspects of this topic to varying extents (e.g., see [1], [2], [3]●, [4]●, [5], [6], [7], [8]●. Without wishing to duplicate any of this excellent effort, it is worth beginning with some key definitions, concepts and issues surrounding Pickering emulsions.

Although there has been a tremendous burgeoning of interest Pickering emulsions in recent years, it turns out the history of the topic, like so many things in science and technology, is longer than expected. The key monograph by Binks and Horozov [9] traces it back to S.U. Pickering (1907) and even earlier to W. Ramsden (1903), whist more recent publications point to an even more ancient exploitation (if not full understanding) of the phenomena [10]. It is perhaps not surprising then that there has been some blurring of the concept over these years.

Fundamentally, Pickering emulsions are strictly defined as emulsions that are stabilized by an adsorbed layer of solid particles at the emulsion drop surface. Unfortunately, this still leaves open the definition of how non-deformable a material has to be classed as ‘solid’. Probably one can say that this refers to materials with shear and Young’s moduli > 0.1 MPa, in other words materials such as mineral particles or organic crystals. Such particles therefore undergo relatively minimal changes in their size and shape on adsorption, since they are insoluble in both phases of the emulsion. This allows one to explain and characterize the adsorption of such true Pickering stabilizers in terms of a finite contact angle with the phases in question, i.e., the particles have a clearly defined surface. Particles of pure polymer, like polymer lattices, might just meet the above criteria, so that the fundamental equation determining anchoring of particles at interfaces applies. This is $\Delta G = -\pi R^2 \gamma (1 - |\cos(\theta)|)^2$, (where ΔG is the energy of desorption, R the particle radius (i.e., assumed spherical in this case); γ the interfacial tension between the two phases and θ the contact angle of the particle with one of the phases. In other words, the closer θ is to 90°, the higher γ, or the larger R (or the higher cross-sectional area at the interface for non-spherical particles), the stronger the particle adsorption.

On the other hand, for microgel particles, which are gaining increasing interest as ‘Pickering’ stabilizers, this might well not be applicable, depending on the degree and strength of their internal cross-linking and the timescale of their exposure to the media of each phase. Indeed this has lead to coining of a separate term – ‘Mickering’ stabilizers – which it might be good to keep separate [11].

What is increasingly confusing, however, is where reference is made to macromolecules [e.g., [12]), their naturally occurring supramolecular aggregates, or artificial combinations of biopolymers, as Pickering particles. This is confusing because such materials generally undergo considerable internal re-organization on adsorption, far more complex than even for microgels, so that to refer to them simply as particles seems to ignore the concerted effort that has gone on previously to understand changes in biopolymer conformational at interfaces.

Whilst the Pickering Police do not yet exist to enforce such regulations regarding use of the term, this does not and should not prevent us from trying to find materials that as far as possible impart the characteristics and properties of true Pickering emulsions. These characteristics are fundamentally emulsions with very high stability to coalescence (at least in the absence of shear) and to ripening. Other perceived advantages in food and drink are the replacement of low molecular weight surfactants as emulsifiers, which may cause irritation to skin and that are seen as more 'chemical', with the negative connotations that this word frequently conjures up in the minds of consumers.

Certainly there may be other advantages in moving to materials that are based more on renewable resource materials that require only benign processing and lower input of energy, water and other increasingly precious resources. However, this raises the immediate problem of finding true, natural, green, 'clean-deck' Pickering stabilizers – there are very few – but these are the subject of the bulk of the references mentioned later. Workers have sought to use combinations of natural biopolymers, fats, etc., to create natural 'Pickering-like' particles [13]●. It should be emphasized that, in the current regulatory climate, the chances of introducing new stabilizers into foods that rely on any synthetic cross-linking of biomaterials, use of harsh chemicals or large quantities of organic solvents, are very small. In addition, there is strong resistance to adding nanoparticles to food deliberately (even if such particles are completely natural). Studies of less natural particles may still illustrate some important principles, but the materials themselves are unlikely to find much practical usage in personal consumer goods. This has influenced to some extent the selection of references mentioned below.

2. Ongoing Fundamental Issues

In view of the apparent widespread application of the Pickering stabilization principle to all sorts of emulsions in the scientific literature, one might be forgiven for assuming that the mechanisms of Pickering stabilization are easy to characterize and are completely understood. This is not necessarily the case.

(a) Firstly it is difficult to measure contact angles of micron or sub-micron solid particles at interfaces, especially if they are non-uniform in shape and have surface homogeneities, i.e., different regions of the surface have different surface energies ΔG.

