

Surprises in the Self-Assembly of Hard Spheres in Spherical Confinement and Long-Ranged Repulsive Rods in an Electric Field

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In research aimed at making colloidal crystalline supraparticles by having monodisperse spherical nanoparticles crystallize in slowly evaporating oil emulsion droplets we discovered icosahedral symmetry in the resulting dried colloidal crystals [1]. Subsequent work with different kind of nanoparticles and a similar study using micron-sized silica colloids all confirmed that crystallization of hard spheres in a spherical confinement results in crystals with an icosahedral symmetry, up until roughly 100.000 particles. Icosahedral packings are known not to be able to regularly pack in 3D space. Subsequent computer simulations confirmed the experimental observations and were able to also show that indeed for roughly this number of particles (or less) the free energy of icosahedral packings is lower than that of e.g. an FCC crystal in a spherical confinement. Moreover, the simulations also provide clues to the actual crystallization pathway/mechanism [1].

Micron-sized and fluorescently labeled rod-like silica colloids [2] were recently found by us to form so-called rotator phases or plastic crystals if the Debye screening length was made sufficiently large (~particle length) [3]. In a plastic crystal positions are long-ranged ordered on a 3D lattice, while rotations are still free and therefore orientational order is short-ranged or even absent. When such systems are confined between two charged flat walls we find alternating 3D ordinary and plastic crystal phases as function of the plate-plate separation [4]. This surprising sequence was found to originate from subtle differences in the charge repulsions between the rods themselves and a rod with the wall. Moreover, at higher densities and in bulk, plastic glasses are found that can be reversibly switched back and forth between 3D crystal phases by the application of an external electric field.

- 1) [Entropy-driven formation of large icosahedral colloidal clusters by spherical confinement](#), B. de Nijs, S. Dussi, F. Smalenburg, J.D. Meeldijk, D.J. Groenendijk, L. Fillion, A. Imhof, M. Dijkstra and A. van Blaaderen, *Nature Materials* **14**, 56-60 (2015).
- 2) [Synthesis of monodisperse, rodlike silica colloids with tunable aspect ratio](#), A. Kuijk, A. van Blaaderen, and A. Imhof, *JACS* **133**, 2346-2349 (2011);
[Colloidal Silica Rods: Material Properties and Fluorescent Labeling](#), A. Kuijk, A. Imhof, M. H. W. Verkuijlen, T. H. Besseling, E. R. H. van Eck, and A. van Blaaderen, *Particle & Particles Systems Characterization* **31**, 706-713 (2014)
- 3) [Switching plastic crystals of colloidal rods with electric fields](#), B. Liu, T. H. Besseling, M. Hermes, A. F. Demirörs, A. Imhof, and A. van Blaaderen, *Nature Communications* **5**: 3092 (2014).
- 4) Confinement Induced Plastic Crystal-to-Crystal Transitions in Rod-Like Particles, with Long-Ranged Repulsion, Bing Liu, Thijs H. Besseling, Alfons van Blaaderen, and Arnout Imhof, *PRL*, accepted (2015).

From physics of adhesion to organ repair

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Adhesives and glues are made of polymers. We introduce a novel concept of adhesion by particle solutions. We will demonstrate that to make a strong junction between two surfaces it suffices to spread a drop of a particle solution on one surface and press the other into a contact for few seconds. We will show the efficiency of the method, which we call nanobridging, for natural and synthetic hydrogels and various sorts of particles such as silica or iron oxide. We then extend the concept of nanobridging to biological tissues and demonstrate that the method can be used *in vivo* to close wounds even for soft organs such as liver and in hemorrhagic conditions. We will also show how particles can be used for hemostasis after organ resection. The approach proved easy to apply, rapid and efficient in situations when conventional methods of suturing or stapling are traumatic or fail

Surface Properties of Gas Bubbles in Liquids Studied with a New Laser Interferometric Technique

