Colloidal spheres confined by liquid droplets: geometry, physics, and physical chemistry

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Abstract

I discuss how colloidal particles organize when they are confined by emulsion droplets. In these systems, the interplay between surface tension and interparticle repulsion drives the formation of complex, non-crystalline 3D arrangements. These can be classified into three groups: *colloidosomes*, or *Pickering emulsions*, structures that form when particles are bound to the interface of a spherical droplet; *colloidal clusters*, small polyhedral configurations of colloids formed by capillary forces generated in an evaporating emulsion droplet; and *supraparticles*, ball-shaped crystallites formed in the interior of emulsion droplets. I discuss the preparation, properties, and structure of each of these systems, using relevant results from geometry to describe how the particles organize.

1. Introduction

When colloidal particles are suspended in an emulsion—a blend of two immiscible fluids such as oil and water—the competition between interfacial energy and interparticle forces causes the particles to arrange in ways that are not observed in bulk colloidal suspensions. Under certain conditions, the spherical droplet interfaces can adsorb particles or confine them to the interior. Also, selectively removing the liquid inside the droplet can generate capillary forces that cause the particles to aggregate together. Although these systems have no obvious analogue at the atomic or molecular scale, a spherical container is one of the simplest geometrical constraints that one can impose on a collection of particles, and studying how particles arrange under such a constraint can reveal some generic principles of how matter organizes itself when confined. Indeed, the structures I present here bear some similarities to those of smaller-scale assemblies, including viruses [1], molecules [2], and quantum dots [3].

I will discuss three different scenarios (see Figure 1): 1. When the particles stick to the surface of the droplets, they organize themselves into spherical shells, also called "colloidosomes". 2. When the particles stick to the interface and the interior fluid is removed, capillary forces draw the particles together into polyhedral clusters. 3. When the particles are confined at high volume fraction inside the droplets, but are prevented from sticking to the interfaces, they form close-packed spherical crystallites called "supraparticles." For each case I will discuss how the systems are prepared, the physical chemistry underlying the interfacial properties of the systems, and the physics and geometry of how the particles organize. First, however, I outline the types of interactions found in emulsions containing colloidal particles.

2. Interactions

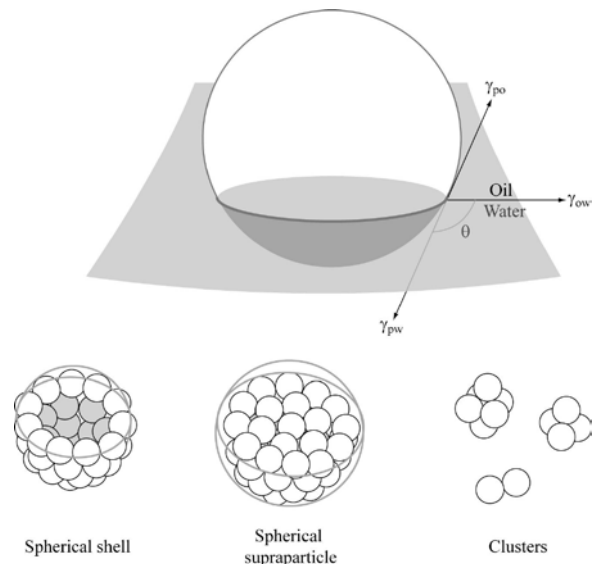### 2.1. Interaction between a particle and an interface

Figure 1: Top: Diagram of a particle at the interface of an oil-in-water emulsion droplet (interface shaded gray), showing the three interfacial tensions and the contact angle. Bottom: Cutaway diagrams of the three types of particle arrangements we discuss in this article.

Consider a simple macroscopic model of a colloid and the interface between two fluids, for example oil and water (see Figure 1). There are three interfacial tensions in the system: γ_{ow}, between oil and water, γ_{pw}, between particle and water, and γ_{po}, between particle and oil. If the interfacial tension between fluids is sufficiently high, the total energy of the system is reduced when a particle that is originally dispersed in one of the two fluids migrates to the interface between them [4,5]. "Sufficiently high" means that the adsorption or binding energy E is much larger the thermal energy kT:

$$E = \pi a^2 \gamma_{ow} \left(1 \pm \cos \theta \right)^2 \qquad (1)$$

where the sign is positive when calculating the energy to move the particle into the oil phase and negative for moving the particle into the water phase.