(b) Secondly, although the fundamental equation above defines the thermodynamic energy difference between a particle adsorbed and not adsorbed at the interface, the energies required to actually enter or remove the particle from the interface are not necessarily the same. Ettelaie and Lishchuk [14]●●

have shown that the energy can be considerably greater than this when one considers the energy of formation of a 'neck' of fluid attached to the particle on its removal/entering the interface.

(c) Depending on the emulsion droplet coverage by particles and their contact angles, particles can stabilize (or destabilize) the thin liquid film between droplets, leading coalescence or aggregation of droplets. Aggregation of droplets and/or trapping of droplets with highly aggregated particle networks can immobilize droplets and enhance their kinetic stability, but it can be argued that this is not true Pickering stabilization, merely trapping droplets with a particle network or particle gel.

(d) In addition, although these and true Pickering emulsions may show limited coalescence and Ostwald ripening in the absence of shear, shear can be quite disruptive to Pickering emulsions. Rong et al. [15] have also shown that if the fluid regions either side of the interface of a droplet in a shear field can distort even a fraction, this concentrates all the transmitted stress between the adsorbed particles to a very small number of particles, such that can easily exceed the desorption energy. This possibly explains the relatively poor resistance of Pickering emulsions to shear, although this has not been studied widely.

(e) In addition most 'natural' particles are not monodisperse as well as being not uniform in shape, so the uniform packing of particles on droplets is not possible.

(f) Finally, one needs to recognize that in real foods Pickering stabilizers will normally have to compete with a range of other surface active materials (e.g., proteins, lipids, surfactants [16]●●) for the interface. These will generally adsorb more quickly and pack more efficiently at the interface due to their smaller size, whilst they may also adsorb to the Pickering particle themselves and so alter θ and the efficiency of particle adsorption to the interface.

Bearing all of the above complications and issues in mind, various studies are worth highlighting, as below. Figure 1 illustrates some of these issues, plus the types of particles described in what follows and further complications in their behaviour.

3. Emulsion types

Since most 'natural' biopolymers are more compatible with water than oil, most Pickering stabilizers are suitable, or specifically designed, to stabilize oil-in-water (O/W) emulsions. In actual fact there is a greater demand for Pickering stabilizers of water-in-oil (W/O) emulsions, since the range of acceptable food-grade W/O emulsifiers is very limited. Therefore, Pickering stabilizers of W/O emulsions deserve highlighting ([17], [18], [19], [16]) which then also expand the possibilities of multiple emulsions, e.g., W/O/W or O/W/O ([6,16], [20], [21]), since the problem of the oil-soluble surfactant is solved. In addition, the adsorbed particle layers might better resist the osmotic pressure gradients that plague multiple emulsions when the two like phases contain different concentrations of solutes. In most multiple emulsion studies the Pickering particle stabilizes the O/W part, whilst the study of Zhao et al. [16] provides a unique study of surfactant desorption of fat crystals in destabilizing W/O emulsions

Water-in-water (W/W) emulsions are slightly more exotic, arising mainly when biopolymer solutions phase separate into discrete microscopic regions far richer in one component than the other. This area has been reviewed recently [5], [8] and all sorts of particles that would prefer not to be in at least one of the phases can end up concentrated at the W/W interface, so effectively stabilizing this region and preventing further growth of the phase regions by fusion or migration of components between them. (Keal et al. [22]●● have provided some fascinating first experimental measurements of the kinetics of particles entering W-W interfaces that reveal added complications in addition to those indicated above).

Although this review is focused on emulsions, it is worth remembering that some of the Pickering particles developed can be used as foaming agents – in aqueous [23] or non-aqueous media. The latter are usually referred to as oleofoams [24], [25], though again there can be some confusion as to whether the gas bubbles in such oleofoams are actually stabilized by particle adsorption or by trapping within a viscous particle network formed in the non-aqueous phase, i.e., an ‘oleogel’ [26], [27]).

4. Particle types

It is easiest to class the remaining studies selected for inclusion via the type of particle used as stabilizer. In the main these are for O/W emulsions, though some exceptions will be pointed out.

4.1 Organic crystal particles

Fat crystals are perhaps the most natural water-insoluble particle in foods that one could think of a Pickering stabilizer [28]●, whilst some lipid materials are also be very insoluble in food oils - indeed this may be one contribution to the stability of W/O emulsions in fatty spreads [16]. Unfortunately, their application in other products may be limited due to the perception that, deliberate addition of solid fats (which are naturally more highly saturated) is undesirable, but also because it may be difficult to control the size and shape of the fat crystals. Nevertheless, fat crystals in combination with proteins or other surfactants may have potential [29], [30] and the formation of novel oleogels or oleofoams using the same types of particles, mentioned above. Polyphenols can also form organic crystals that can act as stabilizers of O/W or W/O emulsions [18].