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A new interferometric technique to measure properties of the gas-liquid interface of a bubble in a liquid is described. The bubble remains still and rests by buoyancy against an electrode. A second electrode is placed below the bubble. In the presence of an electric charge at the interface, an alternative electric field applies an alternating force to the bubble in the vertical direction. The deformation from the equilibrium shape (practically spherical for small bubbles) is detected by the change of the optical path inside the bubble of a laser beam that traverses it in the horizontal direction. High sensitivity is reached by monitoring the fringes due to the interference of the light back-reflected at the two surfaces. Capillary waves are excited at the interface in a set of frequency modes which are independent at small amplitudes. The quadrupolar mode, easily excitable by the alternating field, has a resonance behavior with an amplitude dictated by the applied force, a width which depends on the energy dissipation at the interface and a resonance frequency connected to the bubble geometry and the restoring forces (surface tension) at the interface. Resonances are extremely sensitive to the presence of surfactants. Some new findings will be presented, as the divergence of the energy dissipation at the interface for a bubble immersed in a Sodium Dodecyl Sulfate (SDS) solution at a concentration about two hundreds times below the CMC or the slow down of desorption of SDS molecules from the bubble interface when the surrounding solution is washed with pure water. The technique has been also applied to measure the net surface charge of a bubble in pure water.

Wither colloid science? Imagining the future

Barry Ninham (Overbeek Gold Medal 2014)

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An evolution tantamount to a revolution took place in colloid science and physical chemistry over the last 50 years since DLVO theory took center stage. Three connected advances occurred. The first is in the quantification of Hofmeister (specific ion) effects. These, due to dispersion forces, had been completely neglected in classical theories of electrolytes and molecular forces. The omission rendered theory impotent for prediction.

A second advance recognised a key role for hyperbolic (non Euclidean, bicontinuous) geometries in the self assembly of lipids, surfactants and proteins; and in microstructure generally.

These advances have revolutionised the subject. Our whole intuition has been turned upside down.

The third has to do with the startling recognition that dissolved atmospheric gas, at a molecular level and in micro and macro bubbles, has qualitative effects which we have ignored.

Also ion specific, they are ubiquitous and range over bubble- bubble interactions and enzyme activities to emulsion stability – “hydrophobic interactions” apparently disappear when gas is removed. Gas columns can be exploited for very effective desalination, water treatment and other unanticipated opportunities for novel chemistry.

These matters are not understood. But the phenomena are real and provide rich fields open for application

The weak intersection of physical chemistry with biology and chemical engineering can be traced to flaws in standard theories due to these neglected effects. They affect intuition and interpretation of measurements qualitatively. Of these, problems with pH and buffers and microstructure are just a beginning.

These challenges are encouraging. The consequent removal of conceptual locks provides an open road for future research.

Microfluidics: a tool to design and study new soft matter materials

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In this talk I will describe how microfluidics can be used to both create new soft matter materials, and also study their behavior in flow or fields. In the first part of my talk, I will introduce a new way of interfacing lithography and microfluidics to “optically stamp” complex and functional microparticles. This technique takes advantage of the unique ability to finely structure flows and chemical gradients in microfluidic devices. Next, I will describe a few demonstrative examples of uses of the complex particles that range from anti-counterfeiting to artificial cells to biosensing. All of these examples require the large-scale production of non-spherical and chemically complex microparticles. Lastly, I will describe some recent efforts to arrange particles in well-defined patterns on substrates using novel flow-assembly processes.

Surfactants at the Design Limit

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For common surfactants in aqueous solution the concepts of hydrophilicity and hydrophobicity are well established. Textbooks explain the properties of dilute aqueous bulk surfactant phases in terms of the hydrophobic effect and the Israelachvili-Ninham packing parameter. However, these approaches do not apply so well to surfactant interfacial properties, nor to solvents other than water.

The talk will explore the generality of solvophilicity and solvophobicity, as well as the importance of surfactant chemical structure and architecture on interfacial properties. Using this insight it is possible to design and synthesize effective surfactants for non-aqueous solvents, including supercritical CO₂.

Surfactants at the Design Limit

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