Colloids under External Control

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Abstract

The ability of colloids to self-organize through a minimization of their free energy is a direct consequence of their well-defined thermodynamic temperature that manifests itself through the Brownian motion they perform. In this article, it will be shown that through the use of external fields such as electric and magnetic fields, gravity, structured or confining walls, and shear, this self-organization can be directed to make new advanced materials. Moreover, a start has been made toward colloidal model systems to study fundamental questions relating to materials science such as defect structure and dynamics, grain boundaries, wall and confinement effects, and tribology. Finally, we predict that the enhanced insights on how to use external fields will also lead to "smart" materials with properties that can be changed dynamically.

Keywords: colloids, model systems, self-organization.

Introduction

In 1926, Jean Perrin received the Nobel Prize in physics for putting "a definite end to the long struggle regarding the real existence of molecules" (committee report). In his experiments, which he started about a hundred years ago, Perrin pioneered the use of colloidal particles as a model system when he applied Einstein's insights on how to describe colloids using statistical mechanics to determine Avogadro's number $(N_{\rm A})$. Basically, Einstein realized that colloids have a well-defined thermodynamic temperature. Amazingly, Perrin's experimental approach1 was hardly different from what is described in the rest of this article. First, Perrin realized that he needed a monodisperse dispersion of model particles and therefore went to great lengths to patiently fractionate a dispersion of resin particles he had precipitated by repeated centrifugation over a period of several months. For his first determination of $N_{A'}$ he determined the equilibrium height distribution of a low concentration of colloids by counting particles using a microscope. This so-called barometric height distribution is exactly analogous to that of the distribution of molecules in the atmosphere in the gravitational field of the earth, except that the characteristic gravitational length, which is proportional to the particle's mass and is the height at which the potential energy of a particle equals kT, is not measured in kilometers but in centimeters or millimeters (or even micrometers, as will be discussed). In another determination, he also used a microscope, this time to determine the diffusion constant of colloids. Einstein calculated this diffusion constant on the one hand by taking into account the fact that the erratic diffusive or Brownian motion the particles exhibit is caused by the continuous bombardment of the colloid by solvent molecules, giving rise to forces that do not exactly cancel, while on the other hand calculating the Stokesian drag on the particles (the friction coefficient of the particles in the liquid) using a continuum hydrodynamic description. This Brownian motion of the colloids ensures that a dispersion of such particles can lower its free energy and by doing so self-organize.

During the past hundred years, monodisperse colloids have possibly even increased their role as important model systems. Nowadays, they are used to test theories on strongly interacting systems such as liquids and phenomena important to condensed-matter physics such as melting, freezing, and the glass transition. The last decade has also shown that by using advanced microscopy techniques, quantitative measurements of both structure and dynamics can be made on the singleparticle level inside concentrated dispersions. The understanding gained of the self-organization of colloids is starting to be used to create new materials such as photonic crystals (for example, see the August 2001 issue of *MRS Bulletin*²).

The focus of this review is on how external fields can guide and manipulate this self-organization in desired directions. We have limited this review to papers from the last five years, in order to prevent overlap with a previous issue on colloids published in *MRS Bulletin* in 1998.³ Even with this restriction, space constraints make it impossible to be complete.

Very important to the realization of new materials and model systems are recent advances in synthesis. For instance, core-shell morphologies of particles with similar outside shell materials but different cores can have similar interparticle interactions but can be made to respond to external fields differently.⁴⁻⁵ Moreover, control over more complex shapes in monodisperse form (see Figure 1 and the article by Manoharan and Pine in this issue) is becoming possible, even for particles in the nanometer size range.⁶ This is not, however, the focus of this review.

External Fields Walls and Confinement

Although some may argue that walls or confining boundaries are not exactly an external field, the presence of such a structure can lead to all kinds of phenomena (e.g., wetting, pre-freezing, capillary condensation) that modify the thermodynamic behavior. As such, the wall acts as an external field that modifies bulk behavior and can therefore be used as a relatively simple means of control. In addition, knowledge about the interactions of liquids and solids with a wall of a different material is both of fundamental and applied interest. For instance, in the case of nematic liquid crystals, an understanding on the microscopic scale is still lacking, despite



Figure 1. Scanning electron microscopy (SEM) image of colloidal dumbbells of silica particles created by controlled aggregation of silica spheres (radius, 86 nm) and separated in pure form, by sedimentation, after the method of Perrin. the importance for display applications of aligning these molecules on substrates in a controlled way.

