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Patchy colloids: state of the art and perspectives

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Recently, an increasing experimental effort has been devoted to the synthesis of complex colloidal particles with chemically or physically patterned surfaces and possible specific shapes that are far from spherical. These new colloidal particles with anisotropic interactions are commonly named patchy particles. In this Perspective article, we focus on patchy systems characterized by spherical neutral particles with patchy surfaces. We summarize most of the patchy particle models that have been developed so far and describe how their basic features are connected to the physical systems they are meant to investigate. Patchy models consider particles as hard or soft spheres carrying a finite and small number of attractive sites arranged in precise geometries on the particle’s surface. The anisotropy of the interaction and the limited valence in bonding are the salient features determining the collective behavior of such systems. By tuning the number, the interaction parameters and the local arrangements of the patches, it is possible to investigate a wide range of physical phenomena, from different self-assembly processes of proteins, polymers and patchy colloids to the dynamical arrest of gel-like structures. We also draw attention to charged patchy systems: colloidal patchy particles as well as proteins are likely charged, hence the description of the presence of heterogeneously distributed charges on the particle surface is a promising perspective for future investigations.

1. Introduction

Theories and simulations of liquids in which the constituent particles interact by means of spherically symmetric (i.e., isotropic) interactions have experienced tremendous progress in the last few decades. Together with advances in the corresponding experimental techniques, these approaches have led...
to a deeper understanding of the physical mechanisms governing the structural characteristics, the thermodynamic behavior and the dynamical properties of classical fluids. These advances, however, should not obscure the fact that isotropy in the interactions is an idealization and should be treated either as an approximation or as a zeroth-order point of departure for the analysis of more complicated and realistic situations. Indeed, even on molecular length scales, one readily encounters anisotropy for the simplest of molecules, a fact that has given rise to the development of the theory of molecular liquids and the correspondingly complex theories of anisotropic fluids.

Moving up in the length scale of the associated particles, into the mesoscopic domain of soft matter physics, we are called to deal with effective interactions, the microscopic solvent being usually treated as a continuum. Here, anisotropy in the interactions naturally arises as a result of an underlying anisotropy in shape (colloidal ellipsoids, rods, platelets etc.). Alternatively, one might be dealing with spherical particles carrying embedded or induced dipoles, a vast field with applications in the domain of magneto- and electro-rheological fluids. Anisotropy moreover naturally arises in a different class of soft colloids, which do not have a hard core but rather consist of polymers with various architectures. Though, for instance, star polymers with a high number of arms are very-well approximated as spherical objects and their fluctuations around sphericity are weak, polymer chains display instantaneous shapes that are quite anisotropic, as first shown by Solc and Stockmayer about 40 years ago. In dilute solutions, a characteristic example of patchy particles and the propensity of the patches to associate with one another gives rise to a number of particular intra-star and inter-star association phenomena. Other kinds of soft, patchy nanoaggregates may also originate from the self-assembly of amphiphiles. The latter self-organize into micelles and vesicles when dispersed in the specific solvent. Such aggregates may possibly have patchy surfaces, i.e., the whole surface of the complex aggregate may show extended regions where the solvophobic or solvophilic blocks prevail. It has been shown, for instance, that binary mixtures of two different amphiphiles in aqueous solutions can give rise to two-components vesicles or to soft patchy micelles. The surface patterns and the specific shapes of such aggregates can be tuned by changing the composition of the mixture and via the choice of the hydrophobic–hydrophilic components. A large variety of systems arises, from spherical aggregates to cylindrical ones, which have extended patches on the external surface or even on the internal one. Self-assembled patchy complexes of the above type feature incessant fluctuations in the shape of the final aggregates.

In this paper, we focus on systems in which there are no shape fluctuations of the patchy units. More specifically, we mainly consider spherical units in which the anisotropy of the interaction comes only from specific patterns on the particle surface (see Fig. 1). For such systems, we consider most of the pair potential models that have been developed to date and we describe how they have been used to study the collective behavior of patchy systems from a numerical and, possibly, analytical point of view. Since an extensive, recent review on the experimental side of fabrication and assembly of patchy particles is readily available, here we make the choice to focus on the theoretical and numerical achievements.

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**Fig. 1** Graphical representation of the type of patchy colloid which we focus on: the spherical particle is decorated on its surface by extended patches. Patches are usually discrete and limited in number and the interaction between them, selective or not, gives rise to the formation of strongly directional bonds between otherwise repulsive particles. Here we show the specific pattern of four identical patches arranged on a tetrahedral geometry (the forth patch is hidden behind), whose importance is related to the possibility of using colloidal structures with diamond symmetry to create photonic crystals.
Nonetheless, in section 2 experimental patchy systems are briefly reviewed. In section 3, we describe why, when, and how patchy models have revealed their importance, either as simplified descriptions of molecular fluids and globular proteins or as tunable self assembling systems. In sections 4 and 5, we describe the specific models, the possible theoretical approaches and the physical phenomena that have been investigated up to now. We distinguish between patchy models with spot-like patches on hard particles (section 4), either spherical or not, or extended patches (section 5), either on hard or soft repulsive spherical cores. In all these systems, patchiness is characterized by a correspondence between the patch number/geometrical arrangement and the bonding pattern. Such a correspondence does not hold when considering heterogeneously charged particles. Consideration of particles with charges non-spherically distributed on their surface is a very challenging task. In section 6 we report the few patchy models recently developed for heterogeneously charged systems. Finally, in section 7 we summarize and draw our conclusions.

2. Experimental patchy colloids

Colloidal particles with chemically or physically patterned surfaces are generally referred to as patchy colloids. The presence of discrete patches, usually limited in number, induces strongly anisotropic, highly directional interactions between particles. Low valence, directionality, and selectivity in bonding are the common features of such systems.

Directional, site-specific bonds between colloids can be induced by functionalizing the particle surface with lock and key groups, such as DNA oligonucleotides, protein-base biological cross-linkers, and biotin-avidin or antibody-antigen binding pairs. Nonetheless, in this case, positioning the recognition sites in precise arrangements and numbers on the particle surfaces is a very challenging task.

The first step towards the realization of patchy colloids has been the production of non-spherical colloidal clusters with tunable dimensions, shape and number of constituents. Such colloidal clusters interact anisotropically because of their anisotropic shape but they are still not patchy since they consist of all particles of the same type. The step further has been the fabrication of colloidal clusters made of different materials, such as bidisperse clusters made of particles with different size ratio (nano- and micro-spheres). Anisotropic colloidal clusters made of different materials may be further selectively modified to induce directional specific bonding. An additional intriguing aspect consists in the possibility of controlling the angles between the different cluster components, i.e., by changing, the bonding angles between the patches.

