Beyond beer and bubble baths

Dr Sven Behrens explains the science governing emulsions and foams, and the importance of these liquid mixtures for a variety of consumer products and industrial applications

Can you describe the focus of your research?

Our research aims at understanding and manipulating the forces that act on nanometre- to micron-sized objects suspended in liquids or adsorbed to liquid interfaces, with the goal of controlling assembly or self-assembly processes.

One major focus of our work is on particle-stabilised emulsions and foams, whose applications range from oil recovery to skin care, cosmetics, and the encapsulation and controlled release of drugs, crop protection agents or other active cargoes.

A second focus concerns the electric charging and field-induced assembly of solid particles and surfactant aggregates in nonpolar oils; a poorly understood phenomenon which, nonetheless, plays an important role in many industrial applications and is crucial for the functioning of liquid electrostatic toners and the electrophoretic displays of eBook readers.

A third facet deals with protein stability. This work is relevant for the formulation of therapeutic proteins and for a better understanding of 'prions'; infectious aggregates of misfolded proteins that have been implicated in neurodegenerative diseases like Alzheimer's and Creutzfeldt-Jakob disease.

Why is understanding emulsification processes important for industrial applications?

Emulsions play a huge role in industry; sometimes as raw materials (like milk for dairy

Liquid interfaces

Research from the Behrens Research Group at the **Georgia Institute of Technology** is revealing important insights about the interactions between particles and liquids to improve the stability of emulsions and foams

EMULSIONS ARE MIXTURES of two immiscible liquids, such as oil and water, comprising small, finely dispersed droplets of one liquid inside the other. This is an inherently unstable arrangement, and, similar to salad dressing that has been left to stand, emulsions break down and the two liquids eventually separate.

Despite their instability, emulsions and liquid foams have important applications in industrial processes, household products and biotechnology, to name a few. Associate Professor Dr Sven Behrens, and the members of his research team at the Georgia Institute of Technology in the US, focus their work on understanding the physical and chemical conditions that alter the properties of the liquid interfaces of emulsions and foams in significant and controllable ways in order to improve their application properties.

PICKERING EMULSIONS 101

The key to stabilising an emulsion is to hinder droplet coalescence. When the tiny, suspended droplets come into contact with one another they merge (coalesce) and continued aggregation of droplets results in the eventual separation of the two liquids to their natural, unmixed form. Stability is often achieved using emulsifiers or surfactants with both hydrophilic (water-loving) and hydrophobic (water-repelling) components that bind to the droplet interface to reduce the surface tension and serve as a buffer against coalescence.

An alternative technique to enhance the stability of emulsions and foams is to utilise colloidal particles, ie. nano- or microparticles dispersed within a continuous phase, which have unique 'wetting' properties that dictate their ability to adhere to a liquid. Particle-stabilised mixtures products), sometimes as the final product (like mayonnaise and some cosmetic, pharmaceutical or agrochemical formulations), and often as an auxiliary medium or intermediate stage (like displacing fluids for enhanced oil recovery, media for solute separation processes, or for interfacial reactions).

Depending on the application, it can be crucial to control the droplet size; total interfacial area; droplet coverage by some adsorbing species; or the stability against droplet coalescence, aggregation, creaming or sedimentation; and ripening (ie. the growth of larger droplets at the expense of smaller ones via exchange of dissolved molecules through the continuous phase). Understanding details of the emulsification process is essential to achieve the required level of control.

Can you provide an insight into particle-stabilised emulsions and foams, or 'Pickering emulsions'?

Pickering emulsions and Pickering foams are stabilised by colloidal particles adsorbed to the emulsion droplets or foam bubbles rather than by amphiphilic molecules such as surfactants or block copolymers. Pickering emulsions are appreciated for superior long-term stability, insensitivity to dilution and a lower tendency of causing skin irritations compared with surfactant-stabilised emulsions. Moreover, particle-decorated droplets are used as precursors for liquid-core capsules.

What are the key interactions governing colloidal and interfacial phenomena?