Only recently have theoretical predictions been made in combination with computer simulations for the simpler hard-sphere system at a structured or patterned wall.7 One of the surprising outcomes is that the first layer of spheres stuck to a wall with the symmetry and spacing of close-packed crystals can induce crystallization against the wall at 30% below the bulk freezing volume fraction. On certain crystalline patterns attached to the wall, the crystal that formed on this template was found to wet the structured wall. This implies that there is a logarithmic divergence in the number of crystalline layers approaching the bulk freezing transitionthe crystalline layer induced by the wall grows in thickness according to a power law, and becomes infinitely thick at the bulk freezing transition point. It also means that sizable crystals can be grown on the container wall well before the bulk freezes and that the structured wall causes an appreciable lowering of the free energy of the particles next to it. This is much less the case for an unstructured or unpatterned wall, which will induce freezing, at most, at a volume fraction a few percent below the bulk freezing volume fraction.⁷ This partially explains the experimental realization of the growth of hcp crystals on a wall templated with a crystal plane that would allow only the growth of these metastable (from a bulk point of view) crystals.8 As a matter of fact, it was shown that any stacking sequence resulting in close-packed crystals and, by stretching certain directions, also non-close-packed crystals can be grown by using this approach of "colloidal epitaxy."8 The comparison with theory is not one-to-one, as the experiments were performed by having the colloidal crystals grow on the template in a gravitational field, where the gravitational length was on the order of the particle size. In the case of long-range repulsive potentials, the density of the spheres was matched to that of the liquid; in this case, it was shown that crystal growth could be directed by a 2D pattern of charged lines.9 Here as well, crystals that were not the bulk equilibrium phase could be nucleated against the structured wall. Crystals were also grown on a template in the presence of attractions induced by polymers.¹⁰ It would be interesting to find out which interparticle interaction potential will give the highest-quality crystals.

Another popular and simple method for growing large colloidal crystals, besides growth in a gravitational field, is by drying dilute dispersions slowly on a flat surface drawn out of the dispersion. It is actually not even necessary to move the surface up, as the evaporating liquid surface is moving down by itself.¹¹ Particles sticking up through the surface of the drying liquid are forced together by strong capillary forces, and if the process goes slowly enough, a crystal with a thickness controlled by the particle volume fraction results. We have shown that this process of "controlled drying" still works in the limit of crystals just one layer thick, where, without a template, a close-packed hexagonal arrangement forms. In this mode of layer-by-layer growth, one can alternate particles of different size or composition. In this way, ~ 5 layers of binary crystals can be grown.12 With size ratios close to 0.5, crystals with stoichiometry LS_2 (where L represents large spheres and S small spheres) were grown that have also been found in bulk crystallization. Unexpected crystal symmetries were deposited, both at higher (LS_3) and lower (LS_1) volume fractions of the small spheres. The LS_1 structure is especially intriguing, as it fills the hexagonal array of crevices of the layer of larger spheres in every other hole. This means that the drying liquid film can exert an influence over relatively large distances, probably because the regular structure formed at the lower volume fractions minimizes the surface area in this way. Figure 2 demonstrates that this open structure at lower volume fractions also forms on an arrangement of the first layer with a square symmetry. The first layer in the figure was deposited on a structured

wall with a square symmetry and demonstrates that despite the large drying forces, this process can be directed by a template as well, as long as the number of layers deposited is not too large.¹³ For size ratios of small to large spheres of <0.225, it has been shown that a binary crystal layer can be deposited as a mixture of large and small spheres.¹⁴ Surface patterns with larger dimensions have also been used to orient colloidal crystals for photonic applications.¹⁵

Bringing walls close together not only leads to phenomena such as capillary condensation but also can lead to different packing arrangements that fill the confining spaces more efficiently than crystals found in bulk.¹⁶ A different approach was taken in Reference 17, which also involves packing colloids in confining geometries. Here, 2D arrays of holes in a polymer layer are used to pack the colloids, also by means of drying forces. In this way, small amounts of identical particles with more complex shapes can be designed.

In general, it can be concluded that with the ever-increasing need to make devices and structures on these devices—smaller and smaller, applied and fundamental research into the effects of walls and confinement will only increase in the near future.