Moreover, spherical patchy colloids with distinguishable regions on their surface may be realized by decorating uniform colloidal spheres with metallic patches. For instance, micro-spheres with well-defined interaction spots have been realized by patterning the particle surface with gold nanodots. A variable number of gold patches have been successfully placed in highly symmetric arrangements: two to five gold spots decorate the particle surface in respectively a linear, triangular, tetrahedral or right-pyramidal geometry. Recently, colloidal patchy spheres with multifunctional metallic patches have been synthesized by creating extended patches of metals with different chemical properties, such as gold and silver. The size and the relative orientation of such gold/silver patches have been shown to be tunable to a good extent, while up to now the maximum number of patches on each sphere is two.

Finally, a chemical layer-by-layer surface modification on previously masked-off microspheres has been shown to produce colloids with tunable surface charge patterns made of absorbed nanoparticles on the microsphere surface. Up to now, such partial coating approaches result in the realization of spherical particles with one patch, whose size can be effectively controlled.

One-patch colloids whose patch covers an entire hemisphere are known as Janus particles. The definition of Janus particles is quite broad as it may refer, for instance, to hydrophobic–hydrophilic interactions as well as to charged–uncharged, metallic–polymeric or organic–inorganic functionalizations. In the last 20 years, the fabrication of Janus particles and the fine control of the differences between the properties of the two hemispheres have undergone impressive steps forward, but few of the developed techniques can be extended to produce other geometries of patchy colloids.

Aside of this class of synthetic patchy particles, there are also some natural, biological macromolecules, for example, globular proteins, whose anisotropic interaction may be described by the means of effectively attractive patches on non- or weakly interacting particles.

3. Once upon a time

The first patchy models were introduced in the 1980s, with the goal of numerically studying in a simple and general way a wide class of classical many-body systems, namely the associating fluids. The phenomenon of association (mainly related to hydrogen bonding) is an effect of orientationally dependent attractive interactions between molecules. The basic qualitative features of associating fluids are the presence of strong, directional bonds in the dense phase and, as a consequence, coordination numbers much smaller than 12, which is the average number of nearest neighbors around a molecule in simple fluids. The primitive models developed for associating fluids describe the associating species as repulsive spherical particles carrying a small number of attractive sites, on which the association occurs. The total pair potential is then a sum of the repulsive spherical component plus the attractive anisotropic one. The choice of a hard core repulsive interaction and of an attractive site–site interaction of a square-well type has been favored by the parallel development of an analytical mean field theory able to treat the thermodynamic properties of such systems. This approach is a thermodynamic perturbation theory and it was independently developed by Wertheim to describe fluids with spherically repulsive cores and highly directional attractive forces.

The Wertheim theory is based on the activity expansion of the grand partition function, which can be represented by a sum of topologically distinct diagrams. The decoupling
between attraction and repulsion in the pair interaction potential allows one to simplify such an expansion, as the Mayer function for the full pair potential can be decomposed into the Mayer function for the hard-sphere potential and the Mayer function for the site-site attraction. The Wertheim approach is able to further simplify the complex graphical expansion via the assumption that the conditions of steric incompatibilities are satisfied: (i) no site can be engaged in more than one bond (single bonding condition); and (ii) particles do not form ring-like structures (absence of bonding loops). Thus, only those graphs involving the formation of tree-like bonding structures are considered. The resummed cluster expansion of the grand partition function leads to an expression for the free energy in terms of the densities of particles in different bonding states.60,61 In primitive models for associating fluids, the steric incompatibilities are satisfied due to both the choice of the potential parameters and to the location of the attractive sites on/inside the particle. However, it is worth noting that the theory provides an expression for the free energy of particles with a number \( f \) of attractive sites, independently of the specific geometric arrangement of the same.60,61 The theory only assumes that sites are equally reactive and that the correlation between adjacent sites is missing. Nonetheless, an analytical theory inspired by Wertheim has been derived to describe associative fluids in which a correlation between sites is present.63 In that case, bonding is said to be cooperative, describe associative fluids in which a correlation between sites is missing. Nonetheless, an analytical theory inspired by Wertheim has been derived to describe associative fluids in which a correlation between sites is present.63 In that case, bonding is said to be cooperative, i.e., bonds have a strength related to the size of the cluster they belong to (monomer, dimer, trimer, etc.). The intermolecular potential is not any more pairwise additive but has both two- and three-body terms and thus the analytical approach to describe the system at liquid-like densities has been developed \textit{ad hoc} from the associating ideal gas limit.63

The mean field character of the Wertheim theory can be easily discerned from its reformulation by Chapman and Jackson,64 where the difference in free energy between the associating fluid and the hard sphere reference fluid is given in terms of the fraction of non bonded particles. The theory was also extended to binary mixtures of particles carrying different numbers of attractive sites. In this case, the additional parameter which is taken into account is the molar fraction of the two species.65 Recently, a new formulation of the Wertheim theory in terms of the probability of forming a bond has shown that the free energy due to bonding can be derived in more than one way, assuming that the system of associating clusters is formally equivalent to a system of noninteracting clusters in thermodynamic equilibrium.66 An extension of the Wertheim thermodynamic perturbation theory has been developed to interpret and/or predict the behavior of a wide range of substances with potential industrial applications, as it is possible to treat fluids with strong hydrogen-bonding associations. The statistical associating fluid theory (SAFT) has nowadays given rise to a host of branched developments, which describe for instance chain molecules of hard-core segments with attractive potentials of variable range,67 or even the phase behavior of electrolyte solutions.68

**3.1 Primitive models for water and silica**

Primitive models based on capturing the physics of strong association and low coordination have been developed to describe diverse classes of network-forming liquids. Such models adapt the idea of hard core particles decorated with a fixed number of attractive sites to match the specific features of the system under investigation, \textit{e.g.}, water or silica.

The first anisotropic patchy potential was indeed introduced by Nezbeda to describe the structure and the thermodynamic properties of water.69 In an attempt to mimic the oxygen atom, the model depicts a particle as a hard sphere with four short-ranged interaction sites arranged in a tetrahedral geometry. Sites are of two different types: hydrogen-sites, located on the hard sphere surface, and ion-pair sites, located under the particle surface. The hydrogen bonding is modeled by a square well interaction between hydrogen and lone-pair sites and no interaction between the like sites occurs. The model has been proved to reproduce even the anomalies of water,58,69 and it has also been used to describe the solid–fluid equilibrium behavior as well as the gas–liquid phase separation process. The phase diagram of such a model shows the presence of a high-density crystal and a low density solid with tetrahedral coordination.70 The short range nature of the directional attraction acts, as in simple fluids, towards the destabilization of the liquid phase,71 while the low valence in bonding favors the formation of open networks of bonds which possibly lead to kinetically arrested states.69

A similar primitive model was introduced to describe another network forming material: silica.59 The model is a non-additive hard sphere mixture of particles carrying two or four sticky sites at a fixed distance from the particle center, mimicking respectively the silicon and the oxygen atoms. The only attractive interaction takes place between Si and O sites and it is modeled as a square well potential, while the interaction details are chosen to reproduce the key chemical features of real silica. The model has been proved to be powerful in describing dense phases of real silica59 and it has also been used to investigate the fluid phase close to the dynamical arrest and the gas–liquid critical point location in the phase diagram.72 The phase diagram of this model shows that solid dense phases of the primitive model of silica and experimental data are in good agreement, and that a liquid phase is always observed as a metastable phase with respect to the fluid–solid phase separation, in analogy to the case of the primitive model for water.

