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"Particle-Stabilized Emulsions and Colloids: Formation and Applications"

Edited by To Ngai (The Chinese University of Hong Kong, China) and Stefan A. F. Bon (University of Warwick, UK), RSC Soft Matter Series, No. 3, Royal Society of Chemistry, Cambridge, UK, 2015, 337 pages, ISBN: 978-1-84973-881-1, £175.00, €218.75, US$290.00

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"Particle-Stabilized Emulsions and Colloids: Formation and Applications", edited by To Ngai and Stefan A. F. Bon, is the third book of the Royal Society of Chemistry (RSC) Soft Matter Series, published in 2015. Both editors have extensive expertise in polymer chemistry and its application to colloid science. Professor Ngai's research interests focus on interparticle interactions at fluid interfaces and using emulsions as templates for functional materials, whereas Professor Bon's current research area is supracolloidal polymer chemistry, focusing on the design of assembled supracolloidal structures and the synthesis of their colloidal and macromolecular building blocks through a combination of polymer chemistry, colloid science, soft matter physics and chemical engineering.

This series, edited by Hans-Jürgen Butt, Ian W. Hamley, Howard A. Stone and Chi Wu, provides a review of recent developments in soft matter research. The scope of this volume is quite focused: the book is devoted to the use of solid particles as a means to stabilise emulsions and more complex colloidal systems. The ambition of the book is to offer a comprehensive overview of not only the fundamental science behind Pickering emulsions and their stabilisation mechanism, but also of the current and future range of useful industrial applications, with the aim of fostering further development of these emerging technologies. The target audience is therefore the colloid science community at large, both in academia and in industry, rather than a general, non-specialised audience. Given the broad scope of the applications illustrated, only a selection of the most relevant chapters will be reviewed.

The Pickering Stabilisation Phenomenon

The first chapter is written by Stefan Bon and it is a very short and basic introduction to the Pickering stabilisation phenomenon, with a brief historical perspective. The following chapter, authored by Bum Jun Park (Kyung Hee University, South Korea), Daeyeon Lee (University of Pennsylvania, USA) and Eric M. Furst (University of Delaware, USA), is a more extensive description of the physical-chemical interactions of particles adsorbed at fluid-fluid interfaces: from the wettability of a single particle, homogeneous or amphiphilic, to more complex topics, such as the interactions between pairs of homogeneous and amphiphilic particles, with a focus on effects of geometrical anisotropy and non-spherical objects. Pair interactions are discussed not only from a theoretical viewpoint, but also by illustrating direct measurements done with optical laser tweezers and then related to bulk property measurements; further experiments reviewed include the effect of additives (salt and surfactant) and the evolution of interactions with time.

Polymer-brush Modified Particles

Chapter 3 is nearly entirely dedicated to applications of polymer brush-modified clay layers or gold nanoparticles (AuNPs) in Pickering emulsions. The chapter has been written by Hanying Zhao and Jia Tian (Nankai University, China). Brushes are generally sought after for their responsiveness to environmental conditions. First clay layers with block copolymer brushes are discussed: examples of preparations with poly(dimethylaminoethyl methacrylate) (PDMAEMA) and poly(methyl methacrylate) (PMMA) block copolymers are given. Then clay layers with homopolymer brushes are presented; finally examples of mixed homopolymer brushes and hydrophilic faces with hydrophobic polystyrene (PS) brushes on the edges are introduced.

Next the topic of AuNPs, functionalised with polymer brushes to stabilise emulsions, is highlighted. Interesting NP complexes with core-shell structures are made from AuNPs and iron oxide NPs with PS brushes. AuNP-stabilised emulsions are used as templates to fabricate hollow hybrid capsules.

Finally, the stabilisation of emulsions by Janus disks is summarised, with examples that include preparing amphiphilic Janus Laponite disks at the oil-water interface (**Figure 1**) and using metal-supporting Janus particles as interfacial catalysts.

Pickering Suspension, Mini-Emulsion and Emulsion Polymerisation

The terminology used in Chapter 4 by Stefan Bon is quite technical and confusion is likely for those who are unfamiliar with these topics. The opening paragraph explains the peculiarities of each system, followed by historical perspective and the more recent developments in suspension polymerisation, such as preparing deliberately armoured composite polymer particles. Examples of suspension polymerisations include using titanium dioxide, Laponite particles and iron oxide with different polymers and formulating inverse Pickering suspension polymerisation systems.

Pickering mini-emulsion polymerisation was first reported in the literature by Landfester *et al.* in 2001 (2).

