Institution: The University of Edinburgh		
Unit of Assessment: UoA 9 - Physics		
Title of case study: Dense suspension rheology: from chocolate to ceramics		
Period when the underpinning research was undertaken: 2002–2015		
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:**
Wilson C. K. Poon	Professor	1990 – present
Peter N. Pusey	Professor	1991 – 2008
Michael Cates	Professor	1995 – 2015
Andrew B. Schofield	Research Fellow	1996 – present
Rut Besseling	Research Associate	2004 – 2012
Michiel Hermes	PDRA	2011 – 2016
Simon Titmuss	Lecturer	2011 – present
Stefan Egelhaaf	Senior Research Fellow	1998 – 2005
Period when the claimed impact occurred: August 2013–December 2020		
Is this case study continued from a case study submitted in 2014? N		

1. Summary of the impact

Attribution: Research in suspension rheology, undertaken at the University of Edinburgh (UoE), has been used to improve formulations and manufacturing processes in industries that process dense suspensions of granular (or non-Brownian) particles. This impact was underpinned by a rheometer attachment for visualising suspensions under flow designed at UoE and now marketed by *TA Instruments*.

Impact: Improved industrial practice and, hence, reduced cost and improved sustainability; highly-trained personnel now working in relevant industries.

Beneficiaries: *Mars Wrigley Confectionery* [text removed for publication], *Schlumberger* (oilfield services), *Johnson Matthey* (catalyst manufacturing) and *Corning Inc.* (ceramic catalytic converters) have improved their formulations and manufacturing processes and/or internal research capabilities.

Significance: [text removed for publication] Results from this research have been incorporated into *Schlumberger*'s internal training and professional development. Two highly-skilled researchers have transferred into the R&D teams at *Johnson Matthey* and *Corning*, continuing to generate impact. The new rheo-imaging technique developed by UoE has been commercialised through *TA Instruments* and launched commercially in 2015.

Reach: Applications across highly diverse sectors of industrial practice, including paints and coatings, energy materials, drilling fluids, ceramics and food products.

2. Underpinning research

Professor Poon and the UoE Soft Matter group have developed a research programme on the flow and deformation (rheology) of particulate suspensions. Initial publications focussed on suspensions of Brownian particles (smaller than about 1 micron) [***R1***]. As part of this work, the group pioneered a novel technique to image and track single particle displacements in flowing suspensions, allowing them to probe the shear yielding (solid-to-liquid) transition in dense suspensions in unprecedented detail [***R2***]. They also demonstrated that the technique could be used in geometries other than simple shear, e.g., pipe flow [***R3***].

The publication of [***R2***, ***R3***] attracted significant industrial attention. In particular, *Johnson Matthey* and *Mars Wrigley Confectionery* (then *Mars Chocolate UK)* both approached Prof Poon with a view to better understand the processing of their suspensions (ceramic pastes and molten chocolate respectively), both of which contained non-Brownian (10 microns or larger) particles. Initial stages of this industrial work led the group to the conclusion that non-Brownian suspension rheology was fundamentally different from Brownian suspension rheology. Two successive papers studying 'clean', lab-synthesized model non-Brownian suspensions [***R4***, ***R5***] provided some of the most important experimental evidence to demonstrate that frictional contacts between suspended particles, hitherto thought not possible, in fact dominated their rheological behaviour. Based on this fundamental advance, the group subsequently brought new insights for *Johnson Matthey*, *Mars* and other companies on the processing of non-Brownian suspensions. In particular, it turns out that many effects and processes can all be understood under the single heading of *shifting a frictional jamming concentration*.

The dominance of frictional contact means that details of particle surfaces assume an importance that has not hitherto been customary in suspension rheology. The work we have done with companies has therefore also benefitted from the prior experience of Dr Titmuss in using neutron reflectivity to measure the interfacial structure of polymers at solid interfaces [***R6***], which proved ideal for providing information on the structure of emulsifiers on surfaces as friction modifiers.