The strong glassy behaviour of such network forming liquids has been related to the behavior of thermoreversible colloidal gels.73 Indeed, in the region of intermediate densities where the low bonding valence stabilizes the liquid phase, the Arrhenius slowing down of the dynamics is driven by the attractive interactions rather than packing, as it happens in colloidal gels.

**3.2 Primitive models for proteins**

In the late 1990s, a renewed interest in patchy particles has grown, motivated by the need to tackle the issue of protein crystallization. The existence of low density crystals and the tendency to form gel states instead of ordered structures have been proved to be related to the short range nature and the high anisotropy of attractions between proteins in solution. Already from the seminal work on an aeleotopic model for
globular proteins, a simple pair potential approach to get such features has revealed to be quite powerful.

The minimal model introduced by Sear to study the fluid–fluid and the fluid–solid coexistence in the phase diagram of globular proteins was inspired by the primitive models of associating fluids: patchy particles are modeled as hard-spheres carrying a fixed number of bonding sites in a regular geometry, so that the pair potential between particles is the sum of an isotropic hard-core repulsion and a site–site square-well attraction. In contrast to the majority of primitive models for associating fluids, all sites are on the particle’s surface and have the same interaction strength and attractive range, but they are numbered, so that even sites on a particle interact only with odd sites on a different particle. Due to an appropriate choice of the short ranged attraction and to the location of the bonding sites, the model guarantees the single bonding condition and minimizes the aggregation of closed bonded loops. The Kern–Frenkel model is another hard sphere patchy model with square well attractive patches, and it was introduced to study the gas–liquid critical phenomena when only a reduced coverage of the particle surface was active in the bond formation. Indeed, in such a model, patches are designed to also have an explicit extension on the particle’s surface. Similar to the Sear model, patches are all identical, with the same bonding energy, attractive range and, additionally, the same patch size. In contrast to the Sear model, however, the patch–patch interaction is not selective. The powerful feature of the Kern model is that the angular and the radial characteristics of the patches are independently chosen, while in the Sear model the interaction range and the patch extension are defined jointly. On the other hand, while the Kern model encompasses surface patch coverages both below and above the threshold that guarantees single bonding between particles, the Sear model was built to manifestly avoid the formation of multiple bonds between spot-like patches. The choice of simple discontinuous pair potentials in both models guarantees that bonding is properly defined: a bond sets up when two particles are closer than the patch attraction range and in that case the pair interaction energy is equal to the depth of the square well. The study of such models has shown that the fluid–fluid coexistence moves towards temperatures lower than critical temperatures observed in isotropic systems and that the fluid–fluid phase separation is metastable with respect to the fluid–solid coexistence. Similar results about the metastability of the fluid phase were also found for a continuous patchy model where the (weak) isotropic repulsion and the (strong) anisotropic attraction were both modeled by a 140-35 Lennard-Jones potential.

In the last five years, there have been several studies showing how patchiness affects the phase diagram. Inspired by either the spot-like patch model proposed by Sear (see section 4) or the extended patch model proposed by Kern (see section 5.1), a host of minimal models have been designed to explore in a general way the effect on the phase diagram of the patch extension, the patch geometrical arrangement, the patch interaction strength, the patch interaction range or even the patch specificity. The extensive studies on patchy particles have not only helped to better investigate collective behaviors of proteins in solution, but are of great importance to deepen the understanding of a wide a range of different phenomena as well. Patchy models have indeed played a key role in studying the relation between chemical and physical gelation, the dynamics of supercooled liquids and the formation of kinetically arrested states, the stability of the liquid phase with respect to crystal formation, the interplay between locally favored ordered clusters and crystallization or the assembly of particles into ordered structures.

3.3 Patchy models for self-assembly

Patchy particles are also simple building blocks of mesoscopic and macroscopic self-assembled equilibrium structures. Self-assembly is the spontaneous organization of matter from disordered constituents into well-defined meso- and macroscopic structures with given size and symmetry.

On a molecular scale, traditional examples are the dynamical assembly of molecules into functional clusters, such as actin fibers and tubulin, the formation of micelles from block copolymers or from surfactant molecules exhibiting amphiphilic interactions (e.g. lipids), and virus capsid proteins assembling into monodisperse structures, such as icosahedra in HIV (human immunodeficiency virus) and helical cylinders in tobacco mosaic virus. Inspired by reversible assembly of protein units, a large variety of minimal patchy models have been designed to study the self-assembly of patchy particles into monodisperse clusters of various symmetry. Such models describe the patchy interaction between two particles via an orientationally dependent Lennard-Jones potential (see section 5.2). The mechanisms through which aggregation occurs as well as the interplay between crystallization, kinetic arrest and clustering have been addressed for different platonic solids on varying the arrangement of the patches on the particle surface. Self-assembly of polyhedral cages has also been investigated by the means of rigid, non spherical building blocks carrying anisotropic interaction sites. In particular, truncated pyramids with interaction sites on the lateral faces have been specifically designed to self assemble into viral icosahedral cages, as well as three-legged units with selective interaction sites on both ends of each leg.

On a macroscopic scale, self-assembly is a method to build well defined aggregates ranging from the nanoscale to extended structures. By virtue of the asymmetry in shapes and/or the anisotropy in the interactions, patchy particles significantly extend the possibilities offered by traditional materials. The relationship between patchiness and equilibrium target structures has been extensively investigated via coarse-grained patchy models. In this case, the anisotropy of the interparticle interaction is gained via covering the spherical particles with a number of coarse-grained spherical subunits of different types arranged in a fixed, predefined geometry on the particle surface. The local arrangements of patch units, the total number of surface units and the interactions between like or complementary units are chosen such that selectivity and directionality can be tuned and adapted to the particular system in analysis. Icosahedra, square pyramids, tetrahedra, rings, chains, twisted and staircase structures, and sheets have been obtained, on cooling from a disordered state, by a suitable design of the patches pattern. Particular attention...
has been paid to the specific case of four identical patches in a tetrahedral geometry because of its relevance for photonic crystals with diamond symmetry.

