
Self-Assembly of Colloidal Particles

Prerna Sharma

Colloidal dispersions are suspensions of micron-sized solid particles in a solvent like water or oil. Self-assembly is a widely used approach to create ordered structures of colloidal particles by engineering the inter-colloid potential. This article illustrates how entropy drives disorder to order transitions in a colloidal assembly.

Introduction

Self-assembly is one of the most appealing ideas in science [1, 2]. Imagine buying different components of a computer – mother board, RAM, power supply, cables, cabinet, monitor, keyboard etc., and throwing them in a box. Shake the box a few times and out comes your fully functional computer set-up. That is the promise of self-assembly – stuff that puts itself together [3]. This example of self-assembly is rather a cooked up one and unimportant because each of the components involved here is large enough to be held by a human hand or a machine so that they can be mounted in their appropriate places. Clearly, the idea of self-assembly gains paramount importance when the ‘building blocks’ are microns or nanometers in size. The current and highly successful technologies of nano-fabrication goes to great pains in assembling macroscopic structures using such small building blocks. For example, all ICs/chips in the computers are built using such technologies. An alternate paradigm to nano-fabrication is self-assembly where one engineers interaction between nanoscopic building blocks so that they organize themselves into a target structure without external intervention. In addition to technology, a fundamental understanding of principles of self-assembly holds the promise of deciphering the secrets of nature [2]. All of developmental biology, how a single cell transitions into a functional embryo and later into an organism, seeks to understand how na-



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Keywords

Self-assembly, colloids, liquid crystals, tactoids, cholesterics.



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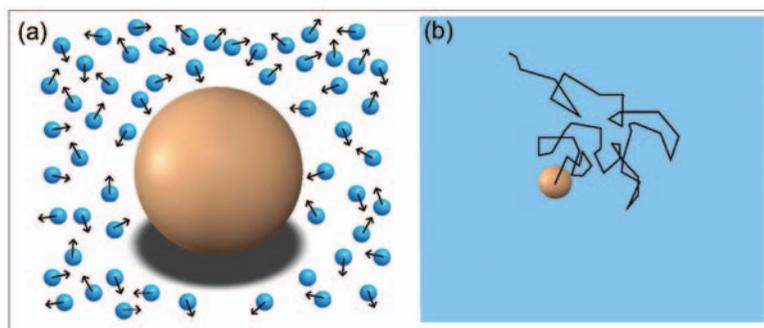
Einstein's theory based on statistical mechanics.

ture utilizes self-assembly. One of the major workhorses of self-assembly studies are colloids.

Colloids

Suspensions of any kind of micron-sized solid particles in a solvent like water or oil are called colloidal solutions. They are all around us. For example, ink and paints are pigments suspended in water, milk is fat globules in water, blood is red blood cells in water etc. Colloidal particles can be easily visualized using simple techniques like optical microscopy. The length scale of the particles being in between the atomic (ångström) and bulk (millimetres) endows them with special features. When one looks at a colloidal solution through an optical microscope, one finds that the particles are not static at one place instead jiggling around. This jiggling was first observed by Robert Brown and quantified by Jean Perrin using Einstein's theory based on statistical mechanics [4, 5]. The jiggling motion of colloidal particles in a solvent is called 'Brownian motion', in the honor of the Robert Brown. This incessant motion can be understood by realizing that a colloidal particle is constantly bombarded from all sides by innumerable collisions from the solvent molecules (*Figure 1a*). In general, the forces acting on such a particle, therefore, do not sum up to zero, and the particle moves in response to such microscopic forces. The particle moves at each time instant to a different direction chosen at random since the net force on the particle due to the solvent molecules is random both in direction and magnitude (*Figure 1b*).

Figure 1. (a) Schematic of a large colloidal particle (brown) immersed in a bath of solvent molecules (blue). (b) Zoomed out schematic depicts the random path of a colloidal particle in a fluid.



