Rational and accidental design of patchy colloids assembly into complex ordered structures

Eva G Noya[1], Enrique Lomba[1], Daniel Tracey[2], Jonathan Doye[2], Francesco Sciortino[3]
[1]Instituto de Química-Física Rocasolano, CSIC, Calle Serrano 119, Madrid, Spain
[2]Chemistry Department, University of Oxford, UK
[3] University of Rome, Italy

Advances in the synthesis of nanoparticles with ever increasing control over the particles interactions have led material scientists to envision a new class of smart, responsive materials which assemble spontaneously from appropriately designed nanoparticles [1]. Thus understanding the effect of the particles shape and interactions on their assembly behaviour is not only an interesting fundamental question, but also one that can have important practical implications. In spite of much effort, designing models that assemble into a desired ordered structure is still challenging, both due to the appearance of competing structures and the tendency of these systems to get stack in kinetic bottlenecks [2]. In this contribution, we will analyse a few relatively simple cases to exemplify these difficulties.

Firstly, we will present two cases in which the assembled structure from simple patchy models challenges our intuition. In the first of these examples we examine the phase behaviour of a simple model of three-patch particles under planar confinement. One would expect that this system forms a honey-comb lattice at low temperature and pressure, but, instead, if the patches are narrow enough, the system organizes into an exotic solid phase consisting of a honey-comb lattice whose voids can be continuously filled without crossing a phase transition [3]. In the second example, we consider the assembly of tetrahedral patchy particles. Our simulations predict that clathrate structures are assembled when the patches are narrower than a given threshold size, a result that again is not intutively obvious[5].

Secondly, we will introduce a simple scheme to design model systems that assemble into complex ordered structures, such as, e.g, clathrate crystals. Our results show that incorporation of specificity and/or torsional contributions to the interactions can be exploited both to design models for which the target crystal is the global free energy minimum and to favour the kinetics of crystallization [4]. What is the minimal amount of information required to assemble complex periodic or aperiodic ordered structures will also be discussed.

[1] S. C. Glotzer, *Assembly engineering: Materials design for the 21st century*, Chem. Eng. Sci. **131**, 3 (2015).

[2] S. Ravaine and E. Duguet, *Synthesis and assembly of patchy particles: Recent progress and fufure prospects*, Curr. Opin. Colloid Interface Sci. **30**, 45 (2017).

[3] E. G. Noya, N. G. Almarza, and E. Lomba, *Assembly of trivalent particles under confinement: from an exotic solid phase to a liquid at low temperature*, Soft Matter **13**, 3221 (2017).

[4] D. F. Tracey, E. G. Noya and J. P. K. Doye, *Programming patchy particles to form complex periodic structures*, J. Chem. Phys. **151**, 224506 (2019).

[5] E. G. Noya, I. Zubieta, D. J. Pine and F. Sciortino, *Assembly of clathrates from tetrahedral patchy colloids with narrow patches*, J. Chem. Phys. **151**, 094502 (2019).