4.2 Prolamin-based particles.

Prolamins are plant storage proteins that are naturally very insoluble in water and/or are quite hydrophobic, which points to their potential as O/W stabilizers. Notwithstanding the fact that many of the prolamin particle preparation processes entail solubilization in organic solvents (usually ethanol), which is a hurdle that might have to be overcome [31], the sheer extent of the work on prolamins illustrates their potential. Good stabilization of O/W emulsions has been demonstrated by many workers, sometimes in combination with other water-soluble polymers that moderate the hydrophobicity of the prolamin particles. Of paramount interest is zein [32] (from maize), glutenins [33,34] and gliadins [26] (from wheat), which are major cereals crops, but also kafirin [21] (from sorghum) and quinoa [21], have been studied quite extensively.

Liu et al. [35]● have used a novel way of cross-linking the gluten molecules via a shearing process that probably promotes the disulfide interchange reaction that occurs on processing bread dough. The majority of the work on zein involves complexing the protein with a more water soluble polysaccharide [36] or second protein [37] or an organic acid [38] to aid its dispersion into water and thence adsorption to the O-W interface. On the other hand, Rutkevicius et al. [17] showed that zein particles can be so hydrophobic that they can stabilize W/O emulsions to a limited extent. A good deal of the prolamin work has focused on their ability to stabilize very high oil fraction dispersed phase O/W emulsions, i.e., high internal phase emulsions (HIPEs). Some authors (e.g., [39]) then refer to such HIPEs as emulsion gels, in view of the bulk rheology of such systems, but it should remembered again that the use of high quantities of insoluble materials to stabilize mayonnaise-type products [40] through 'solidification' of the aqueous phase is not new and not strictly Pickering. It can be difficult to tell what the particles are doing in such densely packed systems, but good evidence of prolamin particle adsorption exists [36].

4.3 Cellulose- and chitin-based particles

Cellulose and chitin [41] may be treated together as examples of food-compatible materials that form particles (crystals) or fibres [42]● of much higher aspect ratio and that are insoluble in both water and oil. Bacterial cellulose is particularly good for very fine fibres and bulk gels [43] that can immobilize emulsion droplets within them. Again, one should be careful to distinguish true Pickering emulsion stabilization from droplets immobilized in a gel network. Citrus fibre is well known to act like this in high internal phase emulsions (HIPEs), i.e., mayonnaise-type products.

As polysaccharides, it is not obvious why such materials alone would adsorb to the O-W interface, but some extraction and processing methods are believed to change the cellulose crystal habit (e.g., nanocellulose particles [44]). Again, such processing may involve lengthy application of acids, alkalis and other solvents to disrupt the cellulose fibre amorphous regions, bringing the perceived disadvantages of non-natural material mentioned earlier [45]. Although these chemicals may be easy to wash away, they can also impart charge to the materials so that they become less surface active on their own and this introduces unwanted ionic strength- and pH-dependence [46], [47]. Some workers get around this by using salt to screen the charges but the formation of complexes with other surface active materials such as food-permitted cellulose derivatives or preferably proteins [48] may be the way forward to utilize cellulose in a more benign way. Here the adsorbed films must be some sort of mixed film of cellulose particles and the other surfactants. Cellulose complexed with carboxy methyl cellulose can even aggregate in oils to form oleogels [27]. There are many other examples of such combinations in the literature, but materials that when extracted already have desired combination of protein and cellulosic material may have more practical application [49]. Indeed, it is always important to check whether low levels of naturally present surface contaminants are responsible for the apparent surface activity of these polysaccharide-based particles.

Chitin [41] and its derivative chitosan have also been widely studied [50], [51], though the latter requires significant complex formation with oppositely charged materials to render it surface active.

4.4 Starch-based particles

Starch is another naturally abundant biopolymer that can also be quite water-insoluble depending on the amylose: amylopectin ratio, but it is not expected to be surface active. Starch usually has to be treated with a reagent like octenyl succinic anhydride (OSA) [52], [53] to make it adsorb, or again via physical complexes with surface active agents such as proteins [54] or lipids [55], [56]. OSA-modified starches are permitted food additives and excellent emulsifiers. Amylopectin molecules can have sizes of tens of nm, i.e., similar in size to many true Pickering nanoparticles. Unfortunately, there is sometimes confusion in the literature whether the OSA-starch materials used to stabilize emulsions are the native solid OSA-starch granules [57], [58], [59]●● (or mechanically broken fragments of them [60], [61]) or combinations of the OSA-granular material plus OSA-conjugated amylopectin + amylose molecules released via full or partial solubilization of the granular material. Perhaps only the intact granules or solid fragments of them, such starch nanocrystals [62] should be strictly viewed Pickering stabilizers.