Colloidal particles interact with one other through a combination of forces such as electrostatic and van der Waals forces [6, 7]. Colloidal particles typically carry surface charge groups which dissociate into ionized form when they are suspended in water. Consequently, the particles become charged and repel each other through electrostatic forces. When suspending solvent carries additional salts like sodium chloride, the strength of this repulsive forces decreases significantly. Under such circumstances, once in a while, through thermal fluctuations, they come in close contact (few nanometers in surface to surface separation). At such short distances, van der Waals forces come into play. Van der Waals force is a short-range attractive force whose origin lies in the dipole-dipole interactions. They are the weakest of all intermolecular or inter-atomic attractive forces. However, in the case of two colloidal particles, the surface to surface contact area has millions of atoms and the sum of van der Waals interaction energy between all of these atoms adds up to cause colloidal particles to permanently stick to each other on coming in close contact. Therefore, to prevent the aggregation of colloidal particles due to van der Waals forces, charged colloidal particles are usually suspended in deionised water.

Electrostatic stabilization of colloidal solutions against aggregation is not possible when the solvent is oil because surface groups do not dissociate in a non-polar solvent like oil and van der Waals forces dominate. Therefore, a radically different strategy of grafting short polymer brushes on colloidal particles is employed to achieve stabilisation in oil [6, 7]. These ‘hairy’ colloidal particles neither repel nor attract each other until the brushes of the two particles touch each other. When the brushes on the two colloidal particles interact with each other with few nanometers of distance between their tips, there is an ‘effective’ repulsion between the two brushes, thereby, avoiding the aggregation of the particles. Such particles are called ‘hard spheres’.

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Colloidal Self-Assembly: Phase Diagram of Hard Spheres

¹Mono-dispersity means that the size and shape of all the particles in the solution are identical.

Self-assembly of colloidal particles depends crucially on mono-dispersity¹ of the particles and the interaction potential between them. Chemists over the years have developed successful methodologies to prepare identical spherical colloidal particles with controlled surface properties. These particles are commercially available and used for self-assembly experiments. Let us consider the phase diagram of hard sphere colloidal particles. The interaction potential of ideal hard sphere colloidal particles is zero when the particles do not touch each other and infinite when they touch each other (*Figure 2*). Therefore, the internal energy of the system can only depend on the temperature of the system in the absence of any other interaction. The free energy of the system is given by,

$$F = U - TS,$$

where U is the internal energy, T is the temperature, and S is the entropy. As discussed above, $U = NK_B T$, where N is the total number of particles and K_B is the Boltzmann constant. This implies that $F = T(NK_B - S)$. In other words, temperature simply acts as a scaling factor for the net free energy and therefore, plays no role in the minimisation of free energy. At equilibrium, the colloidal solution will exhibit the phase which has the lowest free energy, which in a hard sphere system will also have the highest entropy. Given this scenario, one may naively think that ordered phases of hard sphere colloidal particles in a solvent are impossible. Yet, it turns out that ordered phases of hard sphere colloidal particles do exist. *Figure 3a* shows a diagram that depicts the different phases of hard sphere suspensions as a function of volume fraction of the particles [8]. At low volume fraction, all the particles are freely moving and are positionally disordered. Such a phase is appropriately called ‘liquid’. At about 54% volume fraction of the particles, a disorder-order transition takes place, wherein the colloidal particles are positionally ordered on a face-centred cubic crystalline lattice and jiggle in a small volume (\sim fraction of particle volume) in the neighbourhood of the lattice points.

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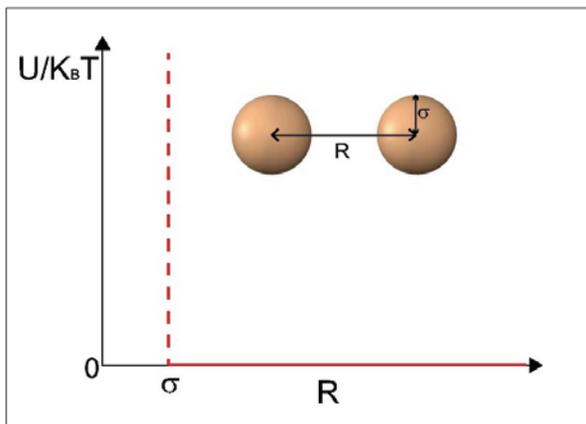


Figure 2. Interaction potential of hard spheres. Hard spheres neither repel nor attract each other until they touch. Being impenetrable, the interaction potential becomes infinitely large when the particles touch each other.