4. Spot-like patch models

Various spot-like patch models have been developed, drawing inspiration from the Sear model for globular proteins. Particles are designed as hard objects carrying on their surface a fixed and small number of attractive patches (from two up to a maximum of six), which are spots on the surface and interact with like or complementary sites on a different particle via a square well pair potential. These models have been designed to satisfy the single bonding conditions of each patch and to minimize the formation of bonded rings. Indeed, because particles cannot overlap, the site–site square well potential can always be made sufficiently short-ranged, so that the formation of multiple bonding at a given site is forbidden. The value of the attraction range for such models is usually around 10–20 per cent of the particle diameter. It is worth noting that the single bonding conditions imply a simple correspondence between the number of sites and the number of bonds, since a particle with a given number \( f \) of patches can form only up to \( f \) bonds and hence \( f \) can be considered the valence or functionality of the particle. Moreover, the geometrical arrangement of the patches on the particle surface is often chosen in such a way that double bonding between the same pair of particles is minimized as well as the effect of correlation between nearby sites. Given such general features of the models, the first-order thermodynamic perturbation Wertheim theory has been widely applied to obtain the free energy contribution due to bonding in terms of bonding probability. The bonding probability can be seen as the ratio between the number of bonds in the system and the maximum possible number of bonds. Considering the bonding process as a chemical reaction between two non-bonded sites in equilibrium into a pair of bonded sites, the bonding probability, \( p_b \), results from the mass action equation as

\[
\frac{p_b}{(1 - p_b)} = \rho \sigma^3 e^{-\beta \Delta F_b}
\]

where \( \rho \) is the density of the system, \( \sigma \) is the particle diameter, \( \beta = 1/k_B T \) is the inverse of the thermal energy (where \( k_B \) is the Boltzmann’s constant) and \( \Delta F_b \) is the free energy difference between the bonded and the nonbonded states. The Wertheim theory provides a simple recipe for \( \Delta F_b \) in terms of the liquid state correlation function of the hard-core reference system and the spherically averaged Mayer function of the site–site interaction. In particular, given two particles 1 and 2, each of them carrying \( f \) sites, the exponential in the right hand side of eqn (1) reads

\[
e^{-\beta \Delta F_b} = f \sqrt[3]{\int g_{HS}(12) f_{SW}(12) d(12)}
\]

where \( g_{HS}(12) \) is the reference hard-sphere fluid pair correlation function, \( f_{SW}(12) \) is the site-i-site-j Mayer function, and \( d(12) \) represents the integration over all the possible orientations and interparticle separations of the pair of particles within the range where bonding occurs.

Since the main assumption of the Wertheim theory is that particles cluster in open structures without closed bonded loops and since this hypothesis is also at the heart of the Flory–Stockmayer theory, a combined parameter-free analytical approach has been developed to describe the equilibrium properties of these spot-like patch models. The Flory–Stockmayer theory, developed in the contest of chemical gelation, provides expressions for the number density of clusters of a given size as a function of the bonding probability, which is called the extent of the reaction in the Flory–Stockmayer language. Combining the cluster size distribution and the chemical equilibrium equation, it has been possible to obtain the structural and connectivity properties of the systems in the temperature-density phase diagram. The Flory–Stockmayer theory has been recently generalized to patchy particles with distinct interaction sites.

An analytical mean-field description is available not only for the thermodynamic properties of point-shaped patch models but also for their dynamics. Indeed, the aggregation kinetics of such systems has been investigated and fully described by combining the static Wertheim expressions with the Smoluchowski equation for coagulation. The Smoluchowski equation was developed to describe the irreversible growth of clusters by coalescence, but it was lately extended to reversible aggregation by taking into account the appropriate bonding and breaking rate constants. As a consequence of conditions (i) and (ii), the bonding and breaking rate constants only depend on the topology of clusters with a given size. The second condition is also equivalent to the assumption that the aggregation process is dominated by bond-formation and not by diffusion of clusters. If the kinetics are mainly controlled by bonding, the system is said to be in its chemical regime. It has been shown that the Flory–Stockmayer cluster size distributions are solutions of the Smoluchowski equation in the chemical limit. Once the appropriate bond-breaking processes are taken into account, the solution of the Smoluchowski equation provides the evolution in time of the bond probability. For patchy systems in which reversible and irreversible aggregation take place in the chemical regime, it has recently been shown that there is a direct correspondence between the bonding probability at a certain time, \( p_b(t) \), and the equilibrium bonding probability at a specific finite temperature, \( p_b(T) \), as it is given from the Wertheim approach of eqn (1) and (2). The role of the time in irreversible aggregation has been related to the role of temperature in reversible aggregation, meaning that the dynamical evolution of the aggregating systems takes place via a sequence of equilibrium states.

A self-consistent mean-field approach is thus available to treat the dynamics and the thermodynamics of spot-like patch particle models, which can be spherical or not, as described more in details in sections 4.1 and 4.2.

4.1 Patchy hard spheres

Patchy models consisting of hard-spheres decorated on their surface by a small number of identical spot-like, short-ranged,
square-well attractive sites have been used as minimal models of self-assembly systems. Self-assembly into non-close packed structures is caused by a very strong inter-particle attraction, significantly larger than the thermal energy, and by interaction geometries far from the spherical one. Equilibrium polymerization of linear polymer chains from monomers having directional bifunctional interactions as well as self-assembly of branched loopless clusters of binary mixtures of bi- and three-functional patchy particles have been deeply investigated.97–99,101 The presence of even a small fraction of polyfunctional particles in a chain-forming system leads to the formation of extended networks and hence it introduces two phenomena which are missing in chain polymerization: a percolation transition and a gas–liquid phase separation. A comprehensive scenario has been developed to describe the basic equilibrium thermodynamic and dynamic properties of such systems.97–99,101

Spot-like patch models have also been widely used to investigate the formation of colloidal gels.66,102–104 A colloidal gel can be defined as a low density disordered arrested state of matter in which stable particle networks are formed due to long-living reversible bonding. Such states are usually observed at large values of the interaction strength (i.e., values of the characteristic energy of the attractive potential $u_0$ much greater than the thermal energy $k_B T$), since such a condition increases the lifetime of inter-particle bonds and stabilizes the bonded network, when excluded volume does not favor caging. On the other hand, large values of $u_0/k_B T$ also favor the liquid–gas phase separation process, since the statistical Boltzmann weight of highly bonded configurations becomes relevant. It has been shown that for particles interacting with attractive spherical potentials (besides the hard-core repulsion) arrest occurs only through interrupted phase separation.105–111 Anisotropically interacting systems in which the bonding valence is significantly reduced show a reduction of the gas–liquid phase separation region. Patchy models66,102,104 as well as systems in which coordination numbers are smaller than 12 have been shown to disfavor dense local configurations.112,113 The average functionality of the system is one of the key parameters controlling the stability of the liquid phase: the reduction of the number of bonded nearest neighbors broadens the region of stability of the liquid phase in the temperature-density plane. Fig. 2 shows the shrinking of the gas–liquid coexistence region in the phase diagram on decreasing the valence of the patchy system.

