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# Self-Assembly of Colloidal Particles

a Combination of Experimental and Simulation Approaches

Riassunto di tesi di laurea sperimentale

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*There is no way around the hard work. Embrace it.*  
**Roger Federer**

# Introduction

A colloidal system can be defined as a dispersion of a certain substance as discrete parts called *colloids*, with size ranging from several nm to few  $\mu\text{m}$ , in a second phase, called a *continuum phase*, which is different either in composition or state of matter. From an industrial point of view, colloidal systems are of prominent importance as widely employed in a set of technological applications ranging from the food industry to paints, detergents and cosmetics. However, colloids attract a prominent interest also from a scientific perspective as they can be regarded as a model systems for understanding the thermodynamic behaviour of atoms and molecules. Like atoms and molecules, colloids experience continuous random motion, which is caused by the multiple collisions of the dispersed phase with the molecules of the solvent. On the other hand, being far bigger in size than atoms and molecules, colloidal dispersions move comparatively slowly and can be observed in real space using relatively simple microscopy techniques such as confocal microscopy or even brightfield microscopy.

In this project, a specific colloidal systems consisting of micron-sized silica particles suspended in a liquid phase was examined. In particular, we employed both real experiments and computer simulations for the study of the self-assembly of rods and spheres in spherical shrinking confinement. A spherical confining system could be experimentally achieved by creating a water-in-oil emulsion and by slowly decreasing the water droplet size through evaporation of the water phase (Figure 1). Due to the complex interactions governing the colloidal system, our investigation is expected to result in supraparticles constituted by colloidal particles arranged in an ordered configuration and stuck together by Van der Waals forces.

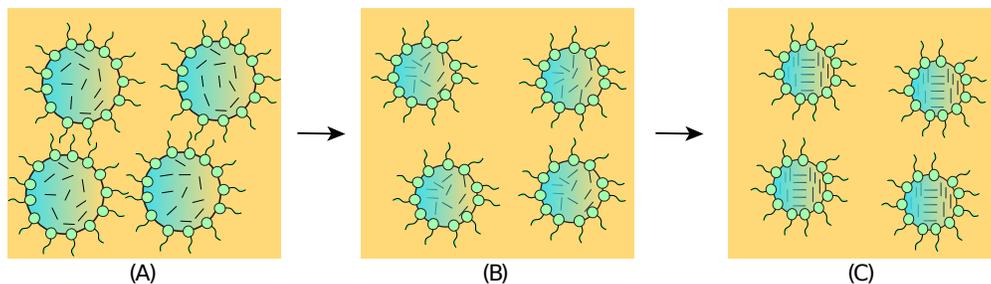


Figure 1: Scheme of the shrinking spherical confining conditions as experimentally explored in the present thesis. After preparation of a water-in-oil emulsion containing colloidal particles (**A**), water content is slowly evaporated so to increase particle concentration inside the water droplets (**B**). The method may in turn induce the *self-assembly* of particles in ordered structure (**C**), thus resulting in supraparticles which may be eventually isolated and collected for further studies.

# Theoretical Background

## Phase behaviour of hard particles

A *hard particle* is essentially a impenetrable particle, which means that the pairwise interaction potential is infinitely repulsive in case of overlap and zero otherwise. A so defined potential not only appears very convenient for both theoretical and computational studies, but was shown also suitable for the description of strongly repulsive atoms and colloids.

One of the research focus involving hard particles has been to explore their phase behaviour, which means their abilities to form physically distinctive form of matter. In particular, it may be shown that hard particles constitute a lyotropic system, which means that their phase behaviour depends only on the concentration of particles and not, for instance, on the temperature.

**Phase behaviour of hard spheres** A bulk system of hard spheres undergoes a transition from a fluid to a face-centred-cubic (FCC) crystalline phase by increasing the particle concentration. However, the crystallization pattern may be strongly reshaped in case spheres are confined in a shrinking spherical cavity. In particular, both computer simulations and experiments have recently showed that spherical colloids in a shrinking spherical confinement crystallize in a five-fold icosahedral structure rather than the usual FCC geometry [1].

