



# Entropic patchiness: Effects of colloid shape and depletion



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## ARTICLE INFO

### Article history:

Received 4 May 2017

Received in revised form 30 May 2017

Accepted 31 May 2017

Available online 06 June 2017

## ABSTRACT

This paper reviews 'entropic patchiness' of colloidal particles. On the one hand this may be due to their intrinsic tendency to form certain shape-dependent configurations in crowded suspensions, on the other hand this can be strongly enhanced by using depletion interactions that are also of purely entropic origin. A brief account of the Onsager theory and its consequences for the formation of colloidal liquid crystals of highly anisometric particles is presented. It is further supplemented by a recap of the description of depletion attraction between colloids and the effects of their shape. A number of recent examples exploiting entropic patchiness are discussed.

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## 1. Introduction

Patchy colloids form an actively developing theme of contemporary research that opens up a wide range of possibilities towards rationally-designed colloidal structures [1,2,3,4]. The term patchiness is often associated with chemical or physical surface modifications using for example patterned coatings [5] or magnetic inclusions [6] inducing strong directionality in the interactions between the particles. In this paper, however, a different type of 'patchiness' is discussed. We shall consider the behaviour of colloids that have a chemically homogeneous surface without magnetic inclusions while the directionality in their mutual interactions has a purely entropic origin.

Entropy determines the behaviour of a dense suspension of colloids with only hard-core excluded volume interactions, i.e. particles that display a steeply rising repulsion at contact but do not interact with each other when their surfaces are further apart. Isotropic spherical particles form close-packed structures with face-centred cubic (fcc) or random-stacking hexagonal crystals (rhcp) at concentrations above the freezing point of about 50 vol% [7,8], where many-body entropic interactions determine the bond-order, i.e. the angles between the directions from a central sphere towards its nearest neighbours (e.g., for fcc one finds angles of only 60°, 90°, 120° and 180°). However, the structure and the bond order can be affected when the particle shape is changed to, for example, that of truncated spheres, various polyhedra or superballs (i.e., cubes with rounded edges) [9–17]. This effect is induced by

facet alignment and has been rationalized as the emergence of "directional entropic forces" [10,11]. For highly anisotropic colloids such as rods, platelets and boards, a number of liquid crystalline phases appear [18–22] as a result of the interplay between different entropic contributions. It can also be seen as an effect of the strong directionality in the entropic interactions between the particles. The entropic interactions can be further modified by adding smaller particles or nonadsorbing polymer to the system [23], which can induce effective attraction between colloids.

The structure of this article is as follows. In Section 2 we briefly overview the phase behaviour of suspensions of hard-core particles forming colloidal liquid crystals. It includes a recap of Onsager theory of colloidal nematic liquid crystals and a discussion of the origin of the biaxial phases and spatially-inhomogeneous phases with positional ordering. An introduction to depletion attraction and to the effects of the particle shape is given in Section 3. A few applications of entropic patchiness are described in Section 4. Finally, concluding remarks are given in Section 5.

## 2. Colloidal liquid crystals

In the 1940s Onsager [24] presented a statistical mechanical theory to describe the isotropic-nematic phase transition observed in dispersions of rod-like and plate-like colloidal particles. For hard-core interactions we may formulate it as the entropy per particle (given as a deviation from its ideal translational value  $S_{ideal}$  and in units of the Boltzmann constant  $k_B$ ) as a function of the number density  $\rho \equiv N/V$ :

$$\frac{S - S_{ideal}}{Nk_B} \approx -\langle \ln f \rangle - \frac{1}{2} \rho \langle \langle v_{excl} \rangle \rangle + O(\rho^2) \quad (1)$$

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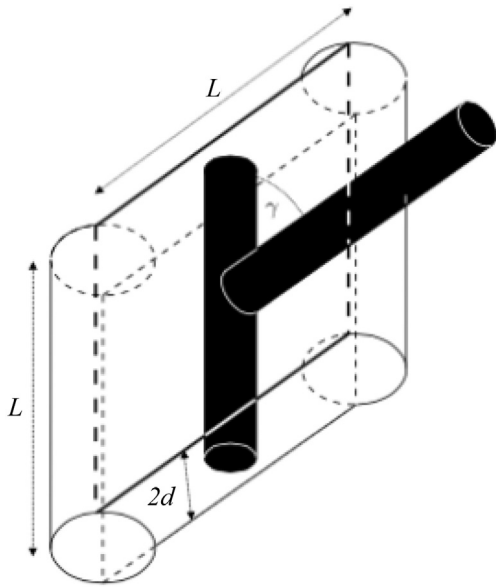


Fig. 1. The excluded volume of two rods of length  $L$  and diameter  $d$  at a mutual angle  $\gamma$ .

