



Inverse patchy colloids: Synthesis, modeling and self-organization



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ABSTRACT

Inverse patchy colloids are nano- to micro-scale particles with a surface divided into differently charged regions. This class of colloids combines directional, selective bonding with a relatively simple particle design: owing to the competitive interplay between the orientation-dependent attraction and repulsion – induced by the interactions between like/oppositely charged areas – experimentally accessible surface patterns are complex enough to favor the stabilization of specific structures of interest. Most important, the behavior of heterogeneously charged units can be ideally controlled by means of external parameters, such as the pH and the salt concentration. We present a concise review about this class of systems, spanning the range from the synthesis of model inverse patchy particles to their self-assembly, covering their coarse-grained modeling and the related numerical/analytical treatments.

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1. Introduction

In the last fifteen years, patchy colloidal particles have emerged as one of the most promising solutions to the problem of designing self-assembling target structures with specific properties at the micro- and nano-scale level [1^{*}]. Patchy particles are indeed able to guarantee a fine control over the features of the equilibrium (ordered as well as disordered) phases due to the anisotropy of their interaction patterns: the orientational and possibly selective bonding mechanism mediated by the patches controls the symmetries of the resulting structures [2, 3^{**}, 4^{**}]. Many synthesis techniques have been developed to produce colloids with chemically or physically distinct surface areas so that directional and possibly site-specific bonds between the particles can be induced: non-spherical colloidal clusters functionalized with DNA strands [5^{**}] and spherical colloids with metallic [6, 7] or polymeric patches [8] are just some examples of the available synthesis advancements. The spontaneous assembly of patchy colloids has been experimentally observed for instance in the site-specific aggregation of finite colloidal clusters [5^{**}] or in the formation of an extended, two-dimensional crystal, known as kagome lattice [9^{**}]; at the same time, numerical and theoretical

investigations in the bulk have pointed out a surprising multitude of phases that significantly extends the many possibilities already offered by isotropically interacting colloids [4^{**}].

Recently, a new direction of investigation in the field of patchy systems has been put forward: soft patchy units have been introduced, combining directional interactions and low bonding valence with soft interactions and mobile patches. Examples of soft patchy particles are colloids or emulsion droplets with mobile DNA linkers [10, 11^{*}], DNA nano-stars [12] and polymer-based aggregates [13^{*}]. The particular feature of these patchy units is an enhanced bond flexibility with respect to conventional patchy colloids. So far, soft patchy particles have shown a general tendency to stabilize disordered phases [14, 15^{*}, 16].

A further direction of investigation in the field of patchy particles has started with the introduction of particles with a heterogeneous surface charge. These units can be described as patchy colloids with differently charged surface regions and have been referred to as inverse patchy colloids (IPCs) [17^{**}]: while conventional patchy particles are realized by adding attractive patches on the surface of otherwise repulsive particles, IPCs have patches that repel each other, while they attract the rest of the colloidal surface that is free of patches. The feature that the respective patches of two IPCs repel each other while they attract the bare regions of the colloid represents a striking difference with respect to conventional patchy colloids – thus the specification “inverse patchy”. The interplay of attraction and repulsion of oppositely and like charged regions leads

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to a complex effective potential between IPCs, which depends on both the separation of the two interacting particles and their mutual orientation.

Although it seems obvious that heterogeneous surface charges play an important role in a wide range of systems, so far there have been only limited experimental studies dedicated to the self assembly of IPCs. One of the first experimental papers demonstrating the possibility to make colloids interact as heterogeneously charged units showed that charged Janus, overall neutral, zwitterionic particles, can indeed act as charge dipoles, forming strings [18*]. The importance of the electrostatic screening length to the interactions between heterogeneously charged colloids was elegantly demonstrated with charged Janus spheres, that were shown to form clusters instead of strings in the presence of salt [19**]. In addition to the screening length, other parameters, such as the particle size and the pH of the solution, are essential to control both the synthesis and the assembly of heterogeneously charged colloids. Charged Janus particles are for instance created by attaching charged polymeric particles to a liquid–liquid interface: if much smaller oppositely charged particles are dispersed in one of the liquids and if the screening length is much smaller than the big particles' size, then the small particles attach to the big particles, thus inverting the surface charge of the involved hemisphere [20*]. Heterogeneously charged complexes can also emerge by aggregation of oppositely charged particles of different sizes [21], the shape of these aggregates being controlled by the size ratio among the charged colloids as well as by the electrostatic screening length. Incidentally, the distribution of the satellite particles on the surface of the larger colloidal particles – within the same aggregate – could also be manipulated by the application of external electric fields. Finally and most importantly in the context of the present review, spherical particles with two positively charged polar patches and a negatively charged equatorial belt have been recently realized by *ad hoc* surface modifications and subsequent pH variations [22**]; this study is explicitly dedicated to the synthesis and the assembly of IPCs in two-dimensions, laying the basis for a vast variety of experimental scenarios.