In the fluid state corresponding to the volume fraction of 0.64, all the spheres are touching each other and there is no room for any movement. That is, the system is physically jammed and constrained.

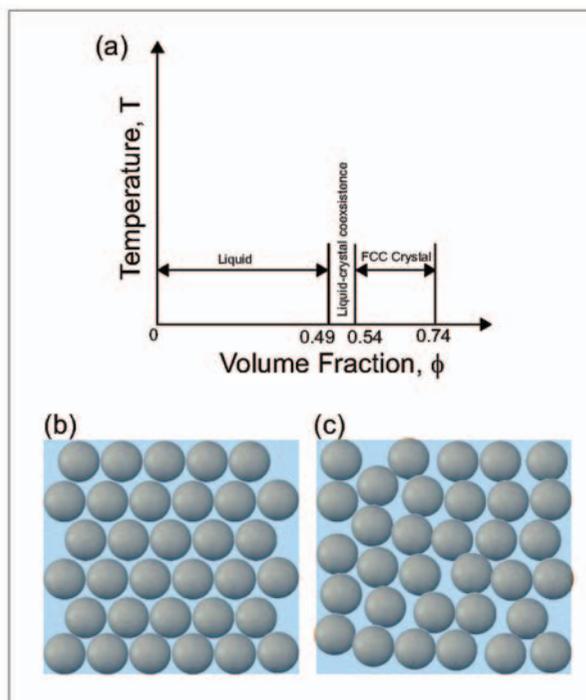
This entropy driven disorder-order transition in hard spheres was of intense speculation and investigation in 1950's because the ordered crystalline phase having higher entropy than the disordered fluid phase was felt to be non-intuitive and irreconcilable. By the late 1980's, computer simulations were robust enough to confirm the existence of this transition, and later experiments confirmed the same as well [9]. One can see for the special case of the volume fraction of 0.64 that fluid phase has lower entropy than the crystalline (*Figure 3b*). 0.64 is the largest volume fraction possible for a disordered random close packing of spheres [10]. Therefore, in the fluid state corresponding to the volume fraction of 0.64, all the spheres are touching each other and there is no room for any movement. That is, the system is physically jammed and constrained. On the other hand, at the same volume fraction of 0.64, if the particles are placed on a crystalline lattice, they have room for movement and have much larger vibrational entropy compared to the case of fluid phase. Therefore, overall the entropy of a crystal is much larger than that of a fluid at the packing fraction of 0.64. A similar argument can be made for other volume fractions where the crystalline phase exists.

Colloidal Self-assembly: Phase Diagram of Hard Rods

So far, this article has focused on spherically symmetric colloidal particles. Novel phases emerge when shape anisotropic parti-



Figure 3. (a) Phase diagram of hard spheres as a function of volume fraction. The phase diagram is independent of temperature. Schematics showing (b) face centered cubic and (c) random close packing of spheres.



cles are used for assembly. Rods are a classic example of shape anisotropic particles. The long axis of the rod marks a unique direction in space. Therefore, a suspension of rods has two kinds of order associated with it – positional and orientational. Partially ordered phases wherein, for example, orientational order exists (all rods pointing in the same direction), but not positional (center of masses of the rods are randomly distributed in space) are called ‘liquid crystalline phases’² [11] (*Figure 4*). It turns out that it is far more intricate to synthesize mono-disperse rods than mono-disperse spheres. Therefore, historically scientists relied on using rod-shaped viruses as model rods [12]. Viruses are typically, single DNA or RNA molecule coated with proteins. DNA acts as a template for the proteins to bind. Therefore, by design, each virus of a given type is identical to another of the same type.