The first term represents the loss of orientational entropy when the orientational distribution function  $f$  becomes non-uniform and is given by the orientational average  $\langle \dots \rangle$  of its logarithm. The second (so called second-virial) term represents the relative reduction of the available volume at the level of two-particle interactions, the ratio of the total excluded volume  $\frac{1}{2}N\langle v_{\text{excl}} \rangle$  per particle to the total volume  $V$  of the system. The higher virial terms, indicated by  $O(\rho^2)$ , involve three- and more-particle interactions and the correspondingly higher powers of  $\rho$ . The driving force of the isotropic-nematic transition occurring above a certain particle density is the reduction of the excluded volume upon aligning the particles as soon as the increase of this “packing” entropy starts to outweigh the loss of orientational entropy.

Fig. 1 illustrates how the excluded volume of two rods at a mutual angle  $\gamma$  depends on their length  $L$  and diameter  $d$ :

$$v_{\text{excl}} = 2L^2d \sin\gamma + O(Ld^2). \quad (2)$$

The angular dependence of the leading term – when averaged over the orientational distribution of each rod as in Eq. (1) – drives the system to the nematic phase at higher densities. The correction terms in  $v_{\text{excl}}$  relate to end effects and are at least a factor of  $d/L$  smaller. They can be neglected for long, thin rods ( $d \ll L$ ) even in the nematic phase; although  $\langle \sin \gamma \rangle$  is obviously smaller than in the isotropic phase, it is found to be independent of  $d/L$  at the phase transition.

The balance between the isotropic and nematic phase is found to tip at a volume fraction<sup>1</sup>:

$$\phi^* (= v_{\text{rod}}\rho^*) = 4 \frac{d}{L}. \quad (3)$$

This shows that the transition takes place at increasingly lower volume fractions for larger aspect ratios  $L/d$  and the fact that in this limit the higher order terms in  $\rho$  in Eq. (1) are also of order  $d/L$  smaller leads to a fully consistent theory. The essential point is that purely

entropic effects favour the approach of the sides of the rods above configurations involving an end face of one of the rods.

Onsager also evaluated the excluded volume between two platelets of diameter  $d$  and thickness  $T$ :

$$v_{\text{excl}} = \frac{\pi}{2} d^3 \sin\gamma + O(Td^2), \quad (4)$$

which has the same angular dependence as rods, Eq. (2), and therefore without any further calculation leads to the analogous result:

$$\phi^* (= v_{\text{plate}}\rho^*) = \frac{16}{\pi} \frac{T}{d}. \quad (5)$$

Above this volume fraction the entropic balance tips from the isotropic to the nematic side and the platelets start to align their short (symmetry) axis. However, as Onsager noted himself, this result is only a rough approximation<sup>2</sup> in this case because the higher order terms in  $\rho$  cannot be neglected anymore. Qualitatively we can argue that the platelets have an entropic preference to lie face-to-face in this case.

The above-mentioned preference for contacts between specific faces of anisometric particles shows up even more clearly when particles have three distinct dimensions in three perpendicular directions: length  $L$ , width  $W$  and thickness  $T$ . In that case the excluded volume is considerably more complicated [25] and the orientational distribution may become biaxial depending on the size ratios (see Fig. 2).

Whereas particles on the rod-like side only align their long axes and particles on the plate-like side only orient their short axes, in a small area of size ratios close to  $L/W \approx W/T$  the longest and the shortest axes both have a tendency to align forming a biaxial nematic ( $N_b$ ) phase at higher volume fraction. This effect was predicted a long time ago [27] and supported by computer simulations for hard ellipsoids [26], but its actual realization in suspensions of purely repulsive, rectangular particles [28,29] took a long time.<sup>3</sup> The existence of biaxial nematic phases implies preferred contacts between the same faces of rectangular particles, although the tendency is not that strong.

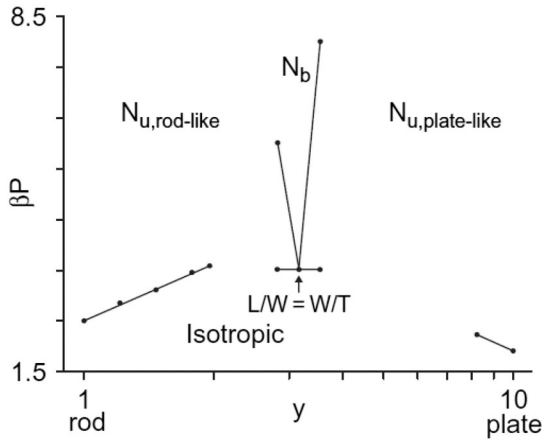
At higher volume fractions the orientational ordering described above can be coupled to spatial inhomogeneities when (some of) the spatial coordinates of the particles come into register, which may lead to additional packing entropy due to the increase of free volume on a local scale. The latter mechanism is analogous to the one behind the famous gas-solid phase transition of hard spheres, and likewise was first found by computer simulations [30,31] leading to a host of additional entropically induced liquid crystal phases, such as different smectic and columnar phases spatially ordered in one or two dimensions respectively. Also this may qualitatively be described as a tendency to maximize contacts between identical faces of the particles.