a is the radius of the particle and θ the contact angle, as defined by Young's equation:

$$\cos\theta = \left(\gamma_{po} - \gamma_{pw}\right)/\gamma_{ow}$$

Given a contact angle of 90° and an interfacial tension of about 0.1 mN/m, the binding energy for a 1 μm diameter particle exceeds 10^4 kT. Thus colloidal particles will stick to an interface unless they are well wetted by one of the fluids, or there is some kinetic barrier that prevents them from attaching. Particles that are dispersed in the exterior fluid of a surfactant-stabilized emulsion will generally not stick to the droplet interfaces, which are coated with a layer of surfactant. On the other hand, particles *inside* surfactant-stabilized emulsion droplets will readily adsorb, because the surfactant does not dissolve in the interior fluid. Particles should also readily adsorb in suspensions of droplets or bubbles with no surfactant, but in practice some agitation or flow appears to be necessary to force the particles onto the interface [6]. The origin of the barrier to adsorption in surfactant-free systems is not well understood.

2.2. Interactions between particles trapped at an interface

The colloidal particles that have been used in experiments are polymer or silica spheres with covalently bound surface groups that stabilize the particles against aggregation due to van der Waals forces. These surface groups can be either polymer chains, which provide a short-ranged steric barrier, or charged groups, which dissociate in water to provide an electrostatic barrier with a range varying from a few nanometers to several micrometers, depending on the dissolved salt concentration.

While the sterically-stabilized particles behave, to a good approximation, as hard spheres, the interactions between charged particles can be quite long-ranged, especially when the particles are trapped at an oil-water interface. Here the low dielectric constant of the oil limits dissociation of the charged groups, so that the portion of the particles in the oil phase carries a much smaller surface charge than the portion in the water, and the particles act as electric dipoles (at least when they are several particle diameters away from each other). If they are on the surface of an oil droplet, they interact primarily through the oil phase, so that the dipole-dipole repulsion can have a range many times the Debye length in water [7]. Thus particles trapped on the surface of an emulsion droplet can organize themselves into an ordered arrangement even at very low surface densities [8].

3. Particles at droplet interfaces

3.1. Preparation

The simplest way to prepare a sample of liquid droplets with particles at the interfaces is to add a colloidal suspension to an immiscible liquid and agitate. Although this yields a distribution of droplet radii R and numbers N of particles on a droplet, one can control the average values of R and N by varying the agitation speed and bulk particle concentration. The resulting particle-bearing droplets have been called "Pickering emulsions" or "colloidosomes" [1,9].

A microfluidic device offers several advantages for preparing liquid droplets or even gas bubbles with adsorbed particles. Subramaniam and coworkers recently fabricated a flow-focusing device with three parallel channels, the outer two of which carry the colloidal suspension while the inner carries a pure fluid [6]. These three flows are fed into one channel, and as the fluids travel alongside one another, particles become attached to the interface. Eventually the central fluid breaks up into spherical droplets or bubbles that are coated with particles. This method allows much better control over the droplet size R, average number of particles N per droplet, and the distribution of N as well.

3.2. Structures

If the emulsion droplets produced by such methods are stable against coalescence, diffusion, and evaporation, the particles have sufficient time to reach an equilibrium arrangement on the surface. As noted in section 2.2, the potential between the particles can vary depending on the solvent properties and the surface coating. Assuming that this potential decays, to first order, as a power law, we can write

the following expression for the total potential energy of the system U:

$$U = \sum_i^N \sum_{j<i} \frac{1}{\left| \mathbf{x}_i - \mathbf{x}_j \right|^p}$$

where the sum is over all pairs, and $\mathbf{x}_i$ is the position of the ith particle. When $p = 1$, the problem of finding the equilibrium arrangement of the particles is known as the Thomson problem [10]. This also corresponds to the problem of finding the minimal energy configuration of N identical point charges on a sphere. In the limit $p \rightarrow \infty$, the potential energy becomes a function only of the smallest distance between any pair of sphere centers, so that minimizing the potential energy becomes equivalent to maximizing the diameter of N equal-sized hard spheres on the surface of another sphere. This is known as the Tammes problem. It is also equivalent to maximizing the area density of spheres on the surface, and the solutions are therefore sometimes called "spherical packings" [11]. Conjectured solutions to the Thomson and Tammes problems differ at most values of N for $N > 6$. At $N = 12$, however, the optimal structure for both problems is an icosahedron.
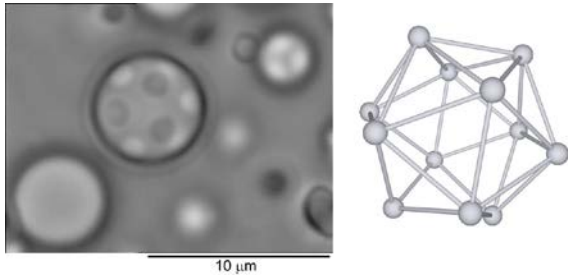