Low-Frequency Electric and Magnetic Fields

Electromagnetic (EM) radiation with frequencies well below the visible range is somewhat arbitrarily termed "low" in this article. A large range of these "low" frequencies can cause coupling of the electric



Figure 2. SEM image of a two-layer square structure made by "controlled drying" on a template with a pitch comparable to the particle diameter. The left inset is an enlargement of the structure; the right inset shows ordering of vacancies in a monolayer of spheres deposited at a lower particle concentration.

field to all kinds of different dynamical processes that involve the colloids or their interactions. Static and constant fields can move charged particles (electrophoresis), can polarize both the double layer and the particle, and can lead to electrode reactions if the electrodes are in direct contact with the liquid. Inhomogeneous fields can move polarized particles (dielectrophoresis). All of these effects have already been used to make new materials. Electrophoresis has been used to accelerate sedimentation.18 Two-dimensional crystals have been created by a combination of interactions caused by the polarization of double layers and dielectrophoresis¹⁹ and by attractions resulting from electrohydrodynamic flows induced by the presence of the particles and current flows.20 Two-dimensional binary crystals of nearly equal-sized polystyrene and silica spheres were made using the different frequency-dependent polarizabilities of the two particles.²¹

Three-dimensional crystallization has been initiated by dielectrophoresis in a hard-sphere system without significant effects arising from induced dipolar interactions between the spheres.²² On the other hand, dipolar interactions by polarization of the "hard-sphere-like" particles (without dielectrophoresis) have been used to grow body-centered-tetragonal (bct) colloidal crystals.²³ In addition, the electric field could in this instance be used to switch between bct and fcc crystals by a martensitic transition. The induced dipolar interactions were also used to grow large fcc or bct single crystals, as well as crystal structures with part-fcc and part-bct layer stackings.24 In other work, it was shown that induced dipolar interactions can also be combined with long-range repulsive potentials if the frequency of the ac field is high enough. A very rich phase diagram with several new colloidal phases is the result of this combination of long-range potentials.25 Moreover, the dipolar interactions can be switched on and off very rapidly, creating interesting possibilities not only for model studies but also for applications. For instance, a lattice constant in a colloidal crystal can be switched between different values, and thus the angle of a light beam that is Bragg-scattered by this lattice can be switched.

Most work on magnetic particles (or magnetizable particles that do not have a permanent magnetic moment) has until now been done on 2D systems in which the dipolar interactions are repulsive only, and the fact that most magnetic particles absorb light is not a problem. Beautiful work identified one of the clearest examples of a 2D hexatic phase,²⁶ having the elastic properties of 2D crystals and characterized by long-range bond order as measured by correlation functions that describe the range of the symmetry between near neighbors, but short-range positional order as measured by the radial distribution function that describes correlation in the position between particles.²⁷

High-Frequency Electromagnetic Fields: Light

The distinction between high and low frequency is based on the fact that if the frequency of the electromagnetic radiation is chosen so high that the wavelength enters the colloidal domain, forces can be generated and limited to the single-particle level. In this regime, light needs to be highly focused, and the refractive index of the particles needs to be larger than that of the suspending medium—although with "beam-shaping" (e.g., donut-shaped beams), even this requirement can be relaxed. If these conditions are met, it becomes possible to locate or trap colloids in the region of high intensity close to the focus. Many ways already exist to generate large arrays of optical tweezers that can be used to simultaneously manipulate many particles (see References 28-29 and cited work therein). Optical tweezers in combination with high-accuracy position detection can be used to measure interaction energies between colloids with sub-kT resolution. Anisotropies in the particle shape or optical properties, moreover, can be used to orient or rotate particles, making it possible to exert torques as well.28

In short, optical tweezers are very versatile and have already been used in several different ways. By sticking colloids to oppositely charged surfaces, 2D arrangements of particles can be made that can subsequently be used to direct 3D crystallization.³⁰ Such a procedure can also be used to build up structures in 3D;³¹ however, this procedure falls more into the category of "do-it-yourself" organization instead of manipulated self-organization. Two-dimensional traps have also been used in combination with interference patterns to arrange multiple colloids on one trapping site, creating 2D "molecular" colloidal crystals.32 Holding multiple particles trapped in three dimensions has also been demonstrated.³³ In Figure 3 and Reference 29, we demonstrate that these techniques can also be applied in concentrated dispersions by using tracer particles with a high-index core in a dispersion of matched particles with a fluorescent core. It is possible to image in 3D the effect that the 3D trapped structures have on the rest of the dispersion because multiple trapping planes can be generated through a different lens than that used for the 3D confocal