Colloidal and interfacial phenomena can be influenced by a wide variety of physicochemical interactions, including electrostatic forces; Lifshitz-van der Waals forces; and acid/base interactions, steric forces and effective interactions derived from these forces – such as interfacial tension forces, capillary forces or depletion interactions. In some systems, gravity or interactions with external electric or magnetic fields are important. Material properties often depend on a subtle balance of several types of interaction, and external stimuli, such as changes in temperature, solution pH or salinity, can alter this balance, triggering major transitions in macroscopic behaviour.

As for the interaction of particles with liquid interfaces relevant for Pickering emulsions and foams, simple theoretical descriptions often consider interfacial tension forces only, yet we know that effects of surface charge and particle roughness can also be important.

Which direction do you envisage interface chemistry research taking in the near future?

Our technical ability to chemically modify and pattern solid surfaces has improved tremendously in the recent past, but I believe that the practical work of exploiting this ability in the fabrication of new devices, materials and machineries is still in its infancy.

Self-assembly processes and stimulus-responsive materials will be explored further, and energy-dissipating materials (both biological and bioinspired) will likely attract much more attention and raise interest in processes far from equilibrium. Interfacing living systems with non-biological devices and machinery is bound to become increasingly important and to bring about new challenges for interfacial science. At the same time, classical questions surrounding the stability of complex fluids, phase behaviour and structure formation are not likely to lose their relevance any time soon.

Future foam

Behrens and colleagues have discovered an entirely new class of liquid foam, called 'capillary foams', that share properties of Pickering emulsions and Pickering foams. By mixing both air bubbles and oil into a water-based particle dispersion, one can form a unique foam structure with fascinating material properties. In contrast to the surfactant-stabilised foams familiar in beer or bubble baths, the resulting foams can be stable for months or years.

are called 'Pickering emulsions' or 'Pickering foams', and operate as follows: colloidal particles adsorb to a droplet surface and, as droplets fuse together, the particles rearrange in a more compact manner on a reduced surface area. The process continues until droplets are fully coated with particles such that further coalescence is physically prevented. This is how Pickering emulsions impart their superior stability: "Particles with appropriate wettability can lower the total interfacial free energy so strongly that adsorption becomes irreversible," Behrens explains.

CHARGED PARTICLES

Although Pickering emulsions have been known for almost a century, their properties are still not well understood. Scientists are not yet able to reliably predict the formation of a stable emulsion, even when all ingredients are well known.

To better control emulsion properties, the Behrens group studies how physical and chemical interactions involving particles and liquid interfaces influence droplet formation and stability. For example, in order for a Pickering emulsion to form, particles must successfully adsorb to the oil-water droplet interface. Just as two matching magnetic poles will repel each other, equivalent surface charges on particles and the oil-water interface create a similar repulsion that can prevent adsorption and emulsion formation.

One might expect that particles bearing an opposite charge to the droplet interface would reliably adsorb due to attractive forces, but Behrens and colleagues found that particles with any form of strong surface charge (whether positive or negative) could prevent emulsion formation: "We could explain it as a result of the so called 'image charge' interaction between the particles and the oil-water interface; a polarisation effect known to occur in systems with electric charges near dielectric discontinuities, which has been largely ignored by the research community interested in Pickering emulsions," Behrens emphasises. The key finding is that the amount of particle surface charge can dictate whether and how an emulsion forms, and its associated stability.

ROUGH AROUND THE EDGES

In addition to electrostatic particle charges, surface 'roughness' can also influence particle adsorption behaviour at liquid interfaces. In order to isolate the specific role of particle roughness on emulsion stability, Behrens and his team

Student Yi Zhang with a dried capillary foam.

INTELLIGENCE

BEHRENS RESEARCH GROUP

OBJECTIVE

To understand and manipulate the forces that act on particles suspended in liquids or adsorbed to liquid interfaces in order to control assembly or self-assembly processes.