Similarly to some cellulose-based materials, it has been shown that the apparent surface activity of some starch granules is due to naturally proteins adsorbed to their surface [63], [54]. The thick adsorbed layers of starch material seem to impart particularly good freeze-thaw stability to emulsions [63] and one potential advantage of starch particles is their ability to gelatinize together after adsorption and increase emulsion stability further [57]. Reviews of the whole starch Pickering area have recently been provided by Li and Zu [64] and Ge et al. [65], including synthetic and enzymatic surface modification [66]. It might be mentioned that OSA can be used make hydrophobic any polysaccharide material, including bacterial cell walls apparently [67].

4.5 Microgel particles

The final particle class selected for discussion is microgels, or microgel particles. Each microgel particle is a network, i.e., a gel, of some sort of material, formed by either controlled network growth ('bottom-up' formation) or controlled fragmentation of a bulk gel to the particles ('top-down' formation). This is a fascinating class of materials that in itself forms a very active area of research

[68]●, [69]●●. One advantage from the food point of view is that microgel particles of reasonably well-controlled size can be formed from a wide range of biopolymers. Thus one can convert natural protein sources that consist of complex mixtures of different proteins that have limited solubility and/or complex aggregation properties, into just one type of supramolecular aggregate, i.e., microgels. Plant proteins are an obvious candidate [70], [71], [72], but also plant polysaccharides, e.g., cellulose [73]. Chen et al. [74] have even shown that soy protein microgels can even form 'spontaneously' on simple changes in physical conditions.

Since protein microgels are composed of surface active material, most protein microgels also seem to be very surface active, combining the high desorption energies of Pickering particles with the ability of proteins to adsorb to almost any interface, whilst the adsorbed layer is much thicker than a protein monolayer. This increased thickness may have some uses in modifying the rate and extent of enzymatic digestion of either the stabilizing layer or the enclosed droplet material [48], [75]. Microgels can be formed from any polysaccharide that gels, and even though the polysaccharide material is non-surface active, it can again be combined with other ingredients, such as proteins or lipids, to make them so.

The interaction between microgel particles in the bulk and at the interface – the electrosteric repulsion between them, their interpenetration and/or deformation – are factors that are still not fully understood [69]. It has been suggested that at interfaces both bulk phases interpenetrate such particles [76], illustrating that it is misleading to conceive of microgels as having a fixed and finite contact angle like true Pickering particles [77]. Nevertheless, for the reasons given above, it is likely that there will be increasing study of the conversion of food materials into microgel particles for uses as Pickering stabilizers, rheology modifiers or controlled release vehicles.

Finally in this section, it is also worth mentioning examples of biopolymer co-aggregates that one might not exactly regard as microgels, in other words, insoluble particles produced via complex formation between combinations of proteins and/or polysaccharides [13], [78]. Such particles do not have a typical gel-like structure, i.e., a characteristic pore size and strand thickness, but have a much more heterogeneous internal and surface composition, so that it is harder to relate their surface activity to the particle properties.

5. Conclusions

Pickering emulsions for food and drinks is a very fertile and active area of research. There are many other studies that have not been covered in this review and many other types of material and combinations of material that are being tested by imaginative colloid scientists as Pickering stabilizers of emulsions and foams. The effectiveness and compatibility in foods of many of the proposed Pickering particles might be improved by combining with other surface active ingredients [79]. It remains to be seen how many of these new types are actually exploited in real products – though this does not necessarily have to be limited to food and drinks – pharmaceuticals, agrochemicals and cosmetics, for example, are other areas where these could be equally well utilized. Whatever the outcome, we will have learnt a great deal more about the subtleties and complications of particles at interfaces in complex media.