3. References to the research

[***R1***] K. N. Pham, A. M. Puertas, J. Bergenholtz, **S. U. Egelhaaf**, A. Moussaïd, **P. N. Pusey**, **A. B. Schofield**, **M. E. Cates**, M. Fuchs, **W. C. K. Poon**, *Multiple Glassy States in a Simple Model System*, Science 296 (2002) 104-106. DOI: https://doi.org/10.1126/science.1068238 *[609 citations, WoK]*

[***R2***] **R. Besseling**, E. R. Weeks, **A. B. Schofield**, **W. C. K. Poon**, *Three-Dimensional Imaging of Colloidal Glasses under Steady Shear*, Phys. Rev. Lett. 99 (2007) 028301. DOI: https://doi.org/10.1103/PhysRevLett.99.028301 *[187 citations, WoK]*

[***R3***] L. Isa, **R. Besseling**, **W. C. K. Poon**, *Shear Zones and Wall Slip in the Capillary Flow of Concentrated Colloidal Suspensions,* Phys. Rev. Lett. 98 (2007) 198305. DOI: https://doi.org/10.1103/PhysRevLett.98.198305 *[88 citations, WoK]*

[***R4***] B. M. Guy, **M. Hermes**, **W. C. K. Poon**, *Towards a Unified Description of the Rheology of Hard-Particle Suspensions,* Phys. Rev. Lett. 115 (2015) 088304. DOI: https://doi.org/10.1103/PhysRevLett.115.088304 *[103 citations, WoK]*

[***R5***] N. Y. C. Lin, **B. M. Guy**, **M. Hermes**, C. Ness, J. Sun, **W. C. K. Poon**, and I. Cohen, *Hydrodynamic and Contact Contributions to Continuous Shear Thickening in Colloidal Suspensions*, Phys. Rev. Lett. 115 (2015) 228304.
DOI: https://doi.org/10.1103/PhysRevLett.115.228304 *[151 citations, WoK]*

[***R6***] H. Jia, A. Wildes and **S. Titmuss**, *Structure of pH-Responsive Polymer Brushes Grown at the Gold-Water Interface: Dependence on Grafting Density and Temperature*, Macromolecules, 45 (2012) 305-312. DOI: https://doi.org/10.1021/ma201839y *[46 citations, WoK]*

4. Details of the impact

High-solid-content particulate suspensions are ubiquitous across diverse sectors of industrial practice, including food, paints and coatings, energy materials, concrete, and ceramics. The flow of these suspensions, especially when the particles are non-Brownian (say, > 10 μm), is capricious and sensitive to environmental conditions, suppliers, and small changes in processing. The progress in understanding suspension flow demonstrated by Prof. Poon's group has given these industries a unified framework to understand how they handle these materials.

Separate, collaborative projects between Poon's group and *Mars*, *Johnson Matthey, Corning Inc.* and *Schlumberger* have enabled these partners to integrate new advances in the physics of suspensions into their industrial practice, and thus reduce costs and improve sustainability. The Edinburgh-*Mars* and Edinburgh-*Johnson Matthey* projects were initially spurred by the characterization techniques demonstrated in [***R1–R3***, ***R6***], while the results of [***R4***, ***R5***] catalysed the Edinburgh–*Corning* project and underpins the Edinburgh-*Schlumberger* project.

The new rheo-imaging technique [***R2***] was commercialised through *TA Instruments*. The group developed a prototype that was licensed to the company in 2012 (Figure 1). The resulting instrument (a "Modular Microscope Accessory") is designed for the company's Discovery Hybrid Rheometer and launched commercially in June 2015 [***I1a***]. [text removed for publication]