**Phase behaviour of hard spherocylinders** The phase behaviour of spherocylinders attracts considerable interest due to their ability to display both positional or orientational order, thus forming the so-called *liquid crystal phases*. Well-known liquid crystal phases include the *nematic* - which display a full orientational order - and the *smectic*, in which particles exhibiting orientational order are also accommodated into layers [2]. Note that the spherocylinder phase behaviour depends on their aspect ratio  $L/D$  (with  $L$  the total particle length and  $D$  the diameter) and that liquid crystal phases generally appear only for high values of this parameter [3].

## Molecular Dynamics (MD) simulation

Molecular Dynamics is a simulation technique for computing the equilibrium and emerging behaviour of many-body systems. The main feature of the method is to evolve the dynamic of the system by use of the classical mechanics laws. Since force evaluation over a large collection of particles cannot be solved analytically, Molecular Dynamics approach provides

a numerical algorithm for approximately solve the problem. This goal is achieved by discretization of the temporal variable  $t$  in discrete values  $\Delta t$ . Given a initial set of positions and velocities for all the elements of the system, first the force potential related to each constituent is evaluated. Then, new positions and velocities are calculated iteratively for each timestep  $\Delta t$ .

**Brownian Dynamics (BD) simulation** The dynamic of a colloidal system is not only determined by the interaction between particles. In fact, molecules of the solvent also play a fundamental role, by inducing a random Brownian motion. In principle, we may evaluate the effect of the medium by performing a bigger Molecular Dynamics simulation in which we explicitly take into account the molecules of the solvent. However, a similar approach would be absolutely too computationally onerous. A much more convenient approach is therefore to consider the solvent as a continuum, and to take into account a Brownian random effect into the particle equation of motion [4].

In this project, evaluation of Brownian Dynamics were performed by employment of the *BAOAB-limit* algorithm recently reported by Leimkuhler *et al* [5] and which takes the form:

$$x_i(t + \Delta t) = x_i(t) - \frac{\Delta t}{m_i} \nabla U_i(t) + \sqrt{\frac{k_B T \Delta t}{2m_i}} (R_t + R_{t+\Delta t}) \quad (1)$$

where  $x_i$ ,  $U_i$  and  $m_i$  are respectively the position, force potential and mass of particle  $i$ ,  $k_B$  is Boltzmann's constant and  $T$  the absolute temperature.  $R$  is a random variable with a standard normal (gaussian) distribution of mean 0 and variance 1 and represent the stochastic part of the equation of motion.

In this project, simulated particles were modelled as interacting via a WCA potential, being it a steep repulsive potential which is computationally cheap to evaluate and close to the hard-particles model:

$$WCA \text{ potential} : U(r_{ij}) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] + \epsilon, & \text{for } r_{ij} \leq 2^{1/6} \\ 0, & \text{for } r_{ij} > 2^{1/6} \end{cases} \quad (2)$$

where  $r_{ij}$  indicates the distance between particle  $i$  and  $j$ . A likewise potential was also employed in describing the particle-confinement interaction.

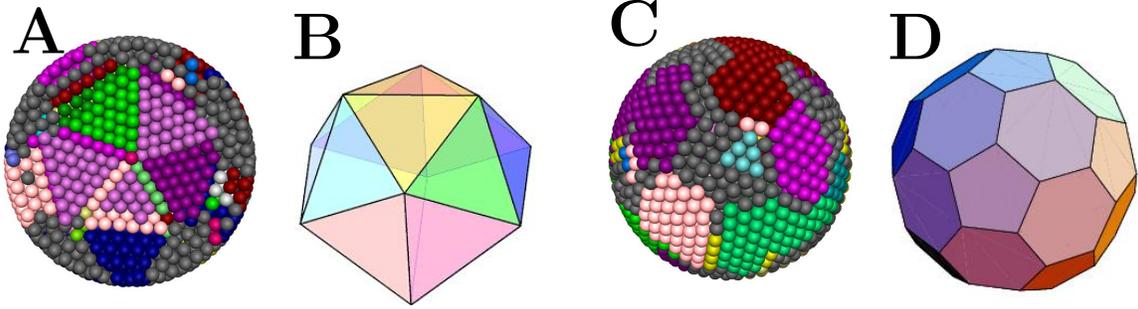


Figure 2: **A** Internal arrangement of  $N = 5000$  spherical particles in a shrinking confining cavity. The typical five-fold symmetry of an icosahedral configuration is visible. **B** Reproduction of a convex regular icosahedron solid. **C** External arrangement of a system composed by  $N = 2000$  spherical particles. Note that the crystalline structure seemingly constitutes a truncated icosahedron structure as shown in **F**. Different crystalline domains are identified with different colours and were determined by using the algorithm described by [6].