In some cases also mixtures of hard particles can be brought under the same heading, such as the formation of a biaxial nematic in mixtures of platelets and rods where the longest dimensions of both particles align in one common direction and the shortest dimensions in another [32]. The same goes for mixtures of rods and spheres, where the surface (or rather projected surface) of the spheres matches better with the end of the rod-like particles than with their length [33,34]. Of course one should be careful not to overemphasize this, since in mixtures also the entropy of mixing plays an important role and ultimately it is the three-dimensional interplay between the particles which determines the entropy rather than the individual contacts between their sides. As described in the next section, this becomes different when one of the components can act as a depletion agent which can really increase the tendency of contact between certain sides of the particles.

<sup>2</sup> In fact computer simulations showed that in this case the transition is very weakly first-order [31].

<sup>3</sup> Biaxiality remains a matter of debate in thermotropic liquid crystals; ref. [67] provides a recent, extensive review of biaxial nematics in different systems.

<sup>1</sup> The full calculation actually shows a first-order phase coexistence between two volume fractions [18]:  $\phi = (3.29 \leftrightarrow 4.19) \frac{d}{L}$



**Fig. 2.** Simulated phase diagram (pressure  $P$  vs.  $y = W/T$ ) of a hard fluid of biaxial ellipsoids with  $L/T = 10$ . Adapted with permission from Ref. [26]; copyright 1997, American Institute of Physics.

### 3. Depletion interaction and directional, entropic attractions

In the 1950s S. Asakura and F. Oosawa [35,36] presented a statistical mechanical theory for the effective interaction between colloidal particles immersed in a solution of ideal polymers. As boundary condition they assumed the polymer segment concentration vanishes at the particle surface [37,38]. This means the polymer segments have no significant adhesive or repulsive interaction with the surface [39] and hence are nonadsorbing. As a result, near the surface of the particles a layer exists in which there is negative adsorption of polymer segments: the segment concentration close to the surface is smaller than in the bulk. This depletion layer (with thickness  $\delta$ ) arises from the excluded volume between a polymer chain and the colloidal particles [40]. When depletion layers overlap in crowded systems, the overlap volume (gray areas in Fig. 3), becomes available for the depletants (in this case polymers). In such cases the polymers can lower their osmotic pressure which lowers the free energy of the system. The resulting effective depletion interaction [41–43], between two particles, separated at a closest distance of their surfaces  $h$ , reads [23]:

$$W(h) = \begin{cases} \infty & \text{particle overlap} \\ -\Pi V_{\text{overlap}}(h) & 0 < h < 2\delta \\ 0 & h > 2\delta \end{cases}, \quad (6)$$

where  $\Pi$  is the osmotic pressure of the depletants and  $V_{\text{overlap}}$  is the overlap volume. It is noted that the depletion interaction [42,43] is an attraction through repulsion, so it is a purely entropic effect. It is an *indirect* attraction between particles driven by excluded volume interactions. In crowded systems, excluded volume interactions can lead to phase transitions [44–46] and ordered structures [47,48]. In recent years the term enthalpic depletion [49,50] is used, but this merely refers to the fact that in real systems the interactions in crowded systems are not only governed by the entropic excluded volume interactions, but can also be affected for instance by direct Van der Waals attractions and double layer and/or steric repulsions. Moreover, in case the particles of interest get small, details of (complex) molecular interactions must also be accounted for. All these aspects however only concern detailed refinement of describing real systems.