Onsager showed theoretically in a landmark work that a first order phase transition exists between completely isotropic phase (positional and orientational disorder) and a nematic phase (positional

²Shruti Mohanty, *Liquid Crystals – The ‘Fourth’ Phase of Matter*, *Resonance*, Vol.8, No.11, pp.52–70, 2003.



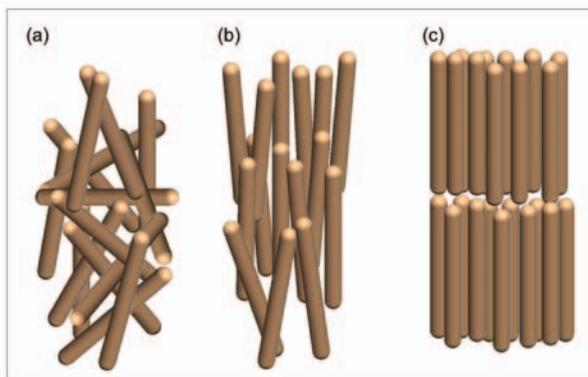


Figure 4. Schematic showing (a) isotropic, (b) nematic, and (c) smectic phases of hard rods.

disorder and orientational order) as a function of volume fraction of the hard rods [13] (*Figures 4a and 4b*). This transition is again entropy driven in the sense that at higher densities, rods orient themselves in the same direction to maximize their propensity to translate and explore the space around them. An interesting feature of the isotropic to nematic phase transition is that it occurs at volume fractions as low as 1%. This is in striking contrast with the assembly of hard spheres where the transition between the fluid and crystalline phase occurs at 55%. Furthermore, this transition is sensitive to the aspect ratio (length to diameter ratio) of the rods. An aspect ratio of 20 or more is typically required to obtain liquid crystalline phases. On further increasing the rod volume fraction, smectic phase appears where rods arrange in layers with each layer having a nematic-like symmetry (*Figure 4c*).

Colloidal Self-assembly: Role of Attractive Interactions

Though hard particle systems are the simplest to understand theoretically, one has to actually take extreme care experimentally to prepare such systems. In addition, combining self-assembly with attractive interactions can potentially give more flexibility and ease in attaining the desired target structure. The most important energy scale in colloidal self-assembly is thermal energy, $K_B T$. The inter-particle attractive interaction strength, therefore, should not be weaker than $K_B T$. Otherwise thermal fluctuations will drive the system to a disordered state. The inter-particle at-



When the number of smaller particles exceeds that of the larger colloidal particles, an effective attraction arises between the colloidal particles that increases the overall entropy of the combined system of colloids and nanoparticles/macromolecules and consequently lowers the free energy of the system.

tractive interaction strength also should not be orders of magnitude stronger than $K_B T$ because that would leave no possibility for the system to come out of the higher local energy minima to the ground state of lowest energy minima. That is, the system will not be able to anneal itself of defects in the assembly if the interparticle attraction strength is significantly larger than the thermal energy. Depletion interaction satisfies this criterion really well.

Depletion interaction is said to be in action when colloidal particles are immersed in a solvent that has larger number of much smaller nanoparticles or macromolecules like polymer coils [14, 15]. The small particles are excluded from a zone around each larger colloidal particle if both particles have hard sphere like interaction potential (*Figure 5a*). Therefore, if surfaces of the two colloidal particles approach one another closer than the smaller particle diameter, then the corresponding excluded volume zones partially overlap (*Figure 5b*). This increases the entropy of the smaller particles since more physical space becomes available for them to move around. When the number of smaller particles exceeds that of the larger colloidal particles, an effective attraction arises between the colloidal particles that increases the overall entropy of the combined system of colloids and nanoparticles/macromolecules and consequently lowers the free energy of the system. The term ‘depletion’ stems from the fact that the smaller particles are ‘depleted’ out of the excluded volume zone. The range of depletion interaction is set by the size of the smaller particles, and the strength of the interaction is set by the concentration of the smaller particles.