Figure 3. Confocal micrographs of the reflection signal of tracer particles (red) in a dispersion of index-matched particles with fluorescent cores (green). In the imaging plane, 3×3 optical traps were created. Traps were created inside (a) an fcc (111) crystal plane and (b) a concentrated colloidal liquid with a volume fraction close to freezing. The images shown are averaged over 10 frames, 1 s apart. Note that the fluorescent spheres are not influenced by the ninth empty trap position. The bulk silica particles are 1050 nm in diameter with 400-nm-diameter fluorescent cores (FITC. fluorescein isothiocyanate); the tracer spheres have polystyrene cores (diameter, 772 nm) with 100-nm-diameter silica shells; the trapping wavelength is 1064 nm.

imaging.²⁹ The fact that the tracer particles have the same outer shell does not only ensure that interactions with the matched particles are identical, but also that optically induced interactions between the cores can be neglected as a result of the increased distance between the cores. In Figure 3a, a square arrangement of trapped particles is shown in a hexagonal (111) plane inside a 3D colloidal crystal. In Figure 3b, the same arrangement is shown inside a colloidal liquid close to crystallizing. The particles close to the trapped spheres have already started to order. The effects were made visible by averaging several frames, causing the particles with no long-range order in the disordered liquid to blur. Also, note that at the ninth position where a trap is present but no tracer is trapped, no effects are visible on the matched fluorescent particles.

In Reference 29, it is also shown that laser beams that are not focused to a diffractionlimited spot can be used to concentrate particles by dielectrophoresis in ways similar to those mentioned in the section on low-frequency electric and magnetic fields.²² The radiation pressure can also be used to press particles against a wall and essentially confine them to a 2D plane. By scanning another more focused laser beam in a square array, a programmable "fence" around the 2D system was realized.³⁴

Gravity

Photonic crystals built up from colloids can be made through crystallization of the particles in a heterogeneous process that starts at the container bottom with the crystals growing in the [111] direction parallel to gravity. The larger colloidal particles (around 1 μ m) used in photonic crystals aimed at bandgaps in the nearinfrared have gravitational lengths close to the particle size. In this limit, a meanfield description is likely to break down. Experiments aimed at investigating earlier theoretical predictions have only been performed recently.35,36 An interesting finding, both in theory and simulations and in experiments, is that the first two layers start crystallizing in unison, while the other layers follow sequentially.³⁵ Another experimental finding is that the stacking errors can be significantly reduced if the crystal growth rate is reduced, but that the same effect, at least close to the bottom wall, can also be induced by having a template there with the symmetry of a (111) plane.36

Usually, a gravitational field is considered a nuisance for binary crystal formation, because the larger particles generally sediment faster. However, in Figure 4, we show that it is also possible to *use* gravity to grow binary crystals that would not even have formed otherwise. Here, two sizes of poly(methyl methacrylate) spheres with different surface charge densities have been used. The large spheres sedimented (upward in this case, because the density of the spheres is less than that of the solvent), first forming a random stacking of closepacked planes. The small and almost hard spheres sedimented later and could move into the octahedral holes, because they did

not experience a repulsion from the charged larger particles.

Shear

Despite the fact that shear-induced crystallization and, at higher shear rates, shear-induced melting have been studied from the mid-1980s, there are only a few papers in the literature in which flow is used to manipulate or improve colloidal crystallization from a materials point of view. Both particles with a hard-spherelike interparticle potential³⁷ and charged spheres³⁸ have been crystallized quite successfully under the influence of shear to obtain larger colloidal crystals. It is interesting that in both cases, the crystals that were pure fcc during shear turned into twinned crystals soon after cessation of the shear. The mechanism responsible for this is still unclear.

Most research until now used scattering methods to infer structural information. In particular, if no clear idea for the structure is known in advance, or if defects or imperfections are an issue, the interpretation of **k**-space (momentum space) information can be quite difficult and indirect. Until now, direct microscopy in combination with shear has been rare; this situation is



Figure 4. Binary dispersion of green (diameter, 740 nm) and red (diameter, 2.16 μ m) fluorescent poly(methyl methacrylate) spheres, showing an image plane between two layers of red spheres. The red spheres interacted with a soft repulsive interparticle potential and crystallized at a volume fraction of around 0.25. For this dispersion, the index was matched and the density was almost matched, creating milligravity conditions and resulting in slow sedimentation of the green, almost hardsphere-like particles in the interstitials of the randomly stacked red spheres.

likely to change soon. Several groups are pursuing real-space rheological experiments.³⁹⁻⁴¹ Our approach makes use of a confocal microscope and allows quantitative analysis of the particles in a thin layer, even during shear. The reason that the particles appear to be stationary in one imaging plane that can be selected by the confocal microscope is because they are stationary with respect to the outside laboratory frame. By moving both the lower plate and an upper cone of the shear cell in opposite directions, it is possible to set up a flow with constant shear (at least in the colloidal liquid) for which there is a plane of zero velocity with respect to the outside world. By changing the relative speeds of the cone and plate, this plane can be moved with respect to the bottom plate through which the imaging is done. Figure 5 shows a metastable liquid at a volume fraction of 0.35 (freezing volume fraction, 0.3) of slightly charged colloids before (Figure 5a)