## Results and Discussion

### Self-assembly of spheres in spherical confinement

**Brownian Dynamics** Brownian Dynamics simulations were first employed for investigating the self-assembly behaviour of spheres in a spherical confinement. By a linear decrease of the confinement size, particle packing fraction  $\phi$  - defined as the ratio between the total volume of the particles and the volume of the confining cavity - was consequently increased. At high values of  $\phi$ , spheres were observed to arrange into distinctive icosahedral geometry, consisting of 20 FCC ordered tetrahedral domains that share a particle at the centre (Figure 2). Additionally, the surface of the supraparticles also exhibited a well-defined arrangement closely resembling the truncated icosahedron geometry, consisting of 12 pentagonal faces and 20 hexagonal faces. The result is in agreement with literature [1]. In particular, higher degrees of crystallization were generally detected by increasing the number of simulated particles and decreasing the shrinking rate of the confinement. The latter trend can be interpreted by considering that for rapid compressions, particles have less time for getting to a stable configuration and likely assemble in disordered structure.

**Synthesis of spheres** In order to experimentally explore the self-assembly of spheres, colloidal particles were synthesized according to Stöber method [7]. The procedure provided fluorescent-labelled silica spheres, which were subsequently coated with several non-fluorescent silica layers. In particular, the latter operation appeared mandatory as we aimed

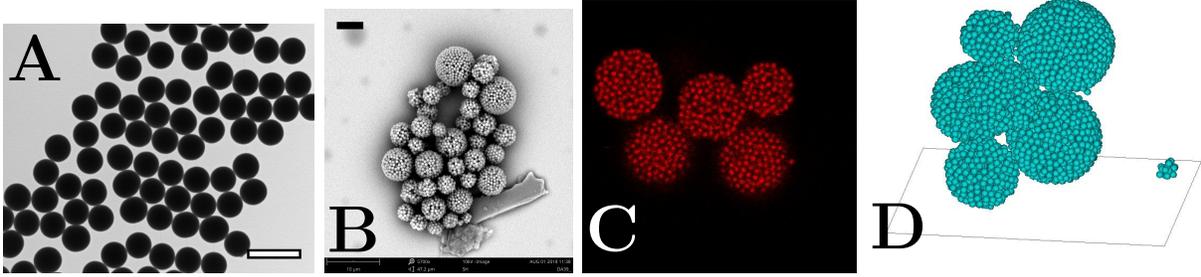


Figure 3: (A) TEM images of colloidal silica spheres (diameter  $D = 541$  nm, polydispersity  $\delta = 0.03$ ). Scale bar refer to  $1 \mu\text{m}$ . (B) SEM images of supraparticles as obtained through experimentally explored self-assembly in spherical confinement. Scale bar refer to  $5 \mu\text{m}$ . A few internal supraparticle structures have been unveiled by confocal microscopy (C) and finally reconstructed as (D).

to observe colloidal particles through laser scanning confocal microscopy (LSCM). In fact, imaging of dense systems with single-particle resolution can be achieved only if fluorescent signals belonging to different particles are separated by a non-fluorescent medium. Furthermore, the coating steps desirable increased the particle dimensions, thus diminishing the value of size polydispersity  $\delta$ . Indeed, it has been shown that high degree of polydispersity could negatively effect the self-assembly process of colloidal particles [8]. Transition electron microscopy images of the obtained spheres are reported in Figure 3, A.