Once the gas–liquid separation is strongly disfavored, it is possible to decouple phase separation from dynamical slowing down, and hence homogeneous states with $u_0 \gg k_B T$ can be approached in a one-phase system.101,102 The stable (or at least metastable) fluid phase at low density, either referred as empty liquid or ideal gel (in the zero temperature limit), can be seen as an extended network of bonds, whose lifetime is essentially controlled by the energy scale. On increasing the bond lifetime (or equivalently on increasing $u_0/k_B T$), the occurrence of the kinetically arrested disordered state of matter at low density becomes possible. The possibility of forming long-lived reversible gels has been proved to be robust against changes in the patches’ geometrical arrangements for systems composed of patchy particles with fixed and equal number of patches (lower than six) and for binary mixtures of particles with a different number of bonding sites such that the average functionality is low (less than three).66,101,102,104 The same scenario has been found also in two-dimensional systems, where the formation of closed bonded loops is highly entropically favored in comparison to the three-dimensional counterpart.114,115 A continuous model designed to mimic the hard-core plus square-well anisotropic potential has been used to study how the valence influences the gel in a binary mixture of patchy particles with different functionalities where the stochiometric ratio of the two species determines the average valence of the system structure.116 The tendency of patchy particles to form bonded, low-density networks has also been exploited to investigate ageing in gel forming systems as compared to glass forming ones and it has been shown that violations of the fluctuation–dissipation theorem occur only for energy-related observables and not for density-related observables, in contrast to what happens in structural glasses.104

The vapor–liquid coexistence, the location in the phase diagram of the critical point and the way it may vanish or not on tuning the patchiness of the system have been also explored via a hard sphere model in which the particle surfaces are patterned with attractive dissimilar spots.117–119 The role of dissimilar patches has been investigated with particular attention paid to the richness of the bonded structures and the possible tailoring of the fluid structural features with temperature. Specifically, each particle carries three spot-like, square well patches, two of one type and one of a different
type. Three different interactions occur between like or unlike patches and the relative values of the strength of such interactions tunes the structures of the fluid: from linear non-interacting chains to non-percolating hyperbranched polymers, from dimers to chains connected by X-like or Y-like junctions. The richness of the model comes from the possibility of tuning the favorite bonding pattern on changing the relative site-site interaction strengths. Moreover, for fixed ratios of such values, the temperature influences the effective functionalities of the particles and hence the prevailing structure. Thermodynamics, percolation and criticality have been then related to the possible structures on exploring the range of the energy parameters. The limit in which the features of the patches favor the formation of chains connected via Y-junctions has also been shown to have a strong analogy with the dipolar hard sphere fluid.

4.2 Patchy hard ellipsoids

A patchy particle model able to combine directional bonding and non-spherical shapes has been used to study gel formation in reversible and irreversible aggregation and to connect the two processes via an analysis of the role of temperature during chemical gelation as compared to the role of temperature in physical gelation. The features of the model have been inspired by the epoxy-amine system but they are representative of colloidal particles functionalized with a small number of patchy attractive sites. The model is a binary mixture of hard ellipsoids of revolution carrying on their surface a fixed number of mutually interactive sites in a predefined geometry. The two species in the mixture differ from each other in size and number of attractive sites, while the stoichiometry of the two species is chosen in such a way that the total number of sites is equal for both species and the average functionality is less than three. The interaction potential is the hard ellipsoid potential plus a site-site square well attractive interaction between sites on different type of ellipsoids. The model turned out to be well suited for the application of mean field approaches, since it disfavors the formation of bonded loops in the clusters and it guarantees a single bonding condition between sites. The entire polymerization process has been described in its structural and connectivity properties both below and above the percolation threshold and it has been shown that the irreversible temporal evolution of the aggregating system can be connected to a sequence of equilibrium states. It has also been possible to investigate the interplay of chemically controlled or diffusion controlled aggregation, finding out that the crossover between the two regimes is related to the probability of two nearby clusters to stick as compared to the probability of two distant clusters to approach each other via diffusion.

5. Extended patch models

Patchy particles with extended patches have been modeled as either hard core particles interacting via orientationally discontinuous pair potentials (see section 5.1) or soft particles (see section 5.2).

The Kern–Frenkel model can be considered the prototype of the first kind of extended patch models. Such a model and its extensions have been used to investigate both ordered and disordered states of matter. Various theoretical approaches have been developed and exploited on the different Kern-inspired patchy models. Once multiple bonding is appropriately hindered, the theoretical mean-field approach provided by the Wertheim theory can be applied to predict the thermodynamic properties of such patchy systems. The Wertheim theory has been successfully applied to Kern systems with a hard sphere reference fluid and four tetrahedral patches or even to Kern-inspired systems with an isotropic square well reference fluid and a variable number of patches. Moreover, standard Kern systems with only one or two patches on the particle surface have been studied by means of an integral equation approach. The two cases have been investigated on changing the areal patch coverage and the integral equation approach has revealed to be quite powerful to study the fluid in the regime where multiple bonding between patches is allowed to occur. In the case of patches with finite interaction range and strength, the Ornstein–Zernike equation for the direct correlation function in terms of the pair correlation function has been solved with the reference hypernetted-chain closure. The corresponding Baxter limit of the Kern model with one or two patches has also been investigated. In that case, a different class of closures has been chosen to solve the Ornstein–Zernike equation.

5.1 Kern and Kern-inspired models

The first patchy model able to independently tune the interaction range and the patch extension on the particle surface has been the Kern–Frenkel model. While in spot-like patchy models the patch extension is determined by the sphere of interaction of a spot site, in the Kern model the width and the range of the patches can be varied independently. The Kern model was introduced to study the fluid–fluid phase separation phenomena when only part of the particle surface can participate in bond formation. To this end, the patch–patch attraction ranges were chosen to guarantee the stability of the critical point in the isotropic limit and the coverage percentage of a small and even number of patches was varied. On reducing the attractive surface of the particles, the gas–liquid coexistence region was found to become metastable. As noted before, the Kern model was conceived to investigate the effect of patchiness in both single and multiple bonding regimes. Successive studies have instead focused on the single bond per patch regime, by appropriately choosing the angular extension and the range of the patches. In such a regime, it has been shown that it is possible to generalize the law of corresponding states developed for isotropic short-range attractive systems to patchy particle systems, at least when they are close to the gas–liquid critical point. Specifically, the critical density and temperature of Kern patchy systems with three, four and five patches arranged in a regular geometry have been determined for different attraction ranges and patch extensions and it has been shown that, if the number of patches is the same, the thermodynamic properties scale with the second virial coefficient, as it happens for isotropic fluids. Particular attention has been paid to the Kern model of patchy particles with four tetrahedrally arranged patches because of the interest in diamond crystal formation. Such studies have focused on the effect of the patch range on
the location of the gas–liquid, the fluid–crystal and the crystal–crystal coexistence regions in the phase diagram. The patch–patch attractive range has been varied from 3% to 25% of the particle diameter, while keeping the patch extension fixed. The stability of the liquid phase has been proved to be metastable when the interaction range becomes less than 15% of the particle diameter, similar to what happens in isotropically interacting systems, but, in contrast to the spherical case, the driving force to nucleate a diamond crystal does not increase upon increasing the interaction range. Moreover, the role of the patch–patch attractive range has been studied with respect to the region of stability of four crystal phases: diamond cubic, body-centered-cubic (bcc), face-centered-cubic (fcc) and plastic fcc crystals.