Figure 5. Confocal micrographs of the plane of zero velocity, located 20 μ m from the lower plate at a shear rate of 0.5 s⁻¹: (a) at time t = 0 s; (b) at time t = 256 s. Particle diameter, 2.25 μ m.

and after (Figure 5b) 256 s of shear. Figure 5b is a confocal image taken while the shear was still being applied. These are preliminary measurements,³⁹ but it is clear that by this method a lot of the theories on shear-induced crystallization and melting can be tested.

Combinations

Quite a few of the examples given here are more or less already combinations of more than one external field. For instance, the hard-sphere crystals grown on a template by colloidal epitaxy were concentrated on the template by gravity.8 However, this example was mentioned in the section on wall effects because the metastable hcp crystals would have probably also formed without this external field, such as in the case of long-range repulsive systems. In several other cases, however, the combination of two external fields is already opening up new possibilities. Combinations with electric fields are especially popular topics of research.

For instance, in the work of Reference 42, the gravitational field plays an essential role in making a martensitic fcc-bct transition go in a layer-by-layer fashion as a function of the electric field used to induce this transition. Here, the electric field was directed perpendicular to the gravitational field. Electrophoresis has been used to move particles to a place where optical tweezers can stick them to a wall.43 In another combination of electrophoresis and light, the position of 2D colloidal crystal growth on an electrode was induced by the currents at the electrode surface, as mentioned earlier,^{20,21} but in this case, the currents were influenced by illumination.44 On tin-doped indium oxide electrodes, the current density can be increased with light, resulting in the ability to spatially arrange the crystallization process. The combination of magnetically induced particle repulsions in 2D systems and optical tweezers or tweezer arrays has led to insights into the effects of pinning arrays45 and the measurement of the elastic constants of a 2D crystal.⁴⁶ In both cases, the external magnetic field controlled the strength of the repulsions and thus the effective temperature of the experiments, giving a kind of control that is difficult to achieve without a field. A combination of magnetic and electric fields has also been used to control the properties of a 2D system of liquid-crystal droplets.4.7

Also, flow and the manipulation of colloids with optical tweezers have been combined. Insights gained from the study of liquids flowing past trapping sites created by optical tweezers may lead to new separation methods.⁴⁸ Controlling the arrangement of colloids inside microfluidic cells can switch flows or even apply a pumping action, causing flow.⁴⁹ Electrorheological fluids, in which an external electric field is used to change the viscosity of a concentrated dispersion in milliseconds by inducing strong dipolar attractions between the colloids, are another example of one field regulating the response to another field.

Outlook

Before spending some words on possible future directions, it is important to repeat that the overview given here is far from complete. For instance, external (thermodynamic) fields set up by gradients in temperature,²² pressure, or solvent composition have not been treated, even though all of these are promising methods for exerting external control over, for instance, the colloidal particle concentration, the interparticle potential, or both. This illustrates how, in the last few years, research on external control of colloids and their self-organization has taken off. It is not hard to predict that this trend, including an increase in combinations of fields, will continue.

It is also likely that there will be a strong increase in the use of colloids as model systems for investigating fundamental questions related to issues important to materials science. Examples are the effect of boundary conditions (e.g., stick-slip boundary conditions in the case of liquid crystals, or issues related to flow past walls), the structure and dynamics of defects, and fundamental issues in tribology. In addition, there is a drive in the photonic-crystal community to investigate the role of polydispersity on longrange order and the effects and possible prevention of defects (point defects, interstitials, stacking errors, grain boundaries). Clearly, the effects of polydispersity are particular to colloids, but the other issues associated with defects are of general interest.

From the examples given, it already follows that the degree of control that external fields allow will make it possible to prepare, in a controlled way, colloidal model systems that are (far) out of equilibrium. This will enable a more systematic study of states (far) out of equilibrium, hopefully clarifying on a fundamental level many processes in both nature and industry.

Finally, electrorheological fluids are considered a "smart" material because their viscoelastic properties can be altered by an external field. This allows for the materials properties to be dynamically adjusted. The increased knowledge that is being gained right now on manipulating selforganization will no doubt also result in an enhanced ability to control the properties of other materials based on colloids.

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