**Experimental self-assembly** A spherical confining environment was achieved by using a water-in-hexadecane ( $\text{C}_{16}\text{H}_{34}$ ) emulsion with particles dispersed in the polar droplets. The confinement was therefore represented by the interface tension between the two phases composing the emulsion. A shrinking spherical confinement is then obtained by slowly evaporating the water content. Remarkably, our method resulted in well-shaped spherical supraparticles between  $2 \mu\text{m}$  and  $8 \mu\text{m}$  of size, consituted by colloidal particles stuck together by Van der Waals forces. By considering a final packing fraction of around 0.65, we could estimate supraparticles being composed by a number of spheres between 30 to 2000. Scanning electron microscopy (SEM) of the obtained supraparticles are reported in Figure 3, C.

In order to disclose the supraparticle internal strcture, confocal scanner laser microscopy (CLSM) was employed. Images taken of an agglomerate of supraparticles are shown in Figure 3, D. After taking a stack of several images at different depth into the sample, the full configuration of the supraparticle was reconstructed by using an appropriate sphere-tracking algorithm (Figure 3, E). As a result,we were able to reproduce the configuration and quantitatively analyse it. However, our results showed that only little order was present,

while no crystalline clusters were identified. This outcome was ascribed to high compression rates due to fast water evaporation.

## Self-assembly of rods in spherical confinement

**Order parameters** In order to quantitatively analyse simulation outcomes, local order parameters were introduced. In particular, the local nematic order parameter  $S_i$  of particle  $i$  was defined as [9]:

$$S_i = \frac{1}{n_i} \sum_{j=1}^{n_i} \left[ \frac{3}{2} \mathbf{u}_i \cdot \mathbf{u}_j - \frac{1}{2} \right] \quad (3)$$

where  $n_i$  is the number of neighbours of particle  $i$ , defined as the particles with center of mass closer than  $(L + D)/2$ , where  $L$  refers to the particle length and  $D$  to its diameter. Note that  $S_i$  ranges from -0.5 to 1.

A novel local smectic order parameter was here introduced with a similar form of the one already reported by Dussi [6]. We first calculated:

$$\Delta_i = 1 - \frac{1}{n_i} \sum_{j=1}^{n_i} \left| \frac{\mathbf{r}_{ij} \cdot \mathbf{u}_i}{|\mathbf{r}_{ij}|} \right|, \quad (4)$$

where  $\mathbf{r}_{ij}$  is the distance vector between the centers of mass of particle  $i$  and neighbour particle  $j$  and  $\mathbf{u}_i$  is the direction of the rod.  $\Delta_i = 1$  corresponds to the orthogonality condition between  $\mathbf{r}_{ij}$  and  $\mathbf{u}_i$ . In order to discriminate between the case rods are parallel or transverse one to the other,  $\Delta_i$  is multiplied by the local nematic order parameter  $S_i$ . We therefore defined  $\tau_i = S_i \Delta_i$  as the local smectic order parameter, so that a particle  $i$  was considered smectic ordered if  $\tau_i > 0.35$ . Finally, different smectic domains were identified for a more effective visualization of the structures. We considered two neighbours rods  $i$  and  $j$  as belonging to the same smectic domain if both particle were identified as smectic ordered and they were aligned one the other. The latter requirement was satisfied in the case their dot product  $\mathbf{u}_i \cdot \mathbf{u}_j$  was determined  $> 0.90$ .

**Brownian Dynamics** Brownian Dynamics simulations revealed that spherocylinders in spherical confinement locally form smectic layers for effectively filling the spherical cavity. However, the confinement clearly frustrated the formation of a single global smectic director. In particular, systems of different dimensions apparently exhibited the tendency to form a single major smectic domain at the core of the cavity. Moreover, two additional smectic domains were observed to form perpendicularly to it and perpendicularly one the other. By