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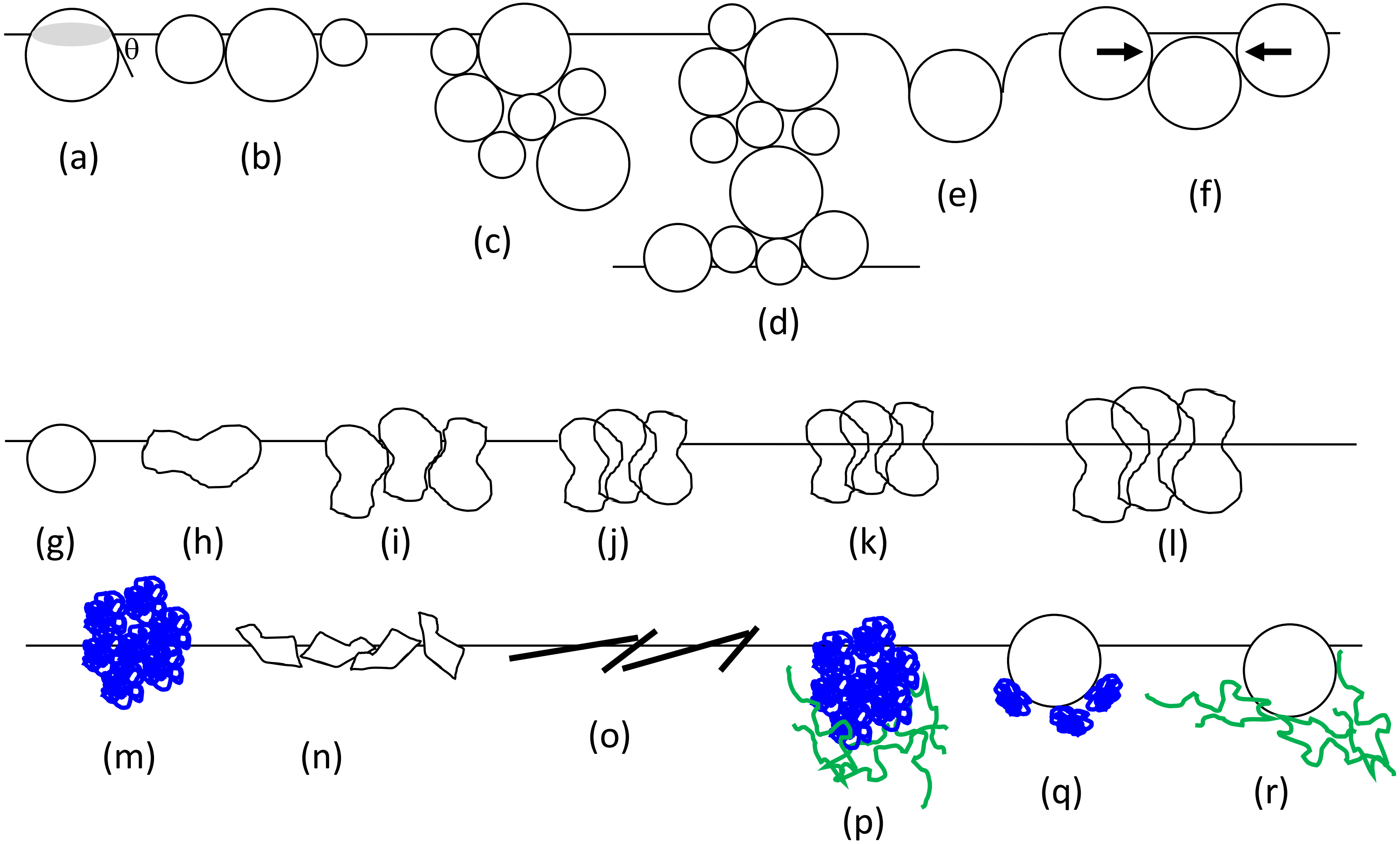
θ
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Figure 1. 'A to Z' of possible Pickering particles in foods and their behaviour. Horizontal line represents an O/W or A/W interface (aqueous phase below the line, hydrophobic phase above): (a) classic Pickering hard sphere with finite contact (θ) with shaded region the interfacial area occupied; (b) multiple particle sizes with varying or similar θ; (c) aggregates of particles adsorbing; (d) bridging of interfaces by particle aggregates and/or trapping of droplets and bubbles within such aggregates; (e) extra energy of necking fluid as particle removed from interface; particle (middle) forced off interface by stress concentration in adjacent particles, e.g., at apex of a bubble or droplet in flow; (g) firm microgel particle; (h) floppy (less cross-linked) microgel particle; (i) deformation & re-orientation of microgel particles as particle coverage increases; (j) interpenetration of microgel particles as coverage increases; (k) penetration of bulk phases into microgel particles, with change in their affinity for each phase; (l) swelling of microgels by aqueous phase, increasing their affinity for aqueous phase; (m) insoluble protein aggregate; (n) single or polycrystalline material of irregular shape and θ; (o) nanofibers of varying aspect ratio and θ; (p) insoluble protein aggregate with increased affinity for aq. phase due to polysaccharide (green) adsorption; (q) particle with increased affinity for aq. phase due to protein (blue) adsorption; (r) particle with increased affinity for aq. phase due to polysaccharide (green) adsorption. [Adsorbed water-soluble lipids would have the opposite effect in the case of (p)- (r)].