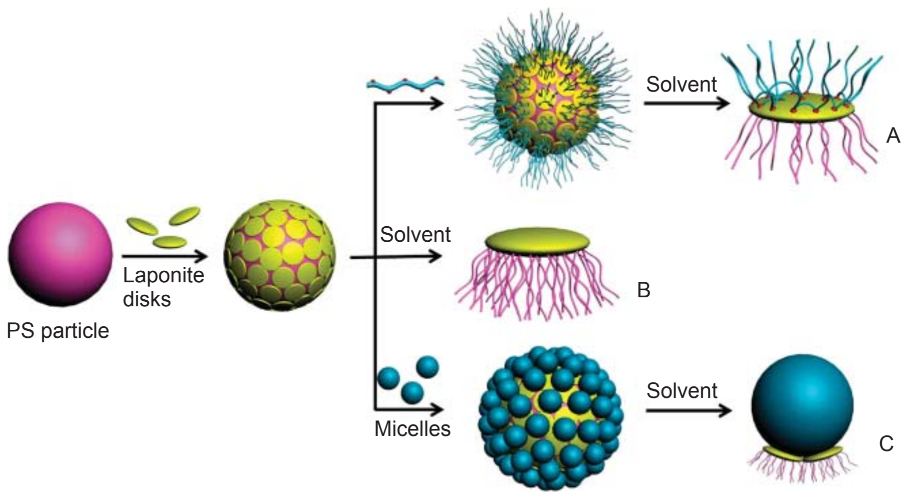


Fig. 1. Schematic outline for the synthesis of Janus Laponite disks: A a Laponite disk with hydrophobic PS brushes on one side and hydrophilic quaternised PDMAEMA on the other side; B a Laponite disk with PS brushes on one side; C a polymeric micelle with Laponite disks (Reprinted with permission from (1). Copyright (2013) American Chemical Society)

More examples of using Laponite disks as stabilisers are given. A successful synthesis needs particles that are able to adhere and cover the emulsion droplet, thus curvature is crucial and constraints on the size of particles are present: typically the particles need to be less than 200 nm in diameter, unless flexibility and bending around the droplet are possible.

The final part of the chapter concentrates on Pickering emulsion polymerisation: general references are suggested for further reading, and then a standard recipe for a free radical emulsion polymerisation is presented. The difference, in the case of Pickering emulsions, is the replacement of surfactants with solid, often nanosized particles: clay disks, amphiphilic polymer Janus particles, and silica NPs. An extensive historical overview of the field is provided with several examples, followed by a mechanistic insight on the process, although work on the area is still limited. The outlook on technological application of armoured nanocomposite polymer latexes is promising, although still in its infancy: the latter developments in the synthesis techniques will allow more applied studies and a potential application has recently been reported by Wang *et al.* (3), where soft armoured latexes added to waterborne adhesives induce a marked increase in tack adhesion energy.

Bicontinuous Emulsions Stabilised by Colloidal Particles

Chapter 6 by Joe W. Tavacoli (Université Paris-Sud, France), Job H. J. Thijssen and Paul S. Clegg (University of Edinburgh, UK) describes how interfaces densely coated by particles can behave like an elastic sheet. Therefore unlike surfactant-stabilised systems, they do not necessarily form spherical droplets and their shape is dependent on the process history, allowing formation of liquid bicontinuous architectures (called bicontinuous interfacially jammed emulsion gels or bijels), which consist of two tortuously entwined percolated liquid phases that are separated and stabilised by solid particles. To adopt a bicontinuous morphology, two immiscible liquids must be induced through a critical quench, while the liquid-liquid interface is populated by neutrally wetted particles. Bicontinuous domains evolve when the system is quenched into the spinodal region of its phase diagram. This process was first described by Stratford *et al.* (4) by computational methods and later experimentally obtained by Herzig *et al.* (5), using a water-lutidine system and Stoeber silica particles. The characteristic size of bijels domains follows from the ratio of the particle diameter and the particle volume fraction used: this allows tuning of this size from the nanoscale to hundreds of microns. Other liquids successfully tested are nitromethane and ethanediol.

Apart from molecular liquids, polymers are also used to obtain bijels. Notably, there are some key differences with molecular liquids, thoroughly discussed in the chapter.

An essential element in the fabrication of bijels is the particles: colloidal silica particles have been used extensively, but more recently more exotic particles have been investigated as alternatives, (mainly with simulations) such as anisotropic or field-responsive particles, magnetic particles and graphene oxide (GO) sheets.

Characterisation of bijel morphology is then introduced, followed by studies on the link between morphology and mechanical properties. Among the up-and-coming applications investigated so far, the use of three-dimensional (3D) bijels (**Figure 2**) to create porous materials is mentioned.