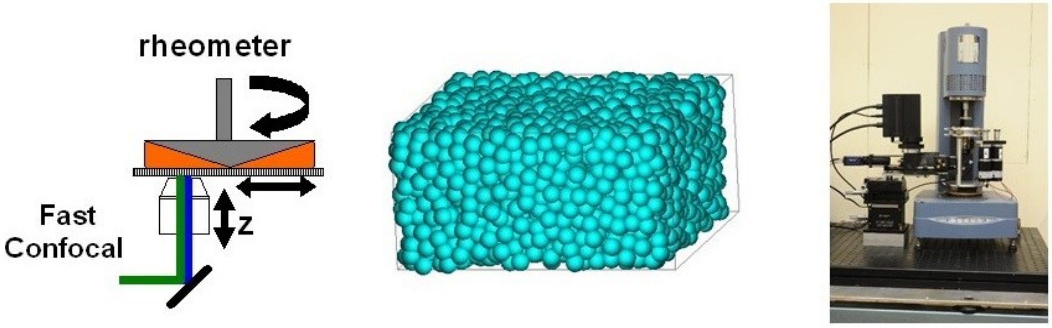

Figure 1: (*Left*) A schematic diagram of the 'rheoimaing' set up. (*Middle*) A 3D reconstruction of particle coordinates during flow of a dense suspension through a channel. (*Right*) The epifluorescent rheoimaging prototype, built around an AR2000 rheometer, licensed to TA Instruments.

The collaboration with *Mars* focused on conching, a critical energy-intensive and time-consuming step in chocolate production. [text removed for publication]

To produce chocolate, solid particulates (sugar, cocoa) must be incorporated into liquid cocoa butter. This process, 'conching', requires sustained mechanical mixing, without which the chocolate remains grainy and un-appetizing (Figure 2). The long mixing time makes conching a huge energy burden, requiring (on average) 100,000Wh/ton of chocolate, which is more than half of the energy *Mars* uses to produce chocolate. Prior to the UoE collaboration, *Mars* scientists based their process control and development decisions on a widely-accepted, text-book picture of conching that understood the process as one of 'spreading cocoa butter on sugar grains'. They further hypothesised that conching could also break apart sugar grains.

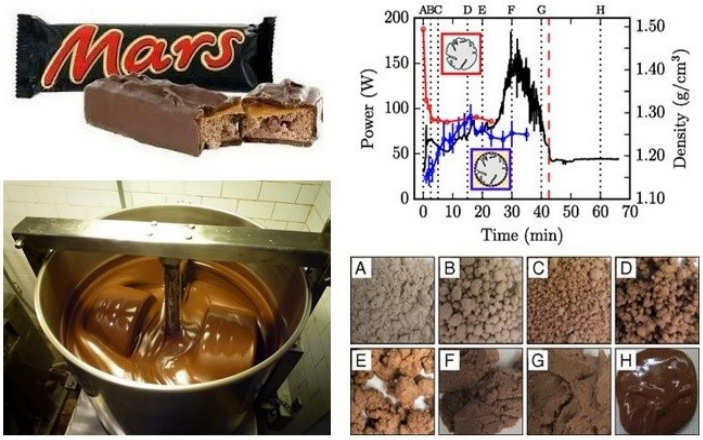

Figure 2: (*Top left*) The familiar sight of a Mars bar. (*Bottom left*) Conching equipment used to make chocolate (Credit: Andrew Pearce, Flickr). (*Top and bottom right*) The power consumption and appearance of chocolate during the conching process (reproduced here from [***I2***] under a CC BY-NC-ND 4.0 license).

Rheoimaging using the instrument developed at UoE [***R2***] first showed that there was little or no grain breakage. Subsequent rheological investigation of molten chocolate, interpreted in the light of parallel work using well-characterised, synthetic particle suspensions [***R4***, ***R5***], completely overturned the text-book picture, and revealed that conching produced smooth-flowing chocolate by shifting the frictional jamming transition of a mixture of sugar grains in oil by breaking powder aggregates, and lowering the viscosity of the final mixture by reducing inter-particle friction using surfactants [***I2***].