The effect of the surface patch coverage on the structure of the fluid has been addressed for Kern patchy systems with one or two opposite patches. In both systems, the patch width values cover the whole range from the full square well system to the hard sphere one. It has been shown that, for a given patch width, the liquid phase is favored by a higher valence and that the structure of the system can be tuned in both its ordered and disordered arrangements. In particular, in the two patches case, the gas–liquid phase coexistence boundaries and the fluid structure can be determined only when the patch coverage is bigger than 30% of the total particle surface. Below such a value, the system tends to crystallize. The ordered crystalline structures are directly controlled by the patchy pattern. On decreasing the patch extension from values such that each patch can form a maximum of four bonds down to two bonds per patch, the structure of the system varies from interconnected planes, with a square or triangular arrangement, to planes interacting only by excluded volume interaction. Eventually, in the single-bond-per-patch limit the stable aggregates are polydisperse chains. Crystal formation does not occur in the one patch case, but the morphology of the surface pattern favors the formation of micelles and vesicles, which can suppress the phase separation process.

The formation of micelles and vesicles in a one-patch Kern system has been thoroughly studied in the specific case of a patch surface coverage equal to half of the total particle surface. Patchy particles carrying only one hemispherical patch are a simple prototype of Janus particles. The phase diagram of Janus particles shows a gas–liquid phase separation phenomenon whose critical temperature and density are much lower than the isotropic counterpart. Interestingly, the fluid–fluid phase separation competes with the aggregation of particles into micelles or vesicles. Indeed, the dense liquid phase has been found to coexist with a gaslike phase composed of micelles or vesicles. In the free energy balance, the entropically favored phase is the liquid, while the gas of micelles or vesicles is the energetically favored phase, in contrast to what happens in simple fluids. Moreover, unlike simple liquids, the densities of the two coexisting phases approach each other on cooling. Investigations on a possible meeting point of the fluid–fluid coexistence boundaries are prevented by the formation of a lamellar crystalline phase. The stability of micelles, vesicles and lamellae has been established for a long-range Janus system, while the effect of interaction ranges closer to the experimental values is still an open question.

Kern patchy systems with one or two patches have also been investigated in their Baxter sticky limit, i.e., when the square well attraction between the patches becomes infinitely deep and narrow. Both systems have been studied under changes of the areal patch coverage and the effect of the two geometrical distribution of the attractive surface has been addressed. Similar to the corresponding cases with finite attractive range and strength between the patches, the liquid phase appears only over a certain threshold of the surface coverage and it is favored by a symmetric two patch distribution rather than by one patch with equivalent attractive surface. The liquid and the percolating phase of the systems are even more favored when a uniform adhesive interaction is added to the isotropic hard sphere repulsion on the top of the patchy interaction.

A different version of the Kern–Frenkel model complements the square well patch–patch interaction with an isotropic square well interaction between particles. The difference between this variant and all the previously described models is that the reference system is not purely repulsive. The isotropic attraction is chosen to be longer ranged and significantly weaker than the patch–patch attraction. At the same time, the patch–patch attractive ranges have been chosen such that, when varying the number of the patches, the total area-coverage of the patches does not allow the formation of more than one bond per patch. The gas–liquid phase separation phenomena, the critical point temperature and density, and the gas–liquid coexistence boundaries have been investigated under changes of the patch number (from three to seven), the patch geometrical arrangement on the particle surface, and the total areal coverage of the patches. Thus, the metastability of the fluid phase has been addressed on varying the system parameters from the square well to the hard sphere isotropic fluid. The generalized law of corresponding states has been proved to hold only for the patch hard sphere system and not for the patchy square well fluid. The specific case of a square well patchy system of particles with six uniformly arranged patches has also been studied with respect to crystal formation. It has been shown that crystallization in such a system is induced by the aggregation of clusters with the same symmetry of the crystal. The self-assembly of long living clusters takes place in a region of the phase diagram in which the critical phase separation phenomena do not take place, and hence it is the self assembly mechanism that leads to the formation of dense liquid-like regions, thus facilitating the formation of a critical nucleus, even in absence of critical fluctuations. The same phenomenon was not observed for five and seven regular patches, meaning that the symmetry of the aggregates has to be compatible with the crystal structure for this phenomenon to take place.

5.2 Patchy soft spheres

Another model in which the patch–patch interaction range and the patch extension on the particle surface are disconnected is a continuous orientationally-dependent pair potential built from an isotropic Lennard-Jones one. Specifically, two particles interact via an isotropic Lennard-Jones repulsive
core and the directional patch–patch attraction is given by the Lennard-Jones attractive part modulated via a Gaussian angular dependent decay. The cutoff distance of the Lennard-Jones potential is chosen to be larger than twice the particle diameter, i.e., patches interact over large interparticle separations, much larger than the usual square well ranges in discontinuous patchy models. Moreover, patches are quite extended on the particles surface, since the Gaussian width ranges typically from 0.2 rad to 0.5 rad. Nonetheless, a patch on a particle cannot bond simultaneously to more than one patch on another particle, since only the smallest of the angles between the interparticle vector and the patch vectors is taken into account when calculating the interaction energy of a given pair of particles. It is worth noting that, in the model, bonds between more than two particles at a given patch are still possible and the wider the patches are the more likely these multiple bonds become. Provided that the patches are sufficiently narrow, each patch is involved in only one bond and the single bonding conditions is recovered.