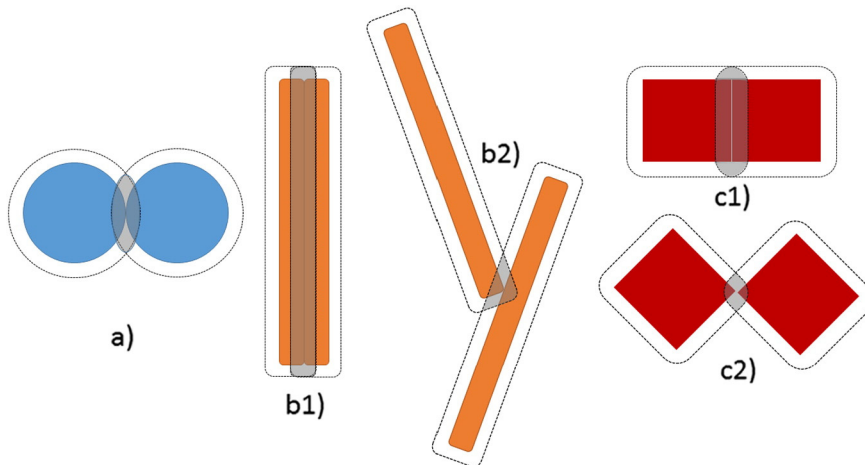
In Fig. 3 overlap volumes are indicated for particles of variable shapes. For isotropic spheres the overlap volume reaches a maximum value,  $V_{\text{overlap}}^{\text{max}}$ , as the spheres touch, see Fig. 3a. For anisotropic particles  $V_{\text{overlap}}^{\text{max}}$  depends on the orientation of the particles. When comparing the overlap volumes in Fig. 3b1 and b2 it becomes clear the overlap volume is maximized for rods as the particles align with their largest surface areas close to each other. Hence aligned rod configurations are induced by the depletion effect. For cubes  $V_{\text{overlap}}^{\text{max}}$  is achieved when two (flat) edges are aligned, see Fig. 3c1 and c2.

It follows that, in contrast to isotropic particles, anisotropic particles assume preferred configurations in order to maximize the overlap volume. In other words, the depletion effect turns anisotropic particles patchy: an indirect attraction between those surfaces that leads to larger overlap volumes is preferred.

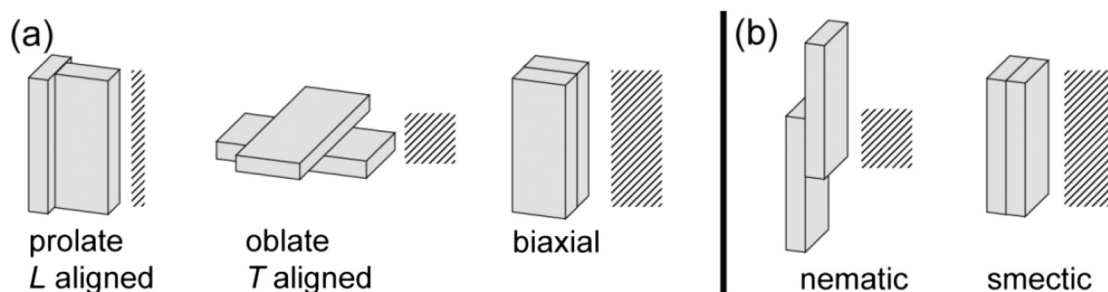
Eq. (6) holds quite generally for the depletion interaction between two particles of various shapes for relatively small depletion thickness. For relatively small values of the depletion thickness  $\delta$ ,  $V_{\text{overlap}}^{\text{max}}$  can be written down in the following manner for spheres, cubes, rods and platelets

$$V_{\text{overlap}}^{\text{max}} = \begin{cases} \sim \sigma \delta^2 & \sim V_{\text{particle}} (\delta/\sigma)^2, & \text{spheres with diameter } \sigma, \\ \sim L d^{1/2} \delta^{3/2} & \sim V_{\text{particle}} (\delta/d)^{3/2}, & \text{rods with length } L \text{ and diameter } d, \\ \sim \tau^2 \delta & \sim V_{\text{particle}} (\delta/\tau), & \text{cubes with edge length } \tau, \\ \sim D^2 \delta & \sim V_{\text{particle}} (\delta/T), & \text{platelets with diameter } D \text{ and thickness } T. \end{cases} \quad (7)$$

It becomes clear that, for fixed depletion thickness  $\delta$ , the overlap volume of depletion zones between cubes, rods and platelets is much larger than the overlap volume between spheres for fixed particle volume. When comparing cubes with size  $\tau$  and spheres with diameter  $\sigma$ , conservation of particle volume implies  $\tau$  is about 80% of  $\sigma$ . Hence it follows



**Fig. 3.** Illustration of the excluded volume between a) spheres, b) rods and c) cubes with fixed particle volume, mediated by depletants that induce a fixed depletion thickness (indicated by the dashes).



