

# Active Colloids: Phase Separation, Clustering, and Directed Assembly

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Active colloids typically comprise Janus particles with two hemispheres of different surface chemistry, e.g. catalytic and inert. When placed in a bath of fuel and/or a light field, they have an inherent self-propulsion mechanism that breaks the time-reversal symmetry of microscopic dynamics, continually generating entropy at a local scale. This means that, even in steady-state conditions, the usual laws of equilibrium statistical mechanics do not apply. For example, the random motion of active colloids (whose propulsion directions rotate by angular Brownian motion) can be rectified into a steady current by placing them in an environment of asymmetric obstacles. I will discuss proof-of-principle computer simulations allowing similar effects to be achieved using light-fields alone, through an optical modulation that causes the propulsive speed to depend on position. In practice, this speed also depends on local particle density due to collisional slow-down of the colloids. This can lead to liquid-gas type phase separation among purely repulsive particles. General theories of phase separation without time-reversal symmetry predict various other new phenomena including the arrest of phase separation in a state of dynamically exchanging large clusters. These theories are complemented in some cases by more specific mechanistic models, for example allowing for cross-terms in the propulsion mechanism whereby the chemical gradient created by one particle causes not only itself, but also its neighbours, to move. I will try to give an overview of recent theoretical developments in this field at a relatively non-technical level.

# “Nanoengineered drug delivery systems for helping drugs to reach their targets”

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Our group, being committed with the translation of ideas from the university through novel pharmaceutical nanotechnology, has designed novel nanostructured materials intended to transport drugs and antigens across biological barriers and to deliver them to the target tissue. During my presentation I would like to overview the different applications of the nanotechnologies we have designed until now, with special emphasis in the area of targeted oncologicals and cancer immunotherapy. Overall, our experience in the field of nanomedicine has greatly benefited from integrative approaches adopted by specifically designed consortia. Hopefully, the results of these cooperative efforts will help to accelerate the progress on the rational design of nanomedicines.

More information about these projects can be found at:

<http://www.usc.es/grupos/mjalonsolab/>

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# Interfacial water: from hydrophobic hydration to osteoarthritis

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Hydration lubrication<sup>1-3</sup> has emerged as a leading paradigm for understanding frictional dissipation in aqueous, especially biological environments. Here I describe recent advances in understanding the role of interfacial water in modulating forces between sliding surfaces, ranging from sliding friction at highly-hydrophobic surfaces<sup>4</sup> to the supra-molecular synergy which may underlie the remarkable lubrication of articular cartilage<sup>5</sup>. The latter in particular holds the key to new insights into the origins of osteoarthritis, the most widespread joint disease.

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# Frictional Drag Reduction in Turbulent Flows Using Passive and Active Super-Hydrophobic Surfaces

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Many different structured surfaces with a wide range of surface chemistries and topographies have been investigated for controlling the wetting (or nonwetting) properties of a fluid/solid interface. Experimental advances in nanofabrication have led to the ability to achieve unprecedented control over the micro- and nano-texture of a substrate and this can result in almost perfect ultrahydrophobicity, at least when probed by the ubiquitous static or dynamically-impacting droplets. An important and ongoing challenge, however, remains developing coatings that are sufficiently and robustly non-wetting or “aerophilic” that they can support an air film or ‘plastron’ when fully immersed in a turbulent liquid flow and thus reduce the frictional drag on the surface. In this talk we explore a number of distinct ways of modifying the dynamic boundary conditions at a three-phase boundary in order to reduce the frictional drag using a bespoke Taylor-Couette fixture that can be mounted onto a commercial controlled stress rheometer. We first show that spray-on superhydrophobic surface treatments can be applied to the rotating inner cylinder that stabilize the resulting plastron in a re-entrant surface microtexture. By carefully controlling the characteristic roughness scales and asperity sizes to match the inherent turbulent lengths we can modify the mixed slip/no slip boundary condition in the viscous boundary layer. This results in frictional drag reductions of up to 20% at Reynolds numbers approaching  $10^5$  and the corresponding interfacial slip lengths can be directly extracted from torque measurements ~~through the use of Prandtl-von Kármán coordinates~~. - Experiments and simulations both show that at sufficiently high Reynolds numbers these passive plastrons are disrupted by intense turbulent pressure fluctuations; however, we also show that the drag reducing properties can be stabilized and further enhanced through the use of a superhydrophobic Leidenfrost surface (which actively regenerates the plastron through electrical heating) and this can further reduce the frictional drag, by up to 80%. Alternate approaches to reinflating collapsed plastrons through surface catalytic means are also investigated and finally we demonstrate how multi-scale structures that combine microscopic streamwise riblets, nanotexturing and liquid impregnation can also be designed to produce multifunctional drag-reducing and non-fouling surfaces.

# Modular design of nanocapsule systems

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Polymeric nanocapsules offer the versatility to cover a wide range of mesoscopic properties for sophisticated applications. By means of the miniemulsion process, we can design custom-made nanocapsule systems for different purposes. The encapsulation and release of a great variety of payloads, ranging from hydrophobic to hydrophilic substances has been successfully achieved in a highly controlled manner and with an unmatched high encapsulation efficiency.