The conclusion in [***I2***] that frictional interaction between sugar grains dominated conching phenomenology meant that surface details mattered. Dr Titmuss therefore developed a planar sucrose substrate to investigate how surfactants modified such interactions [***I3***]. [text removed for publication].

[text removed for publication]

The impact of the dense suspension work at UoE extends beyond chocolate manufacturing. Scientists at *Johnson Matthey* first contacted Prof Poon after they learnt of UoE imaging rheology work [***R2***, ***R3***]. This led to funding for a PhD student working on model systems. The resulting papers [***R4***, ***R5***] helped bring about a paradigm change in non-Brownian suspension rheology, showing the dominant role of frictional contacts. The value of these insights and the skill set used in their acquisition is demonstrated by *Johnson Matthey* hiring Dr Elena Banco, our main postdoctoral researcher engaged in working on chocolate conching with *Mars*, to be a senior scientist working on the extrusion of dense ceramic suspensions [***I5***].

[text removed for publication]

Schlumberger, an oilfield services provider, is a project partner with Prof Poon in an EPSRC Future Formulations grant (EP/N025318/1) on 'Predictive formulation of high-solid-content complex dispersions'. The relevance of this work relates to two of their main products/services: drilling fluids and well cementing, both of which require pumping suspension-based products into and out of wells many kilometres deep. Clogging or unsteady flow degrades performance and impacts wellbore stability; it is again critical to predict and avoid jamming. The company notes that UoE research has brought "*an enhanced awareness of the importance of friction and jamming in suspension flow*" [***I7***]. [text removed for publication].

Further evidence of the reach of UoE suspension rheology research comes from two other sources. First, *AkzoNobel*, a global chemicals company, funded a SOFI CDT student, James Richards, who published a paper elucidating the mechanisms whereby various surfactants manufactured by the company changes the rheology of particulate suspensions [***I8***]. Secondly, *Toyota* Central R&D Labs Inc. (approximately 1000 employees) is funding an employee, Soichiro Makino [***I9***], to do a PhD with Prof Poon on dense suspension flow because they believe that the work in UoE is relevant to the manufacture of battery electrodes. The company typically funds just one overseas research scholarship for PhD work per year, and has the final say in the institution and the project.

5. Sources to corroborate the impact (indicative maximum of 10 references)

[***I1***] a) *TA Instruments* news article announcing module launch in June 2015 ("New Flow Microscopy Measurement System from TA Instruments"): https://web.archive.org/web/20160111040517/https:/www.tainstruments.com/lpage.aspx?id=7&n=4&siteid=11 and b) UoE license fees

[***I2***] Joint Edinburgh-Mars publication on the conching of chocolate. E. Blanco et al., *Conching chocolate is a prototypical transition from frictionally jammed solid to flowable suspension with maximal solid content*, Proc. Natl. Acad. Sci. (USA) 21 (2019) 10303-10308. DOI: https://dx.doi.org/10.1073/pnas.1901858116

[***I3***] Joint Edinburgh-Mars publication investigating interfaces in molten chocolate. Manasi et al., *Planar sucrose substrates f*or investigating interfaces found in molten chocolate, Food Struct. 22 (2019) 100128. DOI: https://dx.doi.org/10.1016/j.foostr.2019.100128

[***I4***] Support letter from Senior Fellow Chocolate at *Mars Wrigley Confectionery* (confidential)

[***I5***] Dr Blanco's LinkedIn page: https://www.linkedin.com/in/elena-blanco-8bb44a29/?originalSubdomain=uk

[***I6***] Support letter from Senior Vice President at *Corning Inc*. (confidential)

[***I7***] Support letter from Centre Manger at *Schlumberger* (confidential)

[***I8***] J. A. Richards, R. O'Neill and W. C. K. Poon, *Turning a yield-stress calcite suspension into a shear-thickening one by tuning inter-particle friction*, Rheol. Acta. (2020) DOI: https://doi.org/10.1007/s00397-020-01247-z

[***I9***] Research gate page: https://www.researchgate.net/profile/Soichiro_Makino