**Fig. 4.** Simplified schematic drawings illustrating two neighbouring particles and their corresponding overlap volumes (equal to the striped areas times the size of the depletant). Panel (a) illustrates that biaxial mutual orientations are promoted relative to prolate and oblate configurations. Panel (b) shows that a smectic rather than nematic structure can be facilitated by depletion. Reproduced from Ref. [56].

that  $V_{\text{overlap}}^{\text{max}}$  is about 25 times larger for cubes than for spheres in the case of (as an example)  $\sigma = 20\delta$ . This is understandable: when the cubes approach with their flat faces and touch, a volume of  $27\delta^3$  overlaps. The 'overlap fish' in case of two big spheres is obviously much smaller, as is also clear from Fig. 3 (compare the overlap volume in 'a' to 'c1'). Two rods with depletion layers surrounding them tend to align [51] in order to maximize the overlap volume; compare Fig. 3b1 and b2. For large aspect ratio  $L/d$ , conservation of volume implies  $L \gg \sigma$ . Hence it follows the maximum overlap volume is much larger for aligned rods. In a way, the case of two parallel platelets can be compared to the case of two cubes: maximum overlap volume implies the platelets orient in a parallel manner and the maximum overlap volume scales as  $D^2\delta$ . Again, since  $D \gg \sigma$  when the volumes of a sphere and a platelet are set equal, the overlap volume will be much larger in case of the platelets. The preferred alignment of anisotropic particles is also reflected in the phase behaviour of such particles with added nonadsorbing depletants [51,52–55]: depletion forces enhance the

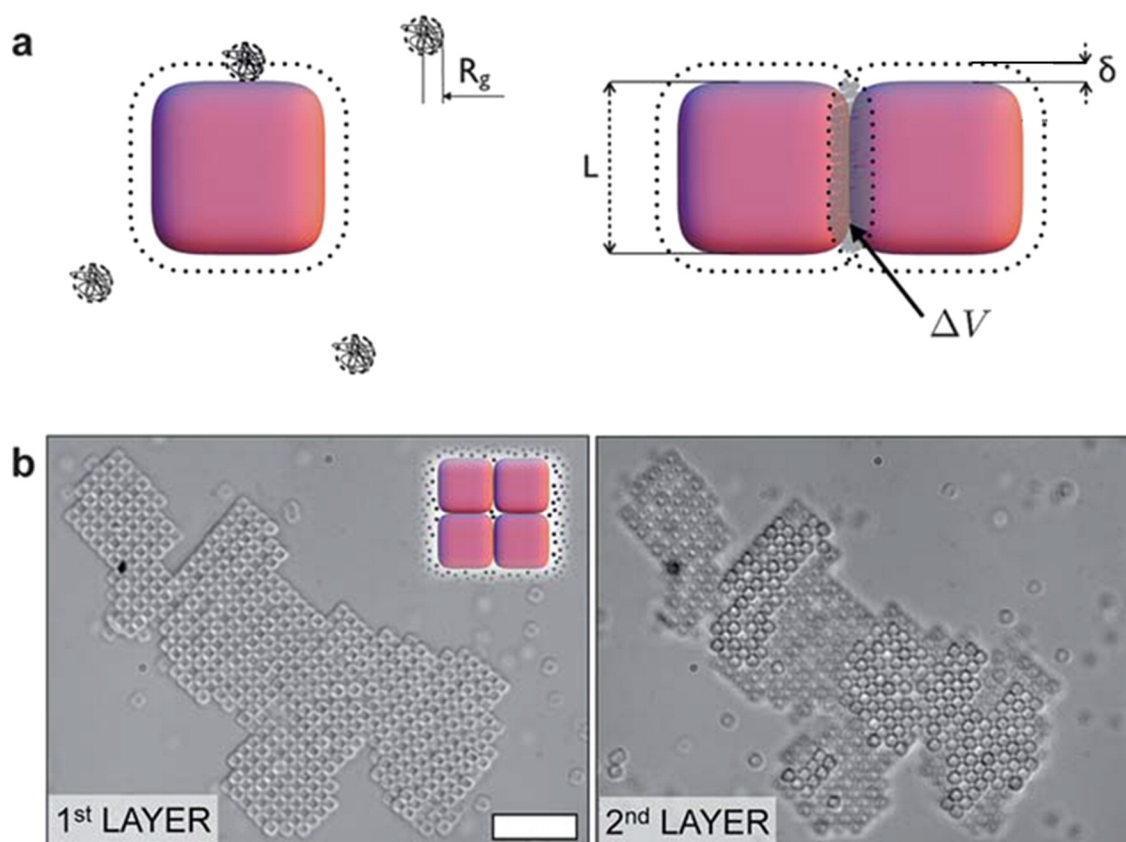
occurrence of liquid crystalline phases, especially when a short-ranged attraction is induced.

#### 4. A few examples of entropic patchiness

In this section we shall illustrate the entropic patchiness of shape-anisotropic colloids and the use of depletion interactions by a few examples from recent literature.

