



# Packing, entropic patchiness, and self-assembly of non-convex colloidal particles: A simulation perspective



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## ABSTRACT

Recent advances in experimental techniques to synthesise particles with non-convex shapes have provided new challenges and opportunities to the modelling community. The availability of such building blocks has motivated many computational studies on the formation of new materials driven by such complex effects as interpenetration, interlocking, and shape complementarity that, if properly harnessed, have the potential of acting as entropic directional (patchy) interactions in particles with non-convex geometries. This article highlights recent molecular simulation studies of anisotropic non-convex colloidal particles with particular emphasis in particles interacting via excluded volume.

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## 1. Self-assembly in colloidal systems

The shape of colloidal particles is one of the most important features that dictates their complex collective behavior. As a result of recent advances in experimental techniques that allow the synthesis of colloidal particles with arbitrary shape and size [1,2<sup>\*</sup>–4], it is currently possible to use these particles as building blocks for the self-assembly of complex structures. Colloidal particles are appealing not only for fundamental studies as they are often large enough to allow direct observation of their self-organisation and dynamics, but also for applications as it is their size what makes them suitable candidates for the fabrication of mesoscopic structures that are not easily attainable using molecular systems [5,6]. Furthermore, the ability to tune the repulsive and attractive contributions of the inter-particle interactions by changing the properties of both the particle surface (surface charge, functional groups, tethered ligands, etc.) and the solvent medium has made possible an unprecedented level of control of complex structural designs [7–10].

In the absence of significant attractive interactions, the properties of colloidal suspensions are mainly determined by packing effects

that tend to increase the particles' translational entropy, thereby decreasing their free energy [11]. Computer simulations of hard-core particles, i.e., particles interacting purely by steric interactions, have played a central role in understanding the structure and order-disorder transitions of colloidal systems [12<sup>\*</sup>]. Numerous simulation studies have been reported focusing on the behavior of spherical particles and many other convex-shaped geometries, including unusual shapes like polyhedra [13–15]. For certain faceted convex shapes, the concept of entropic patchiness has been introduced to describe the entropic directional forces taking place in the systems even in the absence of attractive interactions that promotes the formation of ordered faces. These forces emerge from the collective behavior of the colloidal systems at sufficiently high concentrations [15,16]. Colloidal particles with non-convex geometries, however, have received far less attention despite the significant advances that have been made in experimental techniques for their fabrication. Some examples of non-convex particles available with existing experimental techniques are shown in Fig. 1. A particle is said to be non-convex if, there exist two points inside the particle such that the line segment connecting them does not lie entirely inside the particle. This geometrical representation of non-convex particles is shown in Fig. 1 (a). Different descriptors can be used to characterise the degree of anisotropy of the particles such as aspect ratio, circumscribed sphere radius, and isoperimetric quotient [16–18]. It is also useful to adopt a metric to describe the degree of convexity  $\zeta$  of particles having arbitrary shape. One such choice, sketched in Fig. 1 (b), is to define  $\zeta$  as

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the ratio of the volume of a particle  $V_p$  to the volume of its convex envelop (convex hull)  $V_{ch}$ , i.e.,