Such a model has been mainly used to tune the self assembly of clusters with specific shapes and dimensions. The first and most thoroughly investigated case is the self-assembly of patchy particles into icosahedral clusters, since most of the virus capsid proteins often form cages of icosahedral symmetry.80 On changing the number and the patch location on the particle surface, it is possible to tune the geometry of the interparticle interaction and to study self-assembly paths towards cluster formation as opposed to crystal formation. Within the described orientational Lennard-Jones model, interesting insights have been gained on the role of frustration within the crystallization scenario both in two and three dimensions.88 The competition between local and global order can possibly frustrate the kinetics of crystallization, even if the symmetry of the interactions is compatible with a specific crystal structure. Cluster assembly into monodisperse target structures can be tuned via designing patchy particles with a specific number and geometrical arrangement of patches.80 82,88 The effect of the target geometry on the efficiency of the aggregation process has been studied via comparison of the assembly pathways of different target-shaped building blocks. Different platonic solids can be identified by different patchy particles designed to satisfy the bonding geometry. In particular, cubes, tetrahedra, icosahedra, octahedra and dodecahedra have been considered.80 82,88 The assembly of such structures within the described models occurs via both direct nucleation pathways and a budding mechanism which leads step-by-step to the desired clusters via subsequent rearrangements of the bonded particles. The growth of disordered aggregates and the rearrangement kinetics from random aggregates to monodisperse clusters are sensitive to the size and the degree of order of the final and the intermediate structures: the smaller the aggregates are and the closer to the desired structure the local order is, the easier it is for them to rearrange into the target. Self-assembly via budding mechanisms is suppressed when a torsional constraint in the patch–patch interaction is added.82 Indeed the torsional constraint strongly reduces the number of possible incorrect structures and the competition between target and disordered clusters is reduced as well. The torsional patchy model is hence less sensitive to the geometry of the target structure, i.e., the propensity of the patchy building blocks to aggregate does not show significant differences on assembling cubic, tetrahedral, icosahedral, octahedral or dodecahedral clusters.82 The orientational Lennard-Jones patchy model with the torsional constraint has also been employed to study the self-assembly pathways of homomeric complexes135 made of patchy particles with distinguishable patches. The number and the interaction specificity between the patches have been chosen to focus on the formation of tetramers and octomers. The evolution from monomers and dimers to one of the two final complexes has been investigated with respect to changes of the relative interaction strengths between different patches.135

Both the torsional and the non-torsional soft patchy models with identical patches have been used to investigate the self assembly of the above mentioned platonic clusters.80 82 The role of the patch width, range and strength on cluster aggregation has been addressed and some general rules for optimizing the assembly mechanism can be brought forward.80 82 Narrow patches guarantee the selection of the desired structure, since the lowest-energy clusters are expected to saturate the number of bonds, while non-saturated clusters have a significantly higher energy. Nonetheless, the narrower the patches are, the more difficult it is to rearrange an incorrect structure and the system is likely trapped in glassy kinetic aggregates. On the other hand, wide patches favor the formation of large disordered clusters, since the formation of multiple bonds at a given patch decreases the energy of the aggregates to a value lower than that of the target cluster. The optimal patch width is then a compromise between selectivity, kinetic accessibility and thermodynamics. A similar balance holds for the patch–patch interaction strength, since strong bonds favor the thermodynamic stability of the clusters but slow down the dynamics of rearranging into the correct structure. Rearrangements of particles have to overcome a higher energetic barrier also when the attraction range of the patches is small, so that long ranges increase the yields of the desired monodisperse clusters. Moreover the assembly process has been shown to be quite robust against the patch arrangement on the particle surface, while many and close patches likely tend to stabilize the target structure as compared to the disordered aggregates.

Particular attention has been also paid to the cases of six and four patches arranged on the particle surface in an octahedral and a tetrahedral geometry respectively.80 It has been shown that while for particles with six patches the systems crystallize quite easily in a simple cubic structure, for particles with four patches the formation of the diamond lattice is hindered by the aggregation of dodecahedral clusters. Only for very narrow patches the formation of a diamond nucleus is energetically favorable with respect to the dodecahedron aggregation. The complete phase diagrams of such systems have been lately studied in the case of relatively narrow patches. Particles with six attractive patches in an octahedral geometry show four crystalline phases:134 at low pressures the simple cubic crystal, which is the lowest energy structure; on increasing the pressure the bcc and the fcc, which are high density structures both orientationally ordered; and the disordered (or plastic) fcc for temperatures at which the
entropic effects are most relevant. The phase diagram of patchy particles with four patches in a tetrahedral geometry interestingly shows only three crystal phases, at least for the long ranged Lennard-Jones attraction between patches: a bcc structure, an ordered and a plastic fcc crystal. It has been shown that the bcc structure, which can be viewed as double tetrahedral interpenetrating structure, is energetically favored with respect to the formation of the stable diamond structure, unless the patchy attraction is sufficiently short-ranged.\(^\text{89}\) The formation of bonded and crystalline structures has been investigated in the corresponding two dimensional systems and it has also extended to systems with different average valences, patch extensions and pressures.\(^\text{80,136}\) Some examples of equilibrium open structures in two-dimensional patchy systems are shown in Fig. 3.

A similar continuous patchy model built out of a Lennard-Jones pair potential has been used to describe supramolecular polymerization of patchy particles with two opposite attractive patches.\(^\text{137}\)

A different soft patchy model has been developed to study the structure and the dynamics of gel forming systems.\(^\text{138,139}\) Such a model is described by a potential made of three terms: a soft Lennard-Jones-like isotropic pair attraction, a soft anisotropic repulsion and a three body term which introduce a local rigidity in the bonded structure. Such a model has been exploited to investigate the difference between physical gels obtained \(\text{via}\) slow cooling or \(\text{via}\) quenching: the latter is shown to be more connected and less space-filling than the first.\(^\text{138}\) Moreover, the arrested glassy dynamics in such a system has been related to the formation of a stable network of bonded particles.\(^\text{139}\)

### 6. Perspectives

Colloids and proteins acquire a charge when dispersed in polar solvents, due to dissociation of surface groups and/or preferential adsorption of charged species. The electrostatic interactions between dispersed particles in a liquid medium is a screened Coulomb interaction. The traditional Derjaguin–Landau–Verwey–Overbeek (DLVO) description\(^\text{140}\) is based on the assumption of symmetric charge distributions. Nonetheless, an inhomogeneous surface charge can give rise to anisotropic interactions. Particles with heterogeneously charged surfaces can thus be regarded as charged patchy particles. The main feature of such patchy systems is not any more the limited valence in bonding, but rather a competitive interplay between attractive and repulsive anisotropic interactions. Moreover, the presence of charges implies interaction ranges much longer than the usual bonding distances in patchy systems with limited valence. The design of simple models for heterogeneously charged particles can proceed along two different paths: (i) the building of minimal models from a close match with well-designed experiments; or (ii) the development of models from first principles, in order to keep a connection with the microscopic systems.