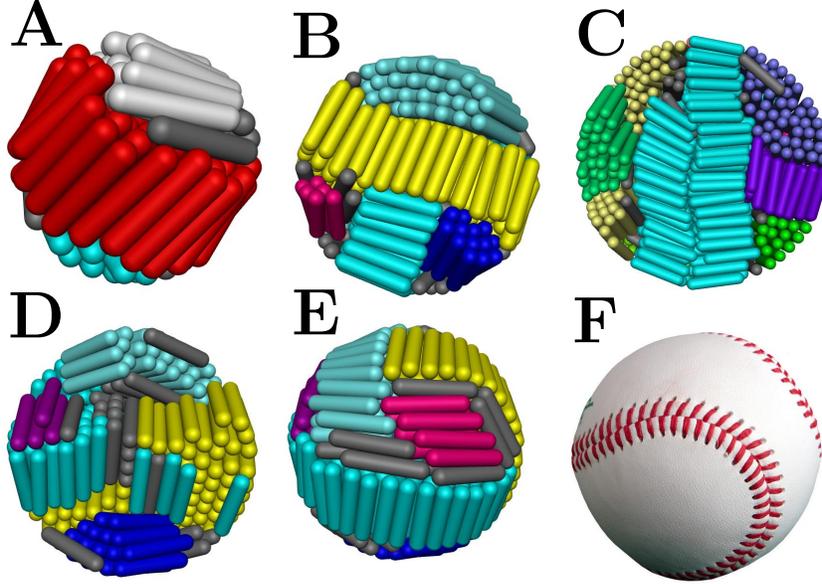


Figure 4: *Top*: Final configurations of simulated rods in spherical confinement. Different smectic domains are identified with different colours. Systems consisting of  $N = 100$  (**A**),  $N = 400$  (**B**) and  $N = 1000$  (**C**) are shown. *Bottom*: Internal (**D**) and external (**E**) configuration of a system of  $N = 400$  spherocylindrical particles at packing fraction  $\phi = 0.70$ . The whole volume of the spherical cavity is occupied by complementary C-shaped smectic domains which form a peculiar fashion resembling a baseball (**F**).

increasing the number of particles, minor domains grows in size so that the spherical cavity result constituted by 3 C-shaped com-penetrating smectic domains. We called this pattern as “baseball” fashion arrangement.

An insight in the formation of this particular structure was obtained by examining the internal organization of the supraparticle during the simulation. After the nucleation of small smectic domains close to the confinement, the domains extend until they form a major single one spread in all the size of the cavity. However, by further increasing the packing fraction, the spherical constrain forces single smectic layers to misalign one the other, so that the major domain is split into smaller complementary ones.

**Synthesis of rods** Silica rods were synthesised according to a procedure reported by [10]. After coating with a single fluorescent-labelled silica layer, several non-fluorescent silica coatings were subsequently grown. TEM images of the obtained particles are shown in Figure 5, A.

**Self-assembly of rods** In this project, silica rods were employed as real models for hard spherocylinders [10]. We first realized our self-assembly experiments by using the standard

