Institution: University of Edinburgh		
Unit of Assessment: UoA9 - Physics		
Title of case study: Research into particle-stabilized emulsions and the discovery of a new material, the bijel, underpin new technologies in industry		
Period when the underpinning research was undertaken: 2004–2016		
Details of staff conducting the underpinning research from the submitting unit:		
Name(s):	**Role(s) (e.g. job title):**	**Period(s) employed by submitting HEI:**
Paul Clegg	Professor	2003–present
Andrew Schofield	Research Fellow	1996–present
Wilson Poon	Professor	1990–present
Mike Cates	Professor	1995–2015
Aidan Brown	Chancellor's Fellow	2012–present
Kevin Stratford	Senior Research Fellow	2001–present
Stefan Egelhaaf	Senior Research Fellow	1998–2005
Joe Tavacoli	Postdoctoral Research Associate	2008–2011
Period when the claimed impact occurred: March 2015–December 2020		
Is this case study continued from a case study submitted in 2014? N		

1. Summary of the impact

Attribution: Research at the University of Edinburgh (UoE) revealed the importance of processing routes in the preparation of particle-stabilized emulsions for the formulation sector. The standout example of what can be achieved was demonstrated through the invention of a new material, the **bicontinuous, interfacially jammed, emulsion-gel** (**bijel**).

Impact: The knowledge generated through UoE's research into the preparation of particle-stabilized emulsions has influenced company policy at *Mondelēz* and prevented failed production runs of an agrochemical product manufactured by *Syngenta*. The invention of the bijel has led to the founding of two companies to commercialise bijel-derived technologies.

Beneficiaries: Multinational companies *Syngenta* and *Mondelēz*, their customers, and start-up companies *UniSieve* and *Innvtek*.

Significance: The research provided underpinning understanding to improve manufacturing robustness of a USD200,000,000 (09-2020) agrochemical product. The two start-up companies founded in Zurich (Switzerland) and Calgary (Canada) to commercialise bijel-derived technologies employ four and two people respectively and have attracted combined investment of GBP4,200,000 during the REF period.

Reach: Particle-stabilized emulsions have become part of a palette of formulation concepts considered to address formulation challenges globally. Applications are found in a range of industries, including agrochemicals, the food industry, energy, and biomaterials.

2. Underpinning research

From 2004 until 2007 experimentalists and computer simulators at UoE worked closely together to develop a novel material: a bicontinuous, interfacially jammed, emulsion-gel (bijel). The UoE team, then led by Cates, employed large-scale computer simulations to demonstrate the possible existence of this new type of composite material [***R1***]. The computer simulations demonstrated that, if particles with appropriate surface chemistry are dispersed in a binary liquid system, undergoing phase separation via spinodal decomposition, they can prevent phase separation from going to completion. Instead, the particles arrest the phase separation process with the liquids arranged in a tortuous bicontinuous pattern.

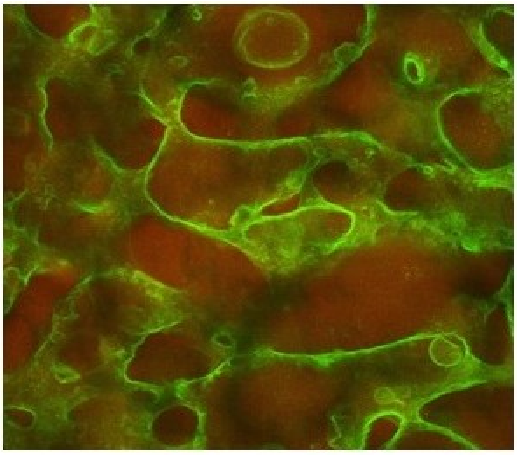

Figure 1: Confocal micrograph (616µm across) of a bijel sample with colloidal particles shown green.

While the computer simulations [***R1***] revealed the existence of the bijel, scaling the simulation variables into a realistic system, they only demonstrate existence for about 1 micro-second. UoE researchers then showed experimentally that the bijel could be fabricated in the laboratory (see Figure 1) and many of the key properties were presented [***R2, R3***]. Having a preferred realisation and an understanding of the practicalities involved in fabrication is also crucial. The structure was demonstrated to be stable for many months. At a conceptual level, this was the first research on particle-stabilized emulsions where the focus was entirely on the fabrication route.

Subsequently, UoE researchers demonstrated the fundamental role that particle wettability plays in both bijel and particle-stabilized emulsion formation [***R4***]. Furthermore, a key insight into processing particle-stabilized systems was revealed: the bijel forms at the point where transitional inversion is occurring (i.e., oil-in-water is changing to water-in-oil). If phase separation via spinodal decomposition is used to create the emulsion, then a bijel forms; if shear is used to create the emulsion, then a multiple emulsion forms in a single step (multiple emulsions have droplets inside droplets).