An alternative way to look at the depletion interaction is to think of the smaller molecules randomly colliding and transferring momentum to the colloidal particles. An isolated colloidal particle will experience such collisions and consequently forces uniformly from all sides with the result that net force on the colloidal particle turns out to be zero. However, when two colloidal particles approach one another closer than the small particle diameter, there is a net force acting on the colloidal particles that pushes them together. This is because the smaller particles are depleted



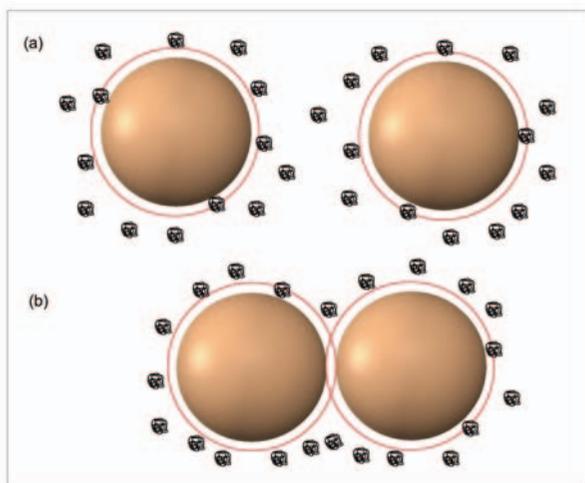


Figure 5. (a) Small polymers (black) are excluded from a zone surrounding the larger colloidal particles (brown) when both polymers and particles are considered as hard spheres. That is, the center of mass of the polymers cannot go within the excluded volume zone whose boundary is marked with red. When the colloidal particles are far from each other, the excluded volumes simply add up. (b) When the surface of two colloidal particles are closer than the polymer diameter, the excluded volume zones overlap and net excluded volume becomes smaller than the case when the particles were far apart.

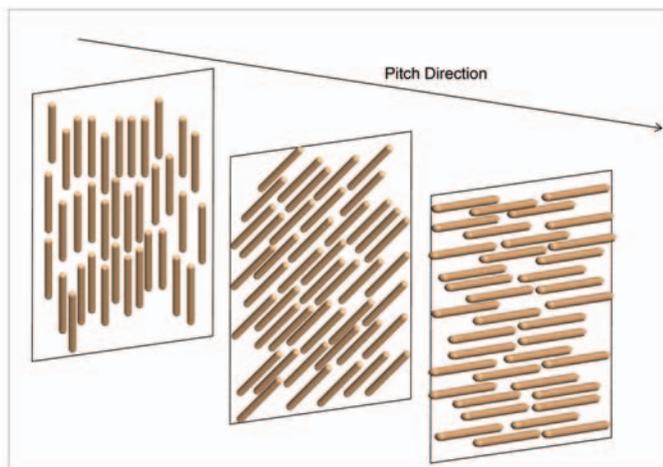
from the region of overlap of the excluded volume zones with the result that the force on individual colloidal particle does not cancel out.

Phase Diagram of Rods in the Presence of Depletion Attraction

The phase diagram of chiral hard rods in the presence of depletion attraction is well studied experimentally and theoretically [16]. Most studies have used fd virus as the model chiral rod. That is, in the hard particle phase diagram, these rods self-assemble into chiral nematics instead of the simple nematic phase described above. ‘Cholesterics’, as chiral nematics are usually called, can be thought of as a nematic phase in which the director (direction of the long axis of the rods) rotates along a helix (*Figure 6*). The origin of chirality in fd viruses is a highly debated topic in literature and no clear understanding is available either experimentally or theoretically. It is generally believed that the helical arrangement of proteins along the DNA of the virus is responsible for its chiral behaviour. Furthermore, it is also a big question in the field how this microscopic chirality of the virus gets translated into the macroscopic rotation of the director that is observed in bulk cholesteric samples.



Figure 6. Schematic depicting the cholesteric phase where the long axis of the rods rotates along a helix.