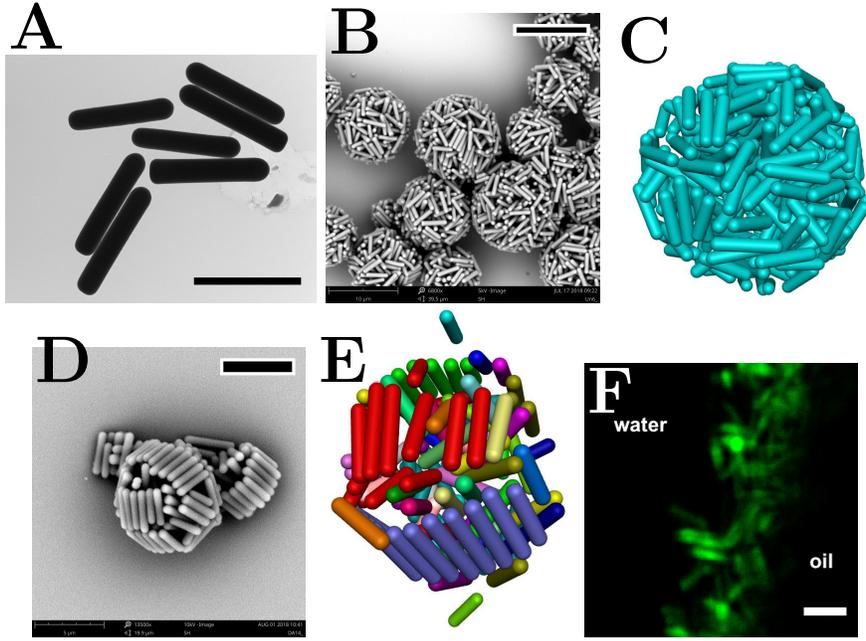


Figure 5: *Top*: (A) TEM images of rod particles ( $L = 3.00 \mu\text{m}$ ,  $D = 598 \text{ nm}$ ). Scale bar refer to  $3 \mu\text{m}$ . Supraparticles constituted by silica rods in a disordered configuration. One SEM image (B) and a reconstructed configuration (C) are reported. Scale bar refer to  $5 \mu\text{m}$ . *Bottom*: Supraparticles constituted by silica rods obtained for slow compression rates. One SEM image (D) and a reconstructed configuration (E) are reported. (F) A water-in-oil emulsion containing rod particles as observed through confocal microscopy. Scale bar refer to  $3 \mu\text{m}$ .

method outlined above (Figure 5, B-C). However, quantitative analysis on the reconstructed configurations displayed only little smectic ordering. Several attempts were therefore performed in order to slowing down the water evaporation rate from the samples. In one case, very slow compression rates determined the formation of hollow supraparticles, which displayed a 2D smectic ordering at the surface (Figure 5, D-E). This outcome was presumably determined by too slow compression combined with attractive interactions between particles and the water-oil interface. The latter condition was confirmed by confocal microscopy investigations (Figure 5, F)

## Self-assembly of mixtures of spheres and rods in spherical confinement

**Order parameter** Bulk mixture of rods and spheres reportedly exhibit a binary smectic phase (Figure 6, A). In order to quantitatively detect the formation of this particular phase in our computer simulations, a novel local order parameter was introduced. As in that

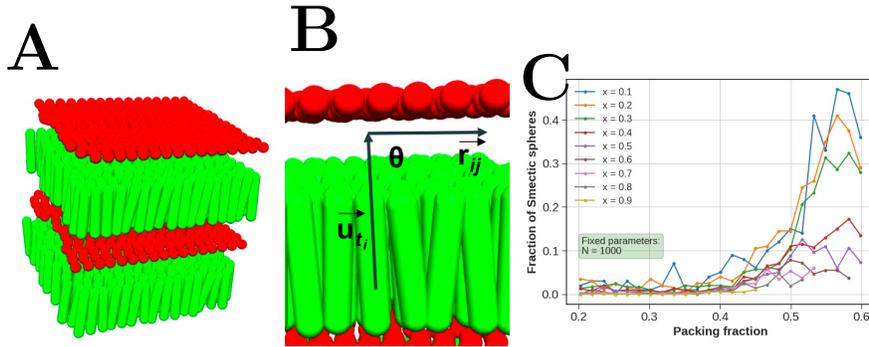


Figure 6: *Top*: (A) Graphic representation of the considered binary smectic order. (B) Orthogonality condition between vectors  $\mathbf{u}_{t_i}$  and  $\mathbf{r}_{ij}$  was considered for evaluating the formation of alternating layers of rods and spheres. (C) Fraction of smectic spheres as a function of the packing fraction for systems of  $N = 1000$  particles.

configuration spheres arrange into orthogonal planes to the rod smectic layer director, for each sphere  $i$  we first determined the rod  $t_i$  with the closest tip to  $i$ . We then evaluated:

$$\Theta_i = \frac{1}{n_b} \sum_{j=1}^{n_b} \left[ 1 - 3 \left( \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|} \cdot \mathbf{u}_{t_i} \right)^2 \right] \quad (5)$$

where  $\mathbf{u}_{t_i}$  represent the direction of rod  $t_i$  and  $n_b$  is the number of neighbour spheres  $j$ , defined as spherical particles which satisfy the condition  $\mathbf{r}_{ij} < 1.4D$  (Figure 6, B).  $\mathbf{r}_{ij}$  is the distance vector between the centres of mass of particles, while  $D$  is the diameter. In order to include in our evaluation also the local tendency to form smectic layers of rods, the *local binary smectic order parameter*  $\tau_{sph,i}$  was eventually defined as:  $\tau_{sph,i} = \Theta_i \tau_{t_i}$ , where  $\tau_{t_i}$  is the local smectic order parameter for rod  $t_i$ . Spherical particle  $i$  was considered ordered in the case  $\tau_{sph,i} > 0.20$ . Note that this seemingly low value is justified by the cutoff of 0.35 employed in the definition of smectic ordered rods.