KEY COLLABORATORS

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FUNDING

US National Science Foundation (NSF) awards #CBET-1134398 and CBET-1160138 and through NSF Industry/University Cooperative Research Centers (I/UCRC) Program Center for Pharmaceutical Development (CPD) Grant 0969003

BASF Corporation

Georgia Tech's Renewable Bioproducts Institute

Bayer-Schering

The Camille and Henry Dreyfus Foundation

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DR SVEN BEHRENS is Associate Professor in the School of Chemical & Biomolecular Engineering at the Georgia Institute of Technology. He received his Bachelor's degree in Physics from the University of Tübingen, Germany, and subsequently his Physics Diploma in 1995 from the University of Göttingen. In 1999, he earned his PhD in Natural Sciences from the Swiss Federal Institute of Technology (ETH) in Zürich. After two years of postdoctoral research at the University of Chicago and five years of industrial research in the polymer research division of BASF, Germany, he assumed his current faculty position at the Georgia Institute of Technology in 2007.

Georgia Institute of Technology

have developed a novel technique to generate systematic alterations in surface texture without simultaneously impacting surface chemistry. They accomplished this by coating colloidal particles with smaller nanoparticles of a special copolymer to create a studded, 'rough' surface. These nanoparticle-covered surfaces were then exposed to acetone to partially dissolve and 'smoothen' the bumpy coating. The acetone concentration and exposure time allowed the remaining surface roughness to be controlled.

Particles of varying roughness were tested as stabilisers for decane/water emulsions. Increasing roughness showed a clear corresponding increase in emulsion stability, although the shape of surface features was also critical: "Rough surfaces with 'overhanging' features and 're-entrant' spaces tend to entrap some of the liquid contacting the surface first, which weakens particle binding to the emulsion droplets and hurts emulsion stability," Behrens postulates. "Less 'porous' types of surfaces, by contrast, promote emulsion stability, possibly by 'pinning' the liquid interface."

NEW FOAM ON THE BLOCK

Foams, which trap pockets of gas in a solid or liquid, present similar challenges with respect to stability. Behrens, in collaboration with Dr J Carson Meredith, also at the Georgia Institute of Technology, discovered a new class of liquid foam by frothing water-based colloidal suspensions as in air/water/particle Pickering foams, but with a small amount of oil added. They found that the colloidal particles can facilitate the formation of a thin oil film around the gas bubbles that helps shield them against coalescence. Further, excess particles in the liquid suspension not adsorbed to bubble surfaces connect via oil bridges into particle networks that anchor the bubbles, thus contributing to foam stability.

Behrens and Meredith have termed this new type of foam a 'capillary foam' due to the capillary force that binds oil-bridged particles together in a network. "This operates much the same way that grains of wet sand in sand castles are held together by small water bridges," Behrens explains. Without the addition of oil, the particles do not have the proper physical characteristics to facilitate network formation.

Oil is a convenient, versatile and economic solution to improving Pickering foams, which often require time-consuming particle treatment procedures, as Behrens elaborates: "Capillary foams are extraordinarily stable and can be prepared using particles that do not normally stabilise foams. We expect they will present advantages over the foams currently used in oil recovery, and find many additional applications".

FROM LABORATORY TO LIFE

Behrens' work has demonstrated that simple alterations to particle shape and surface chemistry can command dramatic differences in Pickering emulsion dynamics. All the above described insights can lead to tangible application benefits in food processing, personal care products, pharmaceuticals and so on. For example, particle-coated droplets modulated by environmental stimuli in predictable ways can be engineered for novel drug delivery mechanisms or other controlled release functions. Additionally, the newly discovered capillary foams can be used as precursors for porous solids whose potential applications include thermal insulation, shock absorption and scaffolds for tissue engineering or other biomedical applications.

The body of work produced by the Behrens group has helped resolve some important and previously unanswered questions relating to emulsion behaviour. Looking ahead, a continued research focus on particles adsorbed to liquid interfaces will unlock new opportunities for emulsion- and foam-based technologies.

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