The ability to control particle wettability [***R2, R4***] led to an understanding of bridge formation in particle-stabilized emulsions [***R5***]. Bridges are points where two droplets in the emulsion share the same particle (or more often particles). They are crucially important because, without bridges, particle-stabilized emulsions are extremely robust. The presence of bridges makes these emulsions suddenly become fragile. The relationship between bridge formation and the emulsification process, the composition of the emulsion, and the wettability of the particle surfaces were explored, demonstrating bridge breaking and its implications for emulsion stability.

Building on the foundations of [***R5***], UoE researchers went on to overturn a long-held dogma in the field of particle-stabilized emulsions. It had been universally accepted that the trapping of single particles to a liquid-liquid interface is sufficiently strong that it is irreversible: i.e., particles do not become detached without also destabilizing the droplet in its entirety. By working with two populations of particles, tagged with different fluorophores, it was shown that, in the presence of bridges, particles are exchanged between droplets even under very gentle stirring [***R6***] (Figure 2 below). This demonstrates the dynamic nature of particle-stabilized emulsions if bridging is present.

3. References to the research

[***R1***] **Stratford, K.**, Adhikari, R., Pagonabarraga, I, Desplat, J.-C., & **Cates, M. E.**, (2005). Colloidal Jamming at Interfaces: A Route to Fluid-Bicontinuous Gels. *Science* 309, 2198–2201. DOI: https://doi.org/10.1126/science.1116589 *[328 citations, WoK]*

[***R2***] Herzig, E. M., White, K. A., **Schofield, A. B.**, **Poon, W. C. K.**, & **Clegg, P. S.**, (2007). Bicontinuous emulsions stabilized solely by colloidal particles. *Nature Materials*, 6, 966–971. DOI: https://doi.org/10.1038/nmat2055 *[278 citations, WoK]*

[***R3***] **Cates, M. E.**, **Clegg, P. S.**, **Poon, W. C. K.**, **Egelhaaf, S. U.** 2010. Fluid-bicontinuous particle stabilized gels. European Patent 1807192B1, filed July 1 2005, granted February 17 2010. https://patents.google.com/patent/EP1807192B1/en

[***R4***] White, K. A., **Schofield, A. B.**, Wormald. P., **Tavacoli J. W.**, Binks, B. P., & **Clegg, P. S.,** (2011). Inversion of particle-stabilized emulsions of partially miscible liquids by mild drying of modified silica particles, *Journal of Colloid and Interface Science*, 359, 126–135. DOI: https://doi.org/10.1016/j.jcis.2011.03.074 *[42 citations, WoK]*

[***R5***] French, D. J., Taylor, P., Fowler, J., & **Clegg, P. S.** (2015). Making and breaking bridges in a Pickering emulsion. *Journal of Colloid and Interface Science*, 441, 30–38. DOI:

https://doi.org/10.1016/j.jcis.2014.11.032 *[55 citations, WoK]*

[***R6***] French, D. J., **Brown, A. T.**, **Schofield, A. B.**, Fowler, J., Taylor, P., & **Clegg, P. S.** (2016). The secret life of Pickering emulsions: particle exchange revealed using two colours of particle. *Scientific Reports*, 6 (August), 31401. DOI: https://doi.org/10.1038/srep31401 *[25 citations, WoK]*

4. Details of the impact

The discovery and experimental realisation of the bijel, along with accompanying advances in understanding particle-stabilized interfaces, have directly impacted a variety of industries, including agrochemicals, foods production, energy materials and filtration. Below we describe specific cases.

New understanding of bridge formation prevents failure of multimillion dollar product

Syngenta Crop Sciences have an agrochemical delivery platform based on particle-stabilized droplets. While they were able to successfully manufacture their product, Jade™, they were aware of a significant fragility associated with process and did not understand "*its origin or the means to avoid it*" [***I1***]. Particle-stabilized emulsions are typically expected to be very robust and long lived due to the rigidity of the interfaces: i.e., the droplets do not coalesce. In practice, *Syngenta* found that small changes to their manufacturing process could lead to the droplets becoming exceptionally fragile. Droplets that coalesce during transport or storage are useless for agrochemical delivery leading to a massive waste of raw materials and energy.