**Brownian Dynamics** Brownian Dynamics simulations of mixture of rods and spheres were performed by varying the fraction of spheres  $x$ . In particular, our quantitative analysis revealed a modest tendency for the system to form a binary smectic (Figure 6, C). However, by increasing the value of  $x$ , segregation of spheres from a rod-rich phase appears (Figure 7). Note that the presence of spheres didn't disrupt the liquid-crystallinity of rods, as well-defined smectic layers were formed in all cases.

An insight into the segregation dynamics can be obtained by inspecting the configuration at increasing compressions. At low packing fractions, rods and spheres are spread in all the volume of the confining cavity and a fully disordered homogeneous phase is formed. However, for increasing packing fractions spheres progressively segregate toward one pole of

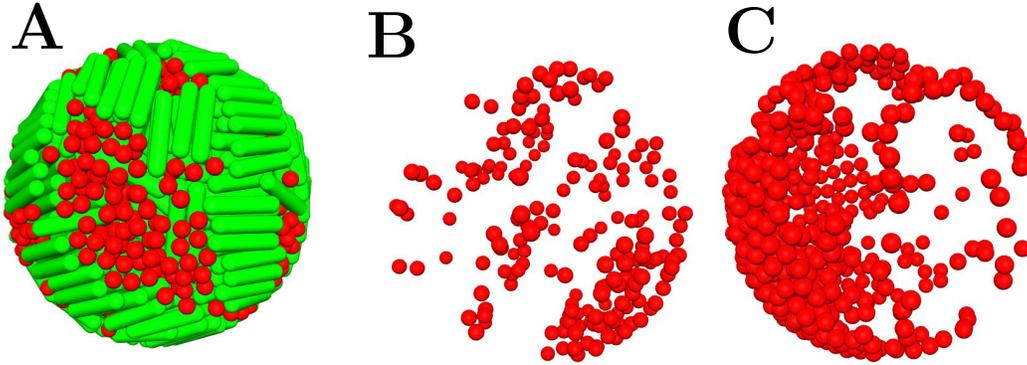


Figure 7: Final configuration of simulated binary mixtures consisting of  $N = 1000$  particles. **(A)** The outside aspect is shown in the case with  $X = 0.3$ . **(B-C)** Spheres arrangements as obtained by removing spherocylindrical particles. While at  $X = 0.20$  **(B)** the organisation of spheres into layers suggests the formation of a binary smectic configuration, at  $X = 0.50$  **(C)** spherical particles clearly concentrated at on pole of the cavity.

the spherical cavity. Meanwhile, smectic layers of rods is shown to nucleate on the opposite pole of the supraparticle.

Segregation of particles of similar shapes can be explained by using the concept of depletion, an entropic force which induce bigger colloidal particles to aggregate by exclusion of smaller ones.

## Conclusions

In this project, self-assembly of rods and spheres in spherical confinement was investigated. Brownian Dynamics simulation studies revealed that for sufficiently slow compression rates, spheres in a spherical cavity crystallized in an icosahedral geometry, while spherocylinders locally formed smectic layers. In the case of mixtures of rods and spheres, quantitative analysis through a novel order parameter revealed a modest tendency for the system to form a binary smectic phase at low fractions of spheres  $X$ . However, by increasing the value of  $X$ , shape-like phase separation prominently appeared.

Particle self-assembly in spherical confinement was further experimentally explored. While our method successfully produced well-defined spherical supraparticles, it generally failed in inducing crystalline or liquid-crystalline ordering. This outcome was supposed to emerge due to fast particle compression inside the confinement. Interestingly, in one case rod self-assembly at the supraparticle surfaces was ascribed to very slow compression rates combined with attractive interactions between colloidal particles and the water-oil interface.

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