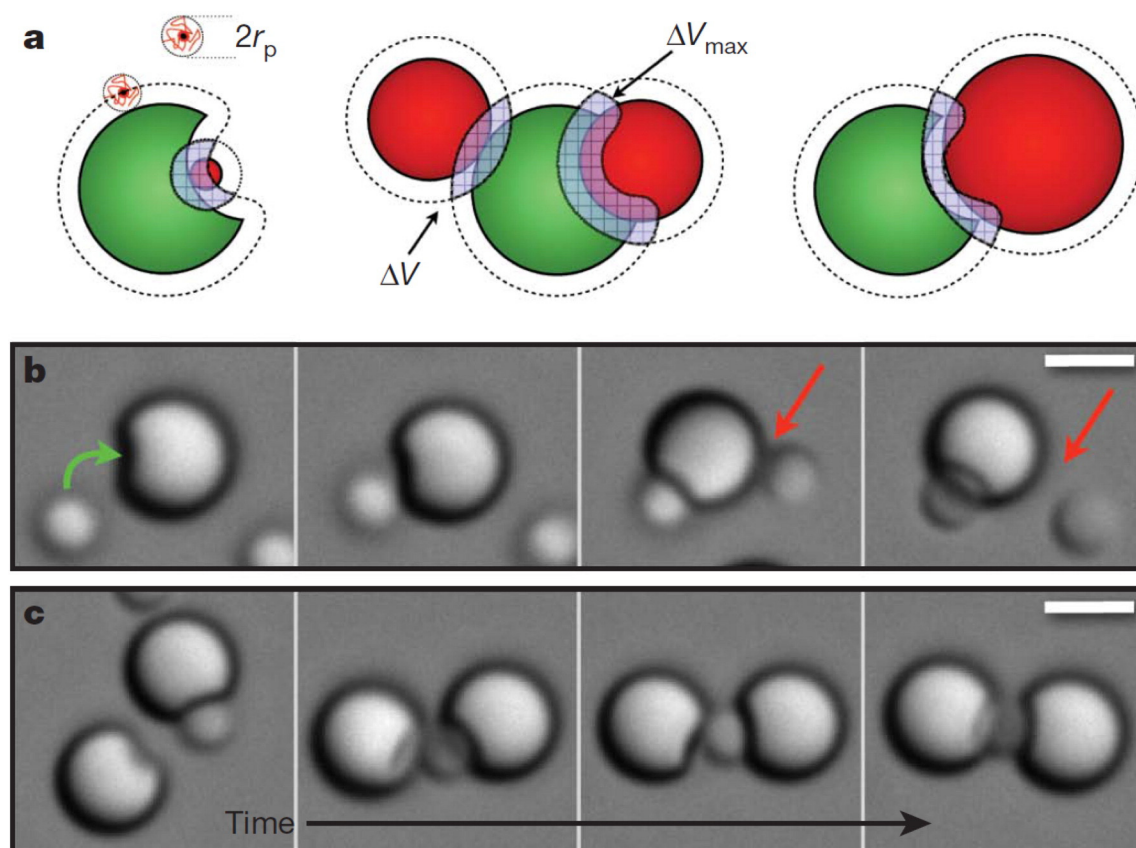
In the previous section, it was already mentioned that the depletion interaction can tune the phase diagram of liquid crystals because of the induced preferential alignment of anisometric particles. This tendency is of particular interest for biaxial rectangular particles which have 3 different faces and could interact differently in different combinations as schematically indicated in Fig. 4.

Fig. 4a shows the difference in the typical area of approach and hence overlap volume of the depletion zones in a uniaxial rod-like (prolate) nematic, a uniaxial plate-like (oblate) nematic and a biaxial



**Fig. 5.** a. Illustration of the depletion effect between cubic particles with rounded edges of size  $L$  induced by a depletant agent of radius  $R_g$ . b. Optical micrographs of a small colloidal crystal with focusing on its bottom layer (left) and the layer above it (right). Adapted from Ref. [59\*] with permission from The Royal Society of Chemistry.





**Fig. 6.** a, Illustration of the depletion interaction between a lock and a key particle. The maximum overlapping excluded volume,  $\Delta V_{\max}$ , is achieved when the key particle precisely fits into the spherical cavity of the lock particle. b, c, Snapshots from a video showing examples of depletion-driven self-assembly of lock and key colloids. In b the site specificity is illustrated showing an example of a successful (green arrow) and unsuccessful (red arrow) attachment. In c the formation of a dimer of two lock particles using one key is illustrated. Reproduced from Ref. [61<sup>\*\*\*</sup>] with permission from The Nature Publishing Group.