A patchy model for lysozyme dispersions has been recently designed as a minimal model with free parameters, which can be determined by experimentally accessible information on the phase behavior of such systems.\(^\text{141}\) The proposed pair potential consists of an isotropic DLVO-type repulsion, complemented by a spherical hard core, and an anisotropic attraction mediated by two opposite patches on the particle surface. Using the Kern–Frenkel scheme,\(^\text{75}\) the patch–patch attraction can be factorized into a radial and an angular part. The angular part of the attraction is the Kern–Frenkel distribution function, while the radial contribution is a Yukawa-like attraction. The depth and the range of the attractive Yukawa, as well as the surface coverage of the patches, are free parameters of the model and they are determined by using experimental information on the gas–liquid critical points. The experimentally matched patchy interaction is found to be stronger and longer ranged than the isotropic repulsion, while the patch extension is about 70% of the total particle surface.\(^\text{141}\) Results for the gas–liquid and fluid–solid coexistence of such a patchy model are in good agreement with experiments on lysozyme solutions.\(^\text{141}\)

A first-principles approach to heterogeneously charged colloids may originate from the statistical mechanical description of electrolytes which goes by the name of Poisson–Boltzmann (PB) theory.\(^\text{142}\) The electrolytic solution is described like a suspension of impenetrable charged colloidal particles in a liquid dielectric solvent containing point-like ions and counterions. By combining the first Maxwell equation of electrostatic for a linear, homogeneous and isotropic dielectric with the third Maxwell equation in absence of external fields, a differential equation of Poisson type is derived to relate the electric potential and the density distribution of the ionic charges. Since the charge density follows the Boltzmann statistics,\(^\text{142}\) the Poisson–Boltzmann theory is intrinsically a non-linear problem. The linearized Poisson–Boltzmann (LPB) theory relies on the assumption of dilute systems, which is referred as the Debye–Hückel approximation.\(^\text{143}\) Under the additional assumption of symmetric charge distributions on the colloidal surface, the LPB approach leads to the DLVO description.\(^\text{140}\)

The PB approach has been recently applied to heterogeneously charged colloids. Specifically, a Poisson–Boltzmann cell model for an homogeneously charged sphere\(^\text{144}\) has been extended to heterogeneously charged surfaces.\(^\text{145}\) The linearized problem has then been solved to study the role of charge
heterogeneity on the fluid orientational order.\textsuperscript{145} Moreover, a 
generalization of the charge renormalization approach\textsuperscript{144} from 
homogeneous to heterogeneous systems has been developed in the non linear 
screening regime, and it has been applied to Janus spheres.\textsuperscript{146} Indeed, Janus particles can be considered as 
the simplest example of charged patchy colloids carrying two 
oppositely charged patches with a surface extension of an hemisphere each.

Complex colloids with heterogeneously charged surfaces 
can also arise from complexation phenomena. Recent studies\textsuperscript{147} 
have shown that the absorption of soft polyelectrolyte stars 
(PE-stars) on the surface of oppositely charged colloids leads to a rich variety of patchy complexes. The equilibrium features 
and the self-assembly of such systems can be externally tuned 
by varying the ratio between the colloid- and polyelectrolyte 
stars- charges and the relative sizes of the two components, as 
well as by changing the salinity of the solution and the 
functionality of the stars. The specific system of two PE-stars 
with low functionality absorbing on a charged colloidal 
particle has been investigated in the case of comparable sizes 
of the colloidal particle and the PE-stars.\textsuperscript{147} The relative 
charge of the two components and the salt concentration are 
ence the key parameters controlling the conformation of the 
complex. When the sum of the charges on the two PE-stars is 
slightly less than the charge on the colloid and there is no 
added salt, the two charged polymers are shown to fully 
absorb onto the colloidal surface.\textsuperscript{147} In this case, the PE-stars 
fully absorb on the colloid on opposite poles and assume on its 
surface a so-called starfish configuration. The addition of salt 
causes a partial detachment of the stars from the particle 
surface, driving them from the starfish to the anemone 
configuration, in the terminology of ref. 148. Fig. 4 shows a 
simulation snapshot of a charged, rigid, spherical colloidal 
particle on which two PE-stars of opposite charge have been 
irreversibly adsorbed, forming in such a way a self-assembled 
patchy colloid. The number of PE-stars that can be adsorbed 
can be controlled via the size- and charge ratios.

The resulting heterogeneously charged complex can be seen 
as a patchy colloid with positively charged polar patches and a 
negatively charged equatorial region, which is free of patches. 
The extent and strength of the patches can be controlled either 
by changing the salinity of the solution, as mentioned before, 
or by using different stars.\textsuperscript{148} The number of the patches could 
be tuned also on changing the charge and the size ratio 
between colloids and stars. In a concentrated system, such 
patchy colloids interact anisotropically among themselves: the 
positively charged patches repel each other, as also do the 
negatively charged equatorial parts, while the interaction 
between patches and non-patchy parts is attractive. The PB 
theory, within the Debye–Hückel approximation, has been 
recently extended to describe the screened electrostatic 
potential of spherical particles with non spherical surface 
charge distributions.\textsuperscript{149} Such an approach is the starting point 
to calculate the effective interaction potential between a pair of 
the above-mentioned complexes, which can indeed be cast in a 
closed form.

7. Conclusions

Although relatively new in the domain of soft matter/colloidal 
science, the research field of patchy colloids has attracted 
inensive attention by a large number of workers in the field 
and has already reached a high degree of maturity and 
richness. The progress achieved and the interdisciplinary 
character of the research performed are yet another instance 
of the ways in which soft matter systems rekindle interest in 
subjects, in this case anisotropically interacting particles, 
which once had been introduced and investigated in the 
realm of atomic or molecular fluids. Evidently, the task of 
investigating the properties of patchy colloids does not 
amount to a mere transcription of recipes and techniques 
known from atomic systems over to colloidal ones: a host of 
novel physical properties and particularities require specific 
treatment of their own. Moreover, the possibilities of 
manipulating the extent, shape, arrangement and nature of the 
patches are much richer in the realm of colloidal science 
than in the atomic one (a property that has its counterpart also 
for the case of isotropic particles), so that the emerging 
phenomena are novel and allow for insights into long-standing 
physical questions.

Among the most prominent classes of problems in which 
patchy colloids have made possible to open new fields and 
address fundamental questions are the ones of self-assembly, 
either to local, well-defined structures or to extended ones, and 
the issue of dynamical arrest at low concentration, also known 
as gelation. Here, limited-valence patchy colloids are a unique 
model system with which one can suppress the liquid–gas 
separation and observe gel formation without the hindrance 
of macroscopic condensation. The game and the investigations 
are far from being over. The same holds true for limited-
valence patchy colloids, which are still under investigation,
regarding their properties on, e.g., formation of ordered crystals or even quasi crystals, the effect of different kinds of attractive patches leading to tuning the structure with temperature, and the inclusion of selective attractions between different sites. Patchy charged systems are, in our view, another field that is just emerging, and in which we are dealing with tunable long range interactions through the addition of salt, the absence of limited valence and the competition between attraction and repulsion between the patches, exemplified in the self-assembled models of inverse patchy colloids mentioned in the main text. We are confident that patchy colloids are here to stay and that their investigations will continue to constitute a very active field of soft matter research for the years to come.

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