The preparation of nanocontainers with a hydrophilic core from water-in-oil emulsions and their subsequent transfer to aqueous medium is of special importance since it enables the efficient encapsulation of hydrophilic payloads in large quantities. However, major challenges are associated with their synthesis including low colloidal stability, leakage of encapsulated payloads due to osmotic pressure, and a demanding transfer of the nanocontainers from apolar to aqueous media. We present a general modular approach for the synthesis of polymer nanocontainers that are colloidally stable, not sensitive to osmotic pressure, and responsive to environmental stimuli that trigger release of the nanocontainer contents. Additionally, the nanocontainers can selectively deliver one or two different payloads. Our modular approach uniquely enables the synthesis of nanocontainers for applications in which aqueous environments are desired or inevitable. It will be also shown that the triplet-triplet annihilation upconversion can be performed in water environment via encapsulation of the upconversion dyes in polymeric nanocapsules. Photon energy upconversion is an assembly of inter- and intramolecular processes in which the low energy of multiple photons is harnessed and recombined into a single photon of higher energy. The challenge is to build effective passive and active protection mechanisms against quenching by molecular oxygen and the subsequent production of highly-reactive singlet oxygen which is imperative for long lifetime and efficient upconversion processes in ambient environments.

# Directed Self-Assembly of Plasmonic Colloids

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The assembly of nanoparticle building blocks is a pre-requisite for the amplification of the properties of the components and/or the generation of new features unique to the ensemble. Usually, nanoparticles employed for these assemblies are spherical and lack a geometrical preference toward directional self-assembly, thus limiting their potential applications. In contrast, controlled self-assembly of non-spherical nanoparticles, such as gold nanorods, enables these arrays to form defined 1D, 2D or 3D structures with a vectorial dependence of the desired properties. We show in this communication several examples where the morphology of gold nanoparticles can be modulated by means of colloid chemistry methods, and in turn exploited to direct the assembly of such nanoparticles into a variety of nanostructures with interesting properties.

## Literature:

References should be placed immediately below end of main text according to citation below:

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# Manipulating and modelling colloids in order to improve knowledge-based greener processes in extraction, separation and recycling

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Developing new experimental techniques aimed to meso- or colloidal scale (recently renamed « nano ») , as well as taking into account not only chemical bindings but all derivatives of the free energy as well as elastic energy when relevant is the key towards new processes at the source of circular economy, based on recycling « wastes ».

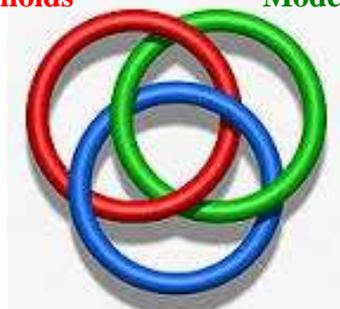
Working since 1979 on “organized molecular matter at nano-scale” in Saclay, later in Canberra and Potsdam and since 2005 in the Institute for separation chemistry I founded in Marcoule, I had the opportunity to participate in several instrumental developments allowing better understanding of complex fluids used in processes: among those USAXS-SAXS-WAXS with high dynamic range associated to measurement of the osmotic pressures over several decades to more recently ultra-centrifugation in complex fluids beyond the Perrin-Svedberg usage in collaboration with Konstanz and Regensburg as well as the detection of nanometric surface oscillation in collaboration with Milano.

Predictive modelling always included meso-scale colloidal terms as an integration over the surface to the macroscopic mechanical elasticity terms as well as the sum of chemical binding. This allowed to explain the first equations of states of colloidal crystals , clay-polymer mixtures, mixed lipids and ionic amphiphiles decorated by counter-ions governed by Hofmeister ion-specific effects.

Linking experimental methods, multi-scale modelling and improved processes based on knowledge processes as Borromean rings -all relevant to ECIS central preoccupations- will be illustrated by a random biased walk from high resolution studies of surfactant bent film, and applications in the discovery and usage of rigid as well as ultra-flexible emulsions, crystalline catanionics with local order and the giant colloids associated as well as synergy allowing better formulations for extraction/desextraction. Developing experimental techniques associated to modelling interactions “beyond the first neighbour” are in this way at the basis of efficient recycling as well as separation and purification, even improving old but unexplained processes such as “Eau de Cologne” or “Bligh and Dyer” lipid extraction routinely used in biochemistry.

**Characterization of colloids**

**Modelling the free energy at meso-scale**



**Better processes based on colloids**

# Polymerisation-induced self-assembly

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We have recently demonstrated that polymerisation-induced self-assembly (PISA) enables the efficient synthesis of a range of block copolymer nano-objects in either water, ethanol or *n*-alkanes. The basic design rules for PISA are generic: a soluble precursor 'A' block is chain-extended using a second monomer that forms an insoluble 'B' block in the chosen solvent. As this second 'B' block grows in the monomer/solvent reaction mixture, micellar nucleation occurs at some critical chain length, leading to the formation of sterically-stabilized nanoparticles. Depending on the relative volume fractions of the 'A' and 'B' blocks, the copolymer morphology can be either spheres, worms or vesicles. In collaboration with a range of industrial partners, various applications for this platform technology are being explored at U. Sheffield. Both aqueous and non-aqueous PISA formulations will be discussed in this talk. We show that small-angle X-ray scattering (SAXS) is a powerful characterization technique that (i) sheds light on the evolution in copolymer morphology during PISA and (ii) can be used to study thermally-induced morphological transitions. In particular, we report the PISA synthesis of a new type of amphiphilic diblock copolymer that can switch reversibly from spheres to worms to vesicles in aqueous solution simply by adjusting the solution temperature – such self-assembly behaviour is unprecedented for a single diblock composition.