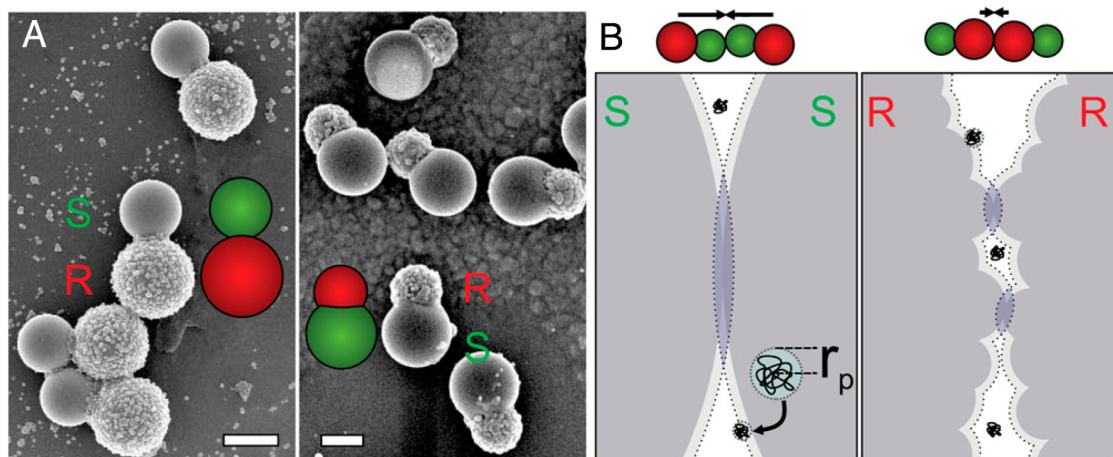
nematic. Depletion-mediated attraction clearly favours the biaxial nematic phase as is also borne out by theoretical calculations of the corresponding phase diagram by Belli et al. [57] using the Zwanzig model.<sup>4</sup> Fig. 4b indicates a preference for two aligned biaxial particles to shift into register under the influence of depletants. This could favour the formation of smectic at the expense of nematic states. These notions were tested in an exploratory study of mixtures of goethite ( $L/W \approx W/T \approx 3.2$ ) with silica spheres of diameter approximately equal to  $T$  [56]. Without depletant, a low (around 15%) polydisperse goethite system displayed *isotropic* - *nematic* - *smectic* phase separation, whereas a very similar but more (27%) polydisperse system showed *isotropic* - *biaxial nematic* phase separation. A higher polydispersity by itself is indeed expected to suppress the smectic phase as well as enhance the biaxiality [58]. Using SAXS (Small-Angle X-ray Scattering) a direct *isotropic* - *smectic* phase transition was identified for both systems upon addition of a depletant, which induced the formation of the smectic phase, while the formation of the nematic phase was suppressed. The depletion induced attraction also decreased the particle spacing within the layers, while the interlayer periodicity increased. This suggests that – similar to what was reported in refs. [33<sup>\*\*\*</sup>, 34<sup>\*\*\*</sup>] – the depletant could have induced microphase separation, where the spherical depletant particles are expelled from the layers and subsequently located in between the layers of goethite particles. The smectic phases also showed signs of biaxiality, although this could not be as fully elucidated as in ref. [28]

because in this case the smectic phase was unresponsive to small magnetic fields possibly also due to the presence of depletants. It would be very interesting to perform a similar study with polymeric depletants.

Another selected example is that of colloidal superballs whose behaviour can be tuned using depletion interactions. As discussed in Section 3 for cubes, adding depletants can introduce an effective attraction, which is the strongest between the flat sides of superballs making them effectively patchy. As a result, a simple cubic arrangement of the particles can be achieved [59<sup>\*\*\*</sup>] as illustrated in Fig. 5. Interestingly, the structure can be tuned by varying the strength and the depth of the depletion attraction. For example, one can use thermosensitive poly(*N*-isopropylacrylamide) (pNIPAM) microgel particles as depletant. These depletant particles can shrink in size upon heating. As a result, the strength of the depletion attraction reduces [cf. Eqs. (6) and (7): the overlap volume reduces for smaller  $\delta$ ] leading to melting of the crystals [59<sup>\*\*\*</sup>]. On the other hand, when a depletion agent is larger than the size of the hole between neighbouring cubic particles with rounded edges, the structure switches to rhombic [15,60]. The latter effect can be also seen as an effect of reduction of the directionality of the depletion attraction.