Syngenta approached the UoE due to the attention UoE were paying to emulsion processing in bijel research [***R2, R3, R4***]. UoE worked with the company to understand their processing vulnerability. *Syngenta* funded an EPSRC Case student (David French) from their pool of studentships. UoE developed a simplified particle-stabilized emulsion that replicated the behaviour of the commercial product, Jade™. UoE researchers went on to demonstrate how droplets can become bridged if the quantity of particles and the processing conditions are not carefully tuned [***R5***]. UoE research also showed how the situation could be recovered [***R6***]. This research has enabled *Syngenta* to avoid failed production runs of Jade™ and has an "*impact on our customers because it obviously affects the homogeneity of the product, and delivering an even dose is essential to achieving good efficacy while eliminating off-target effects.*" [***I1***] *Syngenta* and their customers are the beneficiaries. To give a sense of scale, this product has aggregate sales of over USD200,000,000 (09-2020) in North and South America [***I1***].

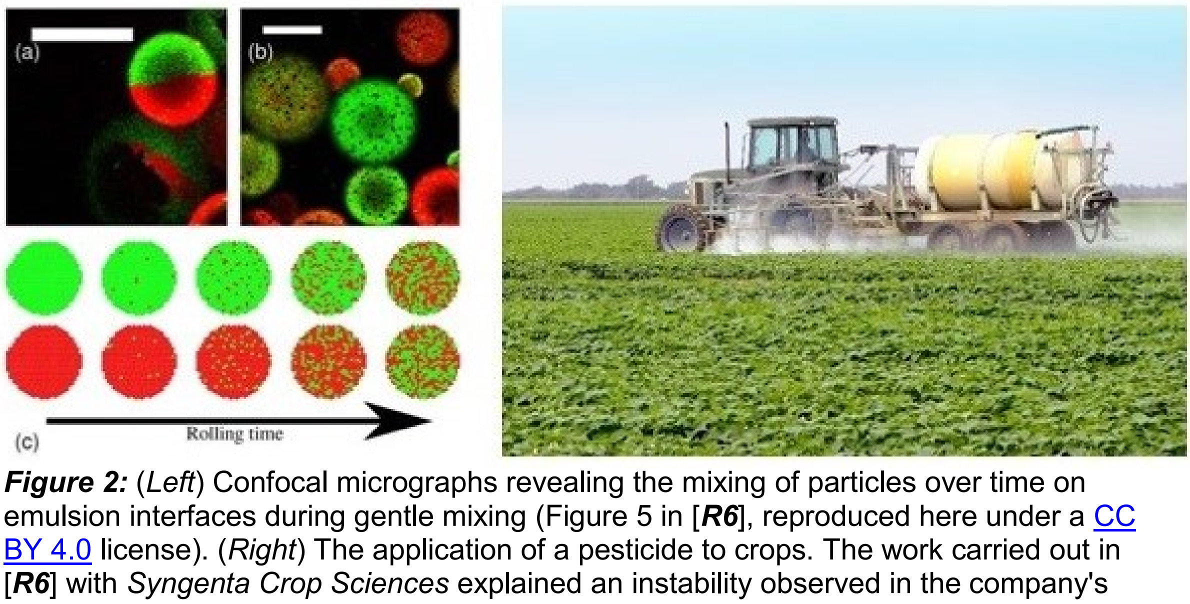

Figure 2: (*Left*) Confocal micrographs revealing the mixing of particles over time on emulsion interfaces during gentle mixing (Figure 5 in [***R6***], reproduced here under a CC BY 4.0 license). (*Right*) The application of a pesticide to crops. The work carried out in [***R6***] with *Syngenta Crop Sciences* explained an instability observed in the company's agrochemical product, Jade™, as well providing a recovery mechanism [***I1***].

Particle-stabilized emulsions as a novel formulation tool for the food industry

For dietary health reasons, *Mondelēz* would like to be able to replace some of the volume of their confectionary products with water droplets. The UoE approach is influencing company policy: the "*ability to reduce the calories in food without impacting sensory properties has, however, long been a challenge for the food industry. As the industry seeks to meet this challenge, I believe the sorts of structures researched by Dr Clegg will play an important role in enabling the coexistence of otherwise incompatible phases and the control of the structures that form, which will be important for simultaneously optimizing calorie-density and sensory properties*" [***I2***]. From 2019, UoE began working with *Mondelēz*'s Science Centre in Reading on the use of droplets with rigid interfaces to constrain the location of water within the product (a rival strategy to the use of osmotic pressure). *Mondelēz* have invested in the UoE approach via a BBSRC CTP studentship from their pool to fund Raj Tadi while he carries out this research [***I2***].

Bijel-derived membranes lead to the founding of two new start-up companies

The invention of the bijel by UoE researchers has created new opportunities for collaborations between academia and industry. Bijel patents have been filed by UoE researchers [***R3***] (for the new material), researchers at the University of Pennsylvania (for a processing route to optimise bijels for filtration [***I3a***])***,*** researchers at the University of California, Irvine (for bijel-derived battery electrodes and bijel-derived materials for biomedical devices and a drug delivery system [***I3b***]), and by a team at the University of Massachusetts Amherst (for bijels with submicron domains [***I3c***]). The technologies are advertised to industry via the universities' technology transfer websites [***I4***]. The team at the University of Pennsylvania are actively exploring their filtration technology with industrial partners and have also collaborated with a company to "*prepare bijels as coating materials*" [***I5***]. The external inventive steps all build on the original UoE discovery of the bijel.