Figure 2: Optical micrograph of an emulsion droplet containing 12 spheres bound to its surface. The 12 spheres are arranged at the vertices of an icosahedron (diagram at right).

The structures of colloidosome systems at low N have not yet been systematically investigated, and little is known about whether they conform to Thomson structures, Tammes packings, or a different class of polyhedra altogether. I show one example in Figure 2: an oil droplet with $N = 12$ charged colloidal particles on its surface. Optical micrographs taken at different depths show that the particles are arranged in an icosahedron. One would expect, based on the qualitative differences between the Thomson and Tammes packings, that the structures at other values of N are sensitive to the interactions between particles. In fact, it might be possible to observe transformations between different types of polyhedra by changing the solvent conditions (pH, ionic strength) and thus changing the range of the interparticle potential.

Systems at large N have been studied more extensively [1,12,13]. To understand the structure of these colloidosomes, it is instructive to first consider the equilibrium phase behavior of a 2D array of particles. On a flat surface, spherical particles at high density will form a triangular lattice in which each particle is coordinated by six others. This arrangement, which has been observed in systems such as monolayers of colloidal particles at a planar air-water interface [8], has the smallest energy and the most efficient use of area. But when the particles are confined to a curved interface, such as the surface of a sphere, it is impossible for each particle to be coordinated by six others. There must be defects.

Some information about the defects follows from Euler's formula,

$$v + f - e = 2,$$

which relates the number of vertices v, edges e, and faces f of a convex polyhedron. If there is some arrangement of particles on the surface of a sphere, and we imagine connecting their centers to form triangular faces, Euler's formula for this polyhedron becomes

$$\sum_i^N \left(6 - z_i\right) = 12$$

where z_i is the coordination number of the ith particle. Thus the total *disclination charge* of the system is constrained. The simplest way to satisfy this constraint is to incorporate exactly 5 five-fold coordinated vertices into the structure, but in general such an arrangement minimizes neither energy nor area. There are many other ways to add defects in order to satisfy the constraint on the total disclination charge.

Using a combination of experiment and theory, Bausch and coworkers revealed the defect structure of a collection of interacting particles on the surface of a sphere [1]. They found that the ground state of the system consists of 12 grain boundary "scars," which are chains of five-fold and seven-fold defects, in a sea of six-fold coordinated particles. The scars are located roughly on the vertices of an icosahedron, and the net disclination charge of each is +1, so that Euler's theorem is satisfied. By creating pairs of five-fold and seven-fold defects, the system can relieve strain and lower its energy without changing the total disclination charge. Although the interparticle potential was not measured in these experiments, it is clearly repulsive, and the results appear to be insensitive to its exact form; observations were consistent for particles with different surface groups and ranges of interaction [12]. This stands in contrast to the situation at low N, where the configuration of the particles does appear to depend on the form of the potential.

4. Particles at the surface of evaporating emulsion droplets

4.1. Preparation of colloidal clusters

A dramatic structural change occurs when the liquid is removed from the interior of a droplet containing adsorbed colloidal particles [2]. As each droplet shrinks, particles come closer together on the surface until they are tightly packed and cannot move. Because the droplet interface is pinned to the jammed particles, it must become non-spherical when more liquid is removed from its interior. In systems containing surfactant, so that the particles do not stick when they touch, the menisci that develop between particles lead to capillary forces that pull the particles into a 3D aggregate, or cluster. This configuration is then "locked in" by van der Waals forces, which become significant once the particles are pulled near contact.