Depletion interaction potential between a pair of rods has both positional and orientational dependence. The overlap of excluded volume zones is maximum when the rods are aligned along their axes and perfectly parallel to each other. That is, it opposes the chiral nature of the rods. Therefore, the equilibrium phase of a chiral rod-polymer system is governed by an interplay of chirality and depletion. When a polymer like long chain dextran is added to a dilute suspension of fd viruses, the first phase that appears after the isotropic phase is that of ‘tactoids’ [17]. Tactoids are three-dimensional nematic droplets with the characteristic shape of an ellipsoid (*Figures 7a and 7b*). This interesting shape emerges due to a competition between the surface tension which prefers spherical droplets, and the tendency of the rods to be oriented along the same direction in the nematic phase. On increasing the concentration of the polymer, metastable self-limited discs, one rod-length thick, of aligned rods form. These discs coalesce to form linear twisted ribbons (*Figures 7c and 7d*). The twisted nature of this assembly stems from the chiral nature of rods wherein the rods are tilted at the edges of the ribbons [18]. At still higher polymer concentration, depletion interaction dominates resulting in monolayer discs of aligned rods to coalesce



laterally and form larger discs [19]. So, such a sample equilibrates to a large number of semi-infinite monolayer of aligned rods (*Figures 7e and 7f*). These monolayers can be considered as two-dimensional fluid membranes since the constituent rods are free to diffuse within the membranes due to comparable strengths of depletion interaction and thermal fluctuations. On the other hand, thermal fluctuations induced deformations of the colloidal membranes along the membrane normal are extremely small as is evident from *Figure 7f* wherein the membrane is visibly flat. That is, one could associate a bending modulus with these membranes which is found to be typically $150K_B T$. These two hallmark properties of colloidal membranes make them an ideal model system to study problems of membrane biophysics [16]. Particularly, the phase behaviour of colloidal membranes has illustrated how chirality affects the physics of membranes.

Conclusion

To summarize, we have discussed simple shapes of colloidal particles like spheres and rods and how entropy drives ordering transitions in their suspensions. Assembly outcomes in the presence of simple attractive potentials have also been discussed. But that

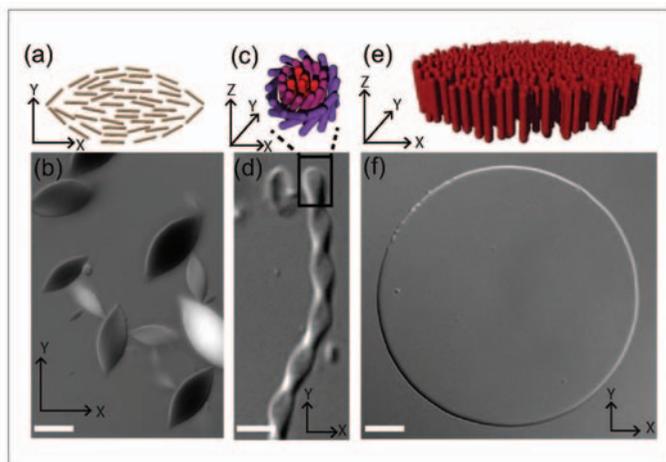


Figure 7. (a) Schematic of cross section of tactoids (b) Optical microscopy image of tactoids (c) Schematic of a section of twisted ribbons outlined by a rectangle in (d) (d) Optical microscopy image of twisted ribbon (e) Schematic of colloidal membrane (f) Optical microscopy image of colloidal membrane. Scale bar, $5\ \mu\text{m}$.

is not all to this emerging field. Boundaries in this frontier area are being continually pushed with designer shaped particles and designer interaction potentials. For example, patchy spherical particles have been synthesized in which one hemisphere is different from the other in terms of sign of the charge or the wettability [20]. Equally exciting is the line of work where colloidal particles are grafted with DNA and self-assembled into complex target structures using the complementary nature of DNA hybridization [21]. Instead of relying on thermal fluctuations, self-driven active colloidal particles use intrinsic energy sources for their motion resulting in a persistent random walk-like trajectory. This has a profound impact on their self-organization with exotic phenomenon like living crystals [22]. In a sense, the field of colloidal self-assembly is simply limited by our imagination to explore and exploit the ever-expanding parameter space of interaction type, shape, and confinement.

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