In addition to the above early-stage industrial collaborations to develop novel bijel-derived products, two new companies that use bijel-derived technology have been established during the REF period.

Professor Wendelin Stark (Swiss Federal University) has commercialised polymer membranes for a range of applications through his company, Novamem, since 2013. In 2015, Stark and his colleague, Dr Samuel Hess, filed a patent on the use of the bijel concept [***R2***] in the creation of metal organic framework-based membranes [***I6***]. Hess went on to found *UniSieve* [***I7, I8***] in 2018 to commercialise this technology. The company sell sustainable sieving membranes for cleaning gases based on the metal organic frameworks reported in [***I6***]. As of May 2020, they have 4 employees (headcount: 4; FTEs: 4) and had raised GBP550,000 in start-up funding [***I7***]. In November 2020, they received a further GBP3,500,000 from Wingman Ventures, the European Innovation Council, and the European Institute of Innovation and Technology [***I9***].

In 2019, *Innvtek Inc.* was spun out of the University of Calgary by Dr Brandy Kinkead (CEO) with the aim of commercializing a bijel variant, a so-called bipjel, for energy materials applications [***I10***]. Bipjels are formed using the same method as reported in *[**R2**]* for bijel formation, with the variation being to pack one of the liquid channels of the bijel full of nanoparticles. *Innvtek* are targeting membrane applications within battery and fuel cell technologies via collaborations with three Canadian companies: AVL, Agora Energy and Salient Energy [***I11***]. Their technology is derived from the bijel [***R2, R3, R4***] and they rely on the research UoE has carried out [***I11***]. *Innvtek* have two employees and have raised GBP150,000 in start-up funding during the REF period.

5. Sources to corroborate the impact

[***I1***] Support letter from Syngenta Fellow at *Syngenta Crop Sciences*, North Carolina, USA.

[***I2***] Support letter from Senior Associate Principal Scientist, *Mondelēz International*, Reading, UK.

[***I3***] Patents filed relating to bijel-derived technologies:

a) Bijels for filtration https://patents.google.com/patent/WO2016196473A1

b) Bijels for batteries https://patents.google.com/patent/US20180375104
Bijels for biomedical devices https://patents.google.com/patent/WO2019236145A1/
Bijels for drug delivery system: https://patents.google.com/patent/US20200139009A1/en

c) Submicron domain bijels https://patents.google.com/patent/US20190375898A1

[*I4*] List of bijel-derived technology transfers:

a) Novel soft material synthesis with liquid phase architecture and interfacially active particles (UPenn): http://upenn.technologypublisher.com/technology/38391

b) Spinodal-Based Co-Continuous Composites For High Performance Battery Electrodes (UCI) https://techtransfer.universityofcalifornia.edu/NCD/25648.html

Non-Immunogenic Coating for Biomedical Devices (UCI) https://techtransfer.universityofcalifornia.edu/NCD/28960.html

Insulin Infusion Cannulas with Superior Performance (UCI) https://techtransfer.universityofcalifornia.edu/NCD/31991.html

c) A Simple, Scalable Method for Producing Bicontinuous Jammed Emulsions (or Bijels) with Sub-micrometer Domains Technology (UMass) http://tto-umass-amherst.technologypublisher.com/tech?title=A_Simple%2C_Scalable_Method_for_Producing_Bicontinuous_Jammed_Emulsions_(or_Bijels)_with_Sub-micrometer_Domains

[*I5*] Support letter from a Professor at the University of Pennsylvania, USA.

[*I6*] European Patent EP3251742A1, Self-supporting MOF membranes: https://patents.google.com/patent/EP3251742A1/en

[*I7*] Support letter from CEO and co-founder of *UniSieve*, Zurich, Switzerland

[*I8*] UniSieve's website www.UniSieve.com has information on their membrane technology for cleaning gases

[*I9*] Article detailing *UniSieve*'s newest investment amount: https://www.eu-startups.com/2020/11/swiss-cleantech-unisieve-lands-e3-9-million-to-help-the-chemical-and-energy-industry-conserve-energy-and-reduce-waste/

[*I10*] Innvtek's website www.innvtek.com/ has information on their membrane technology for chemical and battery processes.

[*I11*] Support letter from CEO and co-founder of *Innvtek*, Calgary, Alberta, Canada