The liquid inside the emulsion droplets can be selectively removed by either evaporation (if the vapor pressure is higher than that of the exterior fluid) or by diffusion of liquid through the exterior fluid into a low pressure reservoir. Either method leads to the same structures, which differ from the colloidosome configurations discussed above.
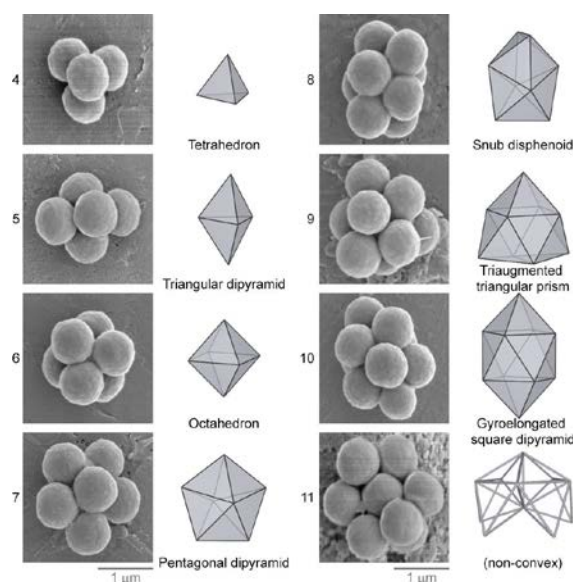

Figure 3: Scanning electron micrographs of polystyrene colloidal clusters and diagrams of polyhedral structures for 4 < N < 11.

4.2. Structure of colloidal clusters

The configurations of the clusters are shown in Figure 3 for small N. The shape of a given cluster depends only the number N of particles that it contains, and identical sequences of structures are formed in a variety of systems, including oil-in-water and water-in-oil emulsions with various types of particles and surface groups [2,14,15].

The clusters do not appear to be minimal-energy configurations of any simple pairwise-additive potential. However, there is a common geometrical feature: All of the clusters for $N \leq 11$ are equivalent to hard sphere packings conjectured to minimize the second moment of their mass distribution,

$$M = \sum_{i=1}^{N} \left| \mathbf{x}_i - \mathbf{x}_0 \right|^2$$

where $\mathbf{x}_i$ is the position of the ith particle and $\mathbf{x}_0$ is the center of mass of the entire cluster. These configurations were originally calculated by Sloane

and coworkers using global optimization procedures [16]. For $N > 12$, the clusters observed in the experiments deviate from the minimal-moment rule, but no other simple mathematical criterion has yet emerged to explain their structures. Also, no experiments have yet systematically examined the shapes of clusters for $N > 15$.

Lauga and Brenner were able to reproduce the observed cluster configurations in simulations of an evaporating droplet with hard spheres attached to its surface [17]. The final configurations they found were independent of the contact angle and the initial configuration of the particles on the surface. This robustness is related to the geometry of the system just before the droplet begins to deform: at this point, if the evaporation process proceeds slowly enough, the particles should achieve maximum density on the interface—in other words, they should be arranged in a spherical (Tammes) packing. Spherical packings are unique for each $N < 19$ and do not depend on contact angle, so that in the course of forming a cluster, each collection of particles at a given N must proceed through the same state, regardless of its initial configuration. The geometry of this state determines all the possible ways in which the droplet can deform upon further evaporation, and for all $N < 12$, an analysis of degrees of freedom shows that there is only one possible rearrangement mode. This explains the uniqueness of the cluster configurations at each N.

Lauga and Brenner were also able to show that most of the final cluster configurations could be calculated by starting from the spherical packing and moving particles iteratively using a linear force law that is valid only for small deformations of the interface. In this limit, the force on a particle is related to the displacements through

$$F_i = c_1 \delta x_i - c_2 \sum_i^N \delta x_i$$

where c_1 and c_2 are functions of the droplet size, particle size, contact angle, and interfacial tension. The second term is due to a volume balance: a change in droplet radius must be coupled to displacements of all the particles. Thus the functional form of this force-displacement relation is the same as that of an effective force law derived from treating the second

moment as a potential energy function. This may well explain why the observed configurations are the same as those of minimal second moment clusters.

5. Particles inside emulsion droplets

5.1. Preparation of supraparticles

As noted in section 3, micrometer-sized colloidal particles are strongly predisposed to adsorb at fluid interfaces. But if the three phase contact angle of the system is large enough for the binding energy of the particle to be on the order of kT (see equation 1), colloidal particles can be confined to the interior of the droplets rather than the interfaces. Thus one way to make droplets with colloids inside is to use a system with an inherently low contact angle. For instance, Velev and coworkers found that polystyrene particles dispersed in water droplets in fluorinated oil do not stick to the water-oil interface, even when there is no surfactant in either phase [18].