An excellent example of purely entropic patchiness is provided by the lock-and-key colloids [61<sup>\*\*\*</sup>]. A combination of colloidal spheres as keys with particles with a spherical cavity as locks can lead to spontaneous binding of the two using depletion interaction as illustrated in Fig. 6. The lock-and-key binding is specific because it is controlled by the match between the size of the key and the radius of the spherical cavity of the lock particle. The strength of the binding can be easily controlled by the concentration of the depletant. Moreover, by using thermosensitive spherical pNIPAM microgel particles, the size of the key can be tuned by the sample temperature. The

<sup>4</sup> Note that the Zwanzig model used in references [57,58] allows for only six possible particle orientations. In future research, it would be important to use a full set of orientational degrees of freedom since this might seriously influence the outcome of these theoretical predictions.



**Fig. 7.** a, Dumbbell colloids synthesised in Ref. [62<sup>•</sup>] consisting of a sphere with rough surface (R, red) and a sphere with smooth surface (S, green). b, In the presence of small depletants (here depicted as polymers with radius  $r_p$ ) the overlap of the depletion zones (dotted line and light-gray area) is much larger for the contact between two smooth surfaces than in the case of rough-rough or rough-smooth surfaces. Small arrows represent the effective forces on both colloids. Adapted from Ref. [62<sup>•</sup>] published by the National Academy of Sciences.

flexibility of the bonding allows production of dimeric, trimeric and tetrameric colloidal ‘molecules’ as well as colloidal ‘polymers’.

Another approach to achieve entropic patchiness is the variation of surface roughness in combination with depletion [62<sup>•</sup>,63–65]. Smooth patches on rough colloids appear to be exclusively attractive due to their different overlap volumes as illustrated in Fig. 7. Such entropically-patchy colloids can serve as a model for molecular surfactants both with respect to their geometry and their interactions. They are shown to be able to assemble into clusters that resemble ‘colloidal micelles’ with the smooth and attractive sides of the colloids located at the interior [62<sup>•</sup>]. By adding larger smooth spheres to this system, their encapsulation by the ‘colloidal surfactant’ particles can be observed [66].

## 5. Concluding remarks and opinion

To summarise, in this review we have presented some of the general principles of the entropy-driven effects leading to directional and site-specific interactions between colloidal particles that can be seen as a kind of “entropic patchiness”. A summary of well-established and widely recognised concepts is here combined with examples of contemporary research, which are, to a large extent, based on the same concepts.

In particular, we have given a brief recap of the Onsager theory [24] that provided theoretical grounds for the entropic effects in liquid crystals. The key ingredient here is the interplay of the orientational and excluded volume contributions to the total entropy of the system. Qualitatively, the produced effect can be also seen as an effective “directional entropic force” [11] that promote strong orientational correlations or “bond order” between neighbouring particles. Furthermore, a short summary of the depletion interactions [23] (attraction through repulsion) is given. Special attention is paid to the effect of the shape of the particles.

The consequences of these fundamental concepts leading to shape-dependent entropic patchiness in the presence of depletion interactions have been illustrated using a few examples from recent literature. These include the influence of the depletion interaction on the stability of the biaxial liquid-crystalline phases, one of the ‘holy grails’ of liquid crystal research [67]. The depletion effect is shown to be able to influence the symmetry of the colloidal crystals formed by cubes with rounded edges [59<sup>•</sup>]. Interestingly, it is not only the strength but also the range of the depletion attraction that is crucial [15]. We have further discussed depletion-mediated lock-and-key assembly that is specific for particles of a certain size [61<sup>•</sup>]. Last but not least the depletion attraction depends on surface roughness and can be used to yield site-specific interaction between colloidal particles [62<sup>•</sup>].

The selected examples presented above are yet relatively simple. Many of the concepts discussed here were recently illustrated in fascinating complex structures by Dogic et al. [68<sup>•</sup>,69]. Furthermore, the use of shape-shifting particles [70] gives the possibility for fine tuning of the entropic shape-dependent anisotropic interactions. Moreover, bio-inspired helical assemblies [71,72] have a great potential for future research of their chiral entropy-induced patchiness. An important role is played by theoretical studies and simulations [10–12,23,27,32,73–75], which provide justifications for the main concepts involved in entropy-induced self-organisation of colloids, help with interpretation of experimental data and are able to inspire new experiments.

This review is focused on entropy-induced effective patchiness of colloidal particles. On the other hand, such entropic patchiness can be complemented by enthalpic contributions [76], possibly also in combination with particle flexibility [77], providing a large parameter space for future research. However, the authors of this article are of opinion that during this obvious trend towards increasing the complexity of patchiness-induced assembly of colloidal particles, the entropic component will always play an important role.

## Acknowledgements

It is a great pleasure to thank Henk Lekkerkerker who is a great teacher and a big inspiration source for all three of us in many topics of colloid science including those discussed here. AVP and RT are indebted to our two universities for the offered possibilities to collaborate within the UU-TU/e alliance.

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