Materials with bicontinuous structures can be used in catalysis, sensors and gas storage, allowing simultaneous optimisation of active surface area and mass transport. Other potential applications include delivery (for example a dye and a bleach in haircare products or separate chemical reactants that form the desired product if released simultaneously at target, through a specific trigger) through bijel capsules and development of cross-flow microreactors. The challenges are the scaling up of fabrication, cost

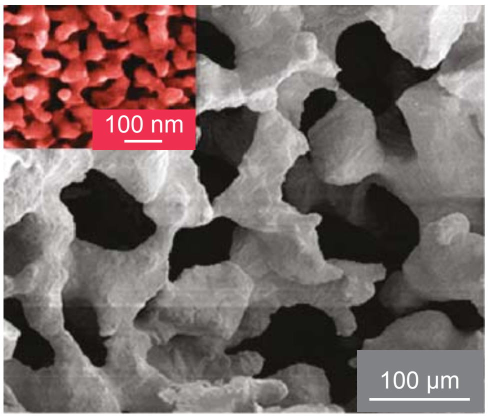


Fig. 2. Silver monolith with continuous pores on two widely separated length scales (Reprinted with permission from (6). Copyright (2011) American Chemical Society)

of materials and use of benign materials instead of hazardous components. Finally, after dealing with liquid-liquid bicontinuous systems separated by a particle-coated, solid interface, the idea of creating a structure which has two co-continuous solid domains separated by a single liquid domain, called a bigel, is considered.

Hollow Spheres and Microcapsules Fabrication through Particle-stabilised Emulsions

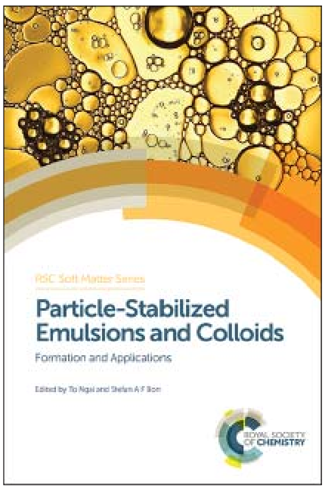
Chapter 9, written by Simon Biggs (The University of Queensland, Australia) and Olivier Cayre (The University of Leeds, UK), explains the fabrication of colloidosomes, hollow core-shell microcapsules in which the capsule wall consists of close-packed colloidal particles that have been permanently locked to each other. Colloidosomes display a range of unique features: the shell thickness can be manipulated by choosing different-sized colloids; the porosity of the shell can be similarly adjusted; the system has inherent flexibility due to the large range of particles that are used; and using particles solely as stabilisers of the emulsion yields enhanced stability.

The manufacture of colloidosomes include three main categories of methods that can lock the particles at the interface. The first method involves using a sol-gel or a polymerisation reaction, either in the droplet or at the interface, leading to the formation of a shell that entraps the colloid particles permanently. A second method uses precipitation, by solvent extraction, of an existing polymer added to the dispersed phase. Another way to solidify the capsule surface is to perform a physical or chemical modification of the particles, for instance fusing, by heating the particles above their glass transition temperature, or by using chemical cross-linkers to bind adjacent particles. Finally it is possible to adsorb one or more additional layers of polymer or polyelectrolyte onto the particle monolayer with two main advantages: adjacent particles are bridged on the surface of emulsion droplets and the permeability of the microcapsule shell so obtained is further controllable, and usually decreased, by this route. The main drawback consists of extra washing steps to remove the excess of stabilising particles and polymer or polyelectrolyte.

When the capsules have been synthesised, post-processing involves removing the oil phase to obtain a water-in-water microcapsule dispersion: often a gelling agent is added to the aqueous phase to impart higher mechanical strength and more control over the release of encapsulated agents. The large variety of particles used allows for an easy introduction of functionality onto the microcapsule surface: magnetic particles can be used to direct the microcapsules into an area of the vessel or onto a specific delivery target. Other responsive materials have been used too. The main use of colloidosomes is for encapsulation and subsequent controlled release of drugs or substances: of more widespread interest for commercial applications are the approaches for encapsulation of highly volatile, low molecular weight molecules which are poorly soluble, or sensitive to their environment (perfumes), however none so far have succeeded in forming an impermeable shell. The variable pore size features have also been explored in order to encapsulate larger molecular weight materials or even NPs.

Conclusion

The book gives a very extensive coverage of particle-stabilised emulsions and it is a useful reference for industrial or academic researchers who are already familiar with the colloid science field, but need to deepen their knowledge into this rather specific, although vast, branch of colloid science. The content is very technical and the style of presentation of the different topics is rather heterogeneous throughout the chapters: both aspects hinder somewhat the overall readability. Frequent overlapping of closely-related themes, developed to a different degree of extent, or across several chapters, can sometimes confuse the reader. As such, the volume is more suitable to a specialised audience rather than to a general one, with little or no previous knowledge of the areas covered by the book.



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The Reviewer

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