Another approach is to reduce the contact angle by adding two surfactants, one in the continuous fluid and one in the droplet fluid [3]. If, for example, the particles are dispersed in oil, and the oil is then mixed with water to form oil droplets, adding surfactant to the water phase will reduce the oil-water interfacial tension as expected, but it will also reduce the particle-water surface energy because the surfactant will coat the portions of the particles protruding into the water phase, rendering them more hydrophilic. The decrease in binding energy due to the reduction in oil-water interfacial tension may be partially offset by the change in contact angle. On the other hand, adding a surfactant to the oil phase before making droplets has the benefit of decreasing the oil-water interfacial tension *and* making the particles more hydrophobic, thus significantly reducing the binding energy. However, this method has its limits. There must be sufficient surfactant in the continuous fluid so that the system does not form an inverse or multiple emulsion. Also, the oil-water interfacial tension cannot be too low, or a microemulsion will form.

Typically the emulsions are prepared with a moderate volume fraction of colloid, from 10–30%. To concentrate the colloid, the fluid inside the droplet
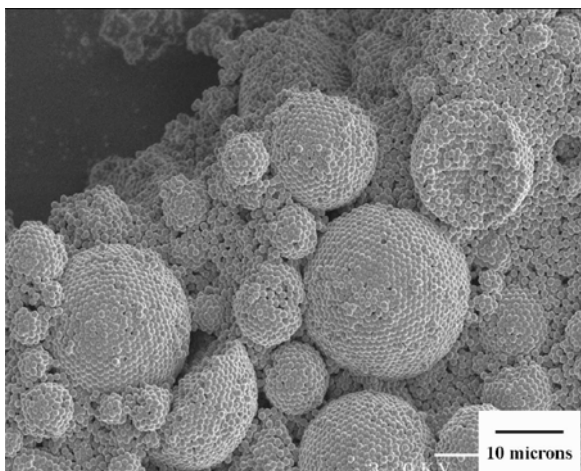
Figure 4: Scanning electron micrograph of supraparticles containing polymer spheres.

can be selectively removed, either by evaporation or by diffusion through the continuous phase. The resulting consolidated structures are called "supraparticles."

5.2. Structure of supraparticles

Although the particles do not stick to the interface of the droplets in these systems, the interface is still a boundary, and because it is curved it can affect how the particles assemble inside. In large systems ($R/a \sim$ 1000, corresponding to approximately 1 mm droplets), the curvature is small, so that when the droplet fluid is removed the particles form face-centered cubic crystals with some stacking faults [18]. Although the curvature of the droplet does introduce some grain boundaries, on the scale of the particles the crystals have flat faces. The supraparticles are sufficiently ordered to diffract light.

In smaller systems ($R/a \sim$ 10–100), the structures are less crystalline. Figure 4 shows a scanning electron micrograph of supraparticles after removal of all the liquid. On the outside the particles are arranged in spherical shells resembling the colloidosome structures, but on the inside there is disorder. Optical microscopy of the interior of the supraparticles reveals small wedge shaped crystallites, approximately 10-20 particle diameters

across, with grain boundaries extending radially from the center of the supraparticle to the outside [3]. Many of these supraparticles are also faceted rather than spherical. This type of reconstruction—a compromise between surface effects and crystallization—has also been observed in nanocrystals prepared in solution [19,20].

6. Conclusions

As shown here, adding a second fluid to a colloidal suspension creates emulsion droplets that can confine particles and change the way they organize. The three types of systems I have discussed all have complex structures that are not seen in bulk suspensions. In part this is because each droplet contains a finite number of particles, so that a true crystal, for example, cannot form. But more importantly, in all of these systems the interface of the droplet acts as a geometrical constraint on the organization of the particles. It can not only confine the particles but also push them around or, when the particles are interfacially active, pull them together through capillary forces. All of these forces are reasonably well understood, and analogous kinds of assembly may well occur in molecular or atomic scale systems subjected to similar kinds of forces. Overall, however, the colloidal systems discussed here, which are both easy to prepare and observe, are convenient tools for discovering new phenomena in condensed matter.

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