It is worth noting that, besides their application in materials science, colloids with differently charged surface regions can be also considered as colloid model systems for more complex biological systems: proteins and virus capsids are known to exhibit heterogeneous surface charges [23*, 24, 25] and their complex behavior is affected by the anisotropic nature of their effective interactions [26, 27, 28].

The first elaborate model for particles with heterogeneously charged surfaces, for which the terminology “inverse patchy” was coined, was put forward some five years ago in Ref. [17**]. The model was inspired by complex units resulting from the condensation of two polyelectrolyte stars on the surface of an oppositely charged colloid [29] (for an artistic view see the cover of Ref. [4**]) and it was later used to describe simpler experimental colloids with a charged surface pattern [22**]. In Ref. [17**] an IPC was modeled as a charged sphere decorated with two oppositely charged regions of finite extent (termed patches), located at the respective poles of the colloid (see Fig. 1) the parameters of the model being related to the experimental physical parameters by a suitably developed description within the Debye–Hückel theory; in Ref. [30] the original model was generalized to characterize colloids with possibly richer surface patterns, such as IPCs with two differently charged or sized patches as well as IPCs with more than two patches. This model has been extensively used to numerically investigate the collective properties of IPCs, such as the gas–liquid phase separation, the formation of gel-like structures or the stability of new emerging crystals.

In the subsequent years, the idea to study particles with heterogeneously charged surfaces proliferated within the community. In Ref. [31**] a charged Janus model was developed, represented by a charged, spherical colloid, decorated with one single oppositely

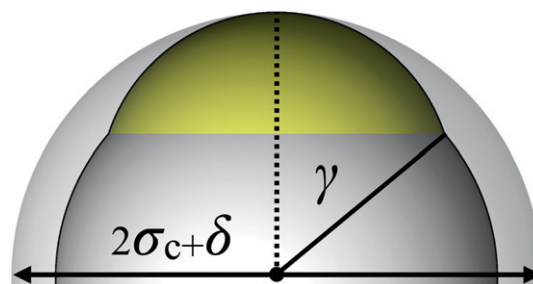


Fig. 1. In the schematic representation of an IPC, the particle core is depicted in dark gray, while patches are colored in yellow. Note that IPCs are spherical units: the yellow caps represent the interaction sphere of the patches, while the light gray halo features the interaction sphere of the bare colloid. The characteristic parameters are as follows: σ_c , the radius of the colloid; δ , the particle interaction range; and γ , the patch opening angle, as labeled. In this model [17**], σ_c is the unit of length, while γ and δ are determined once the position and the interaction range of the out-of-center sites are chosen (see Section 3). In the experimental realization [22**], σ_c and γ are determined at the synthesis level, while δ depends on the overall properties of the system, such as the screening conditions, the charges of the different surface areas, the pH, the salt concentration and the dielectric constant of the surrounding medium.

charged patch. The (pairwise) interaction between these particles is quite simple: the radial part consists of a soft, steric repulsion plus an electrostatic term (for the differently charged regions), treated within the Debye–Hückel theory; the latter contribution is multiplied by a distance- and orientation-dependent prefactor which generalizes ideas of the seminal Kern–Frenkel model for conventional patchy particles [32]. This model has been used to study the aggregation behavior of such units depending on their patch size [31**]. Again along the Debye–Hückel lines, Ref. [33*] proposes a multipolar expansion for the interaction potential between charged Janus colloids: in this work, minimum-energy clusters relative to different orders of the multipolar expansion are compared to experimental clusters, thus showing how the order of the expansion affects the resulting clusters. It is worth noting here a peculiarity of the Debye–Hückel multipolar expansion: each standard multipole carries also all higher multipoles, as first shown in Ref. [34] and later elaborated in Ref. [35]. In the context of globular proteins, a set of charged patchy particle models, introduced in Ref. [36], can be considered as IPC-related particles: here the charged patches are generated by distributing – following well-defined rules – a few hundred charged beads on a spherical surface. This set of entities has been subsequently used to study their adsorption on a polyelectrolyte brush layer [37]. Zwitterionic and protein-like units have been also modeled in Ref. [38] to elucidate the properties of the fluid phase upon small changes of the system parameters, such as the strength of the interactions or the arrangement of charged patches.

A highly sophisticated model for particles with heterogeneously charged surfaces has been put forward in Ref. [39**], which considers homogeneously charged shells, decorated with an arbitrary pattern of opposite charges within the Debye–Hückel approximation; particular emphasis is put on heterogeneous icosahedral, octahedral, and tetrahedral charge decoration. With its complexity, this versatile and rather general model is able to describe, for instance, virus capsids. However, the emerging analytical expressions for the interaction free energy between two such shells seems to be too complex to be amenable to simulations and/or theoretical frameworks.

For completeness one should also mention in this context colloidal particles whose surfaces are not explicitly decorated with charges but rather carry an explicit (dipolar, quadrupolar, etc.) moment, which might originate from an inhomogeneous surface charge decoration.

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