$$\zeta = \frac{V_p}{V_{ch}}. \quad (1)$$

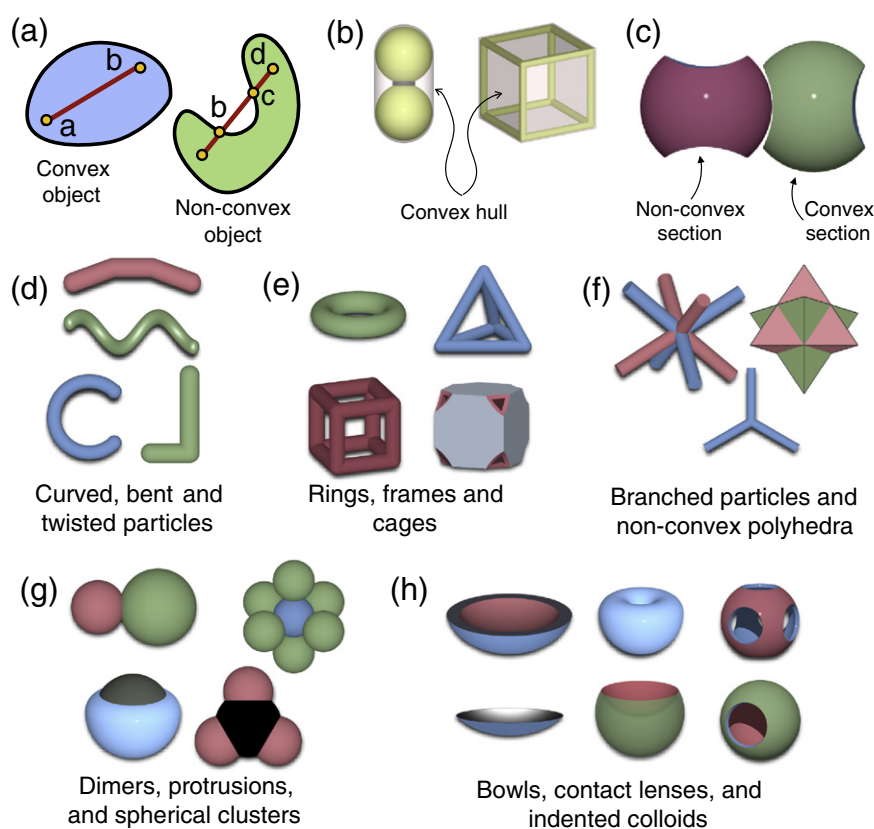
Note that in the limit of  $\zeta \rightarrow 1$  a particle becomes convex, while  $\zeta \rightarrow 0$  indicates high degree of non-convexity. Alternatively, one could identify shape-complementary patches in the particles, e.g., by the convex and non-convex regions of two particles that fit closely together (akin to entropic lock-and-key or patchy attractions, see Fig. 1 (c)). Some of the earlier examples of non-convex shapes investigated were slight variants of their convex counterparts, such as the case of “banana”-shaped particles shown in Fig. 1 (d) [19,20], whose phase behavior provided interesting departures to the known liquid-crystalline phases of rods and spherocylinders. Arguably, polymers, which have been extensively studied and are often modelled as bead-spring chains, can be regarded as “flexible” or re-configurable non-convex Brownian objects. Although some of the peculiar characteristics of polymer–polymer interactions (like the tendency to form entanglements) are ubiquitous in non-convex shapes, this review is only concerned with “rigid” particles that lack conformational entropy; however, small oligomers and dimers in particular constitute a natural point of intersection and divergence between those two classes of materials.

In general, single-component non-convex particles do not pack very efficiently since they are characterised by a free volume within their convex hull that is often inaccessible to neighbouring particles. This is particularly evident when the degree of convexity  $\zeta \rightarrow 0$  such as in the case of thin rings (see Fig. 1 (e)) [21,22\*] and branched

colloids [23\*] (see Fig. 1 (f)). Inefficient packing in this context, however, does not always imply disordered states. In fact, several studies have shown that highly symmetric non-convex particles can form ordered structures having high free volumes, i.e., porous ordered materials [22\*,23\*,24\*,25].

Non-convex particles offer many possibilities for the fabrication of functional materials as a result of their ability to self assemble into unique structures driven by mechanisms absent in convex particles such as particle interlocking, entanglement, and interpenetration [21,24\*,29]. These emerging materials are thus promising in a broad range of applications including drug delivery and therapeutics [30,31], catalysis [32], sensing [33], photonics [34,35], absorption [36\*] and nanopattern scaffolding [37]. From a modelling perspective, NC particles represent multiple challenges. For instance, global ergodic equilibration can be compromised by the occurrence of local interlocking configurations. Furthermore, in most cases, the particle geometry and the interparticle hard-core repulsion cannot be represented via a simple analytical form. With some exceptions, most recent attempts to model non-convex particles involve outlining a shape by an ensemble of smaller convex objects. For example, branched colloids have been modelled as ensembles of rod-like particles [38], rings have been modelled as rigid ensembles of spheres [22\*,29,39], and even more complicated geometries have been represented using triangular tessellation methods [24\*]. While generally effective and adaptable, such “multi-site” particle models tend to be computationally more expensive than those that can describe particle interactions via a single mathematical function.

The introduction of surface roughness to selected areas of convex colloidal particles has been shown to be an effective means to induce directional interparticle attractions in the presence of depletants



**Fig. 1.** Geometrical representation of (a) convex and non-convex objects and (b) the convex hull envelope used to define the degree of convexity  $\zeta$  of an object, exemplified here for a dimer and a cubic frame; (c) example of a particle shape containing both convex and non-convex (patchy) sections. Two particles are shown forming a lock-and-key bond. Examples of non-convex particle shapes that are accessible with current experimental techniques: (d) curved (banana shaped) and twisted particles, and circular segments [39–41]; (e) frames, rings, and cages [30,32,42–44]; (f) branched particles and non-convex polyhedra [23\*,45–48]; (g) dimers, clusters and protruded particles [49,50]; (h) bowls, lenses, indented and multicavity particles [51–